The chemistry of
organophosphorus compounds

Volume 2

The chemistry of organophosphorus compounds, Volume 2, Phosphine oxides, sulphides, selenides and tellurides
Edited by Frank R. Hartley. © 1992 John Wiley & Sons, Ltd. ISBN: 0-471-93056-3

THE CHEMISTRY OF FUNCTIONAL GROUPS

A series of advanced treatises under the general editorship of
Professor Saul Patai

The chemistry of alkenes (2 volumes)
The chemistry of the carbonyl group (2 volumes)
The chemistry of the ether linkage
The chemistry of the amino group
The chemistry of the nitro and nitroso groups (2 parts)
The chemistry of carboxylic acids and esters
The chemistry of the carbon–nitrogen double bond
The chemistry of amides
The chemistry of the cyano group
The chemistry of the hydroxyl group (2 parts)
The chemistry of the azido group
The chemistry of acyl halides
The chemistry of the carbon–halogen bond (2 parts)
The chemistry of the quinonoid compounds (2 volumes, 4 parts)
The chemistry of the thiol group (2 parts)
The chemistry of the hydrazo, azo and azoxy groups (2 parts)
The chemistry of amidines and imidates (2 volumes)
The chemistry of cyanates and their thio derivatives (2 parts)
The chemistry of diazonium and diazo groups (2 parts)
The chemistry of the carbon–carbon triple bond (2 parts)
The chemistry of ketenes, allenes and related compounds (2 parts)
The chemistry of the sulphonium group (2 parts)
Supplement A: The chemistry of double-bonded functional groups (2 volumes, 4 parts)
Supplement B: The chemistry of acid derivatives (2 parts)
Supplement C: The chemistry of triple-bonded functional groups (2 parts)
Supplement D: The chemistry of halides, pseudo-halides and azides (2 parts)
Supplement E: The chemistry of ethers, crown ethers, hydroxyl groups
and their sulphur analogues (2 parts)
Supplement F: The chemistry of amino, nitroso and nitro compounds
and their derivatives (2 parts)
The chemistry of the metal–carbon bond (5 volumes)
The chemistry of peroxides
The chemistry of organic selenium and tellurium compounds (2 volumes)
The chemistry of the cyclopropyl group
The chemistry of sulphones and sulphoxides
The chemistry of organic silicon compounds (2 parts)
The chemistry of enones (2 parts)
The chemistry of sulphenic acids, esters and their derivatives
The chemistry of sulphenic acids and their derivatives
The chemistry of enols
The chemistry of organophosphorus compounds (2 volumes)
The chemistry of sulphonic acids, esters and their derivatives
The chemistry of alkanes

UPDATES

The chemistry of α-haloketones, α-haloaldehydes and α-haloimines
Nitrones, nitronates and nitroxides
Crown ethers and analogs
Cyclopropane-derived reactive intermediates
Silicon–heteroatom bond
Synthesis of carboxylic acids, esters and their derivatives

Patai's 1992 guide to the chemistry of functional groups—*Saul Patai*

The chemistry of
organophosphorus compounds

Volume 2

Phosphine oxides, sulphides, selenides and tellurides

Edited by

FRANK R. HARTLEY

Cranfield Institute of Technology
Cranfield, UK

1992

JOHN WILEY & SONS
CHICHESTER—NEW YORK—BRISBANE—TORONTO—SINGAPORE

An Interscience® Publication

Baffins Lane, Chichester, West Sussex PO19 1UD, England

Other Wiley Editorial Offices

John Wiley & Sons, Inc., 605 Third Avenue,
New York, NY 10158-0012, USA

Jacaranda Wiley Ltd, G.P.O. Box 859, Brisbane,
Queensland 4001, Australia

John Wiley & Sons (Canada) Ltd, 22 Worcester Rd,
Rexdale, Ontario M9W 1L1, Canada

John Wiley & Sons (SEA) Pte Ltd, 37 Jalan Pemimpin #05-04,
Block B, Union Industrial Building, Singapore 2057

Library of Congress Cataloging-in-Publication Data

(Revised for vol. 2)

The Chemistry of organophosphorus compounds.

(The Chemistry of functional groups)
'An Interscience publication.'
Includes bibliographical references and indexes.
Contents: v. 1. Primary, secondary, and tertiary phosphines, polyphosphines, and heterocyclic organophosphorus(III) compounds — v. 2. Phosphine Oxides, sulphides, selenides, and tellurides.
1. Organophosphorus compounds. I. Hartley, F. R. II. Series.
QD412.P1C444 1990 547'.07 89-22591
ISBN 0 471 92607 8 (v. 1)

British Library Cataloging in Publication Data

A catalogue record for this book is available from the British Library

ISBN 0 471 93056 3

Typeset in Times 9/10 pt by Thomson Press (India) Ltd, New Delhi and
Printed and bound in Great Britain by Biddles Ltd, Guildford, Surrey

To

V. H., S. M. H., J. A. H. and E. J. H.

Contributing authors

Alok K. Bhattacharya	FACT Engineering and Design Organisation, New Delhi 110019, India
Manfred Dankowski	Degussa AG, Inorganic Chemical Products Division, D-6000 Frankfurt, Germany
George Davidson	Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK
Ronald S. Edmundson	Retired from Department of Chemistry, University of Bradford, Bradford, West Yorkshire BD7 1DP, UK
Michael J. Gallagher	School of Chemistry, University of New South Wales, PO Box 1, Kensington, New South Wales 2033, Australia
Declan G. Gilheany	Department of Chemistry, St Patrick's College, Maynooth, Co. Kildare, Ireland
Tarlok S. Lobana	Department of Chemistry, Guru Nanak Dev University, Amritsar 143005, India
Nripendra K. Roy	Indian Agricultural Research Institute, New Delhi 110012, India
Kalathur S. V. Santhanam	Chemical Physics Group, Tata Institute of Fundamental Research, Colaba, Bombay 400005, India

Foreword

The Chemistry of Organophosphorus Compounds is a multi-volume work within the well established series of books covering *The Chemistry of Functional Groups.* It is proposed to cover the extensive subject matter in four volumes.

Volume 1 covers primary, secondary and tertiary phosphines ($PR_3H_{3-n}, n = 1-3$), polyphosphines [both $P(C)_nP$ and $R(P)_nR'$, $n > 1$) and heterocyclic compounds containing phosphorus.
Volume 2 covers phosphine oxides, sulphides, selenides and tellurides.
Volume 3 will cover phosphonium salts, phosphonium ylides and phosphoranes.
Volume 4 will cover phosphinous, phosphonous, phosphinic and phosphonic acid compounds and their halogen derivatives R_2PY, RPY_2 and $R_2P(X)Y_2$, where Y = halogen and X = O, S or Se.

For many years the nomenclature used in organophosphorus chemistry was extremely frustrating, with different compounds being given the same name by different authors. The nomenclature has, however, now been rationalized and is summarized in Volume 1, Chapter 1, Section IV.

In common with other volumes in *The Chemistry of the Functional Groups* series, the emphasis is laid on the functional group treated and on the effects which it exerts on the chemical and physical properties, primarily in the immediate vicinity of the group in question, and secondarily on the behaviour of the whole molecule. The coverage is restricted in that material included in easily and generally available secondary or tertiary sources, such as *Chemical Reviews* and various 'Advances' and 'Progress' series, as well as textbooks (i.e. in books which are usually found in the chemical libraries of universities and research institutes) is not as a rule repeated in detail, unless it is necessary for the balanced treatment of the subject. Therefore, each of the authors has been asked *not* to give an encyclopaedic coverage of his or her subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself or herself to a reader who is assumed to be at a fairly advanced postgraduate level. With these restrictions, it is realised that no plan can be devised for a volume that would give a complete coverage of the subject with no overlap between the chapters, while at the same time preserving the readability of the text.

The publication of the Functional Group Series would never had started without the support of many people. This volume would never have reached fruition without the help of Mr Mitchell and Mrs Perkins with typing and the efficient and patient cooperation of several staff members of the Publisher. Many of my colleagues in England, Israel and elsewhere gave help in solving many problems, especially Professor Saul Patai, without whose continual support and encouragement this work would never have been attempted.

Finally, that the project ever reached completion is due to the essential support and partnership of my wife and family, amongst whom my eldest daughter provided both moral support and chemical understanding in the more difficult areas of the subject.

Cranfield, England FRANK HARTLEY

Contents

List of abbreviations used

abd	azobisisobutyl diacetate
Ac	acetyl (MeCO)
acac	acetylacetone
Ad	adamantyl
aibn	azobisisobutyronitrile
all	allyl
an	acetonitrile
An	anisyl
Ar	aryl
ATP	adenosine triphosphate
bipy	2,2′-bipyridine
BSA	bovine serum albumin
btsa	*N*,*O*-bis(trimethylsilyl)acetamide
Bu	butyl (also *t*-Bu or Bu^t)
Bz	benzyl
cd	circular dichroism
cod	cycloocta-1,5-diene
cp	cyclopentadienyl
mCPBA	*m*-chloroperoxybenzoic acid
CPMAS	cross-polarization magic angle spinning
Cy	cyclohexyl
dbn	1,5-diazabicyclo[5.4.0]non-5-ene
dbso	dibenzoyl sulphoxide
dbu	1,8-diazabicyclo[5.4.0]undec-7-ene
$DDPN^+$	deamino diphosphopyridine nucleotide
diop	2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino) butane
dme	1,2-dimethoxyethane
dmf	dimethylformamide
dmg	dimethylglyoximate
dmpe	bis(1,2-dimethylphosphino)ethane
dmso	dimethyl sulphoxide
DNA	deoxyribonucleic acid
$dpbO_2$ $dpbS_2$	$Ph_2P(E)(CH_2)_4P(E)Ph_2 \quad E = O, S$

dpbSe$_2$ dpeO$_2$ dpeS$_2$ dpeSe$_2$ dpmO$_2$ dpmS$_2$ dpmSe$_2$ dppO$_2$ dppS$_2$ dppSe$_2$	$Ph_2P(E)(CH_2)_nP(E)Ph_2$ b, $n = 4$ e, $n = 2$ m, $n = 1$ p, $n = 3$ $E = O, S, Se$
dpmPS	$Ph_2P(S)CH_2PPh_2$
dpmPSe	$Ph_2P(Se)CH_2PPh_2$
DPN$^+$	diphosphopyridine nucleotide
DPNH	dihydronicotinamide adenine dinucleotide
dppb	bis(1,4-diphenylphosphino)butane
dppe	bis(1,2-diphenylphosphino)ethane
dppm	bis(1,1-diphenylphosphino)methane
dppp	bis(1,3-diphenylphosphino)propane
dpso	diphenyl sulphoxide
ECE	electron transfer followed by chemical reaction followed by further electron transfer
ee	enantiomeric excess
epr	electron paramagnetic resonance
esr	electron spin resonance
FAD	flavine adenine dinucleotide
FMN	flavine mononucleotide
FT	Fourier transform
Hba	benzoylacetone
Hbfa	benzoyltrifluoroacetone
Hdbm	dibenzoylmethane
H$_2$dehp	di(2-ethylhexyl)phosphoric acid
H$_2$dmg	dimethylglyoxime
H$_2$dz	dithizone (3-mercapto-1,5-diphenylformazan)
Hex	hexyl
Hhfa	hexafluoroacetylacetone
hmde	hanging mercury drop electrode
hmpa	hexamethylphosphoramide
hmpt	hexamethylphosphorotriamide
HOMO	highest occupied molecular orbital
Hox	8-hydroxyquinoline
HPLC	high-performance liquid chromatography
Hpmap	1-phenyl-3-methyl-4-acylpyrazol-5-one
Hpmbp	1-phenyl-3-methyl-4-benzoylpyrazol-5-one
Hpmbup	1-phenyl-3-methyl-4-butyrylpyrazol-5-one
Hpmdbp	1-phenyl-3-methyl-4-(3,5-dinitrobenzoyl)-pyrazol-5-one
Hpmop	1-phenyl-3-methyl-4-octanoylpyrazol-5-one
Hpmsp	1-phenyl-3-methyl-4-stearoylpyrazol-5-one
Hpmtfp	1-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one
Hpva	pivaloyltrifluoroacetone

Hpvta	dipivaloylacetone
Htbfa	thiobenzoyltrifluoroacetone
Htfa	trifluoroacetylacetone
Htfma	1,1,1-trifluoro-5-methylhexane-2,4-dione
Htta	1,1,1-trifluoro-3-(2-thenoyl)acetone
IP	ionization potential
LC_{50}	concentration causing lethality to 50% of the population
LD_{50}	dose causing lethality to 50% of the population
lda	lithium diisopropylamide
lp	lone pair of electrons
LUMO	lowest unoccupied molecular orbital
M	metal
Me	methyl
mibk	methyl isobutyl ketone
MNDO	modified neglect of diatomic overlap
NADP	nicotinamide adenine dinucleotide phosphate
nba	*N*-bromoacetamide
nbs	*N*-bromosuccinimide
NHN	nicotinamide ribose monophosphate
Np	naphthyl
OAc	acetate
ord	optical rotatory dispersion
Pe	pentenyl
Pen	pentyl (C_5H_{11})
pes	photoelectron spectroscopy
Ph	phenyl
phen	1,10-phenanthroline
ppa	polyphosphoric acid
ppm	parts per million
Pr	propyl (also *i*-Pr or Pr^i)
R	any radical
RNA	ribonucleic acid
SCE	standard calomel electrode
SCF	self-consistent field
tbp	trigonal bipyramid (when referring to a structure) or *tert*-butyl peroxide (when referring to a chemical)
tbpo	tri-*n*-butyl phosphate
tfa	trifluoroacetic acid
tfb	tetrafluorobenzobicyclo[2.2.2]octatriene
thf	tetrahydrofuran
tht	tetrahydrothiophen
tmeda	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
tmpo	2,2,6,6-tetramethylpiperidine-1-oxyl

Tol	tolyl ($CH_3C_6H_4$)
topo	tri-*n*-octyl phosphate
tos	tosyl
TPN	triphosphopyridine nucleolide
VSEPR	valence shell electron pair repulsion
X	halide

CHAPTER **1**

Structure and bonding in tertiary phosphine chalcogenides

D. G. GILHEANY

Department of Chemistry, St. Patrick's College, Maynooth, Co. Kildare, Ireland

---

The chemistry of organophosphorus compounds, Volume 2, Phosphine oxides, sulphides, selenides and tellurides
Edited by Frank R. Hartley. © 1992 John Wiley & Sons, Ltd. ISBN: 0-471-93056-3

---

1. INTRODUCTION

The general features of bonding to phosphorus were discussed in Volume 1[1], including likely bonding schemes and the strengths of single and double bonds to phosphorus. Using these, the gross features of the structure and bonding of phosphine chalcogenides are readily predicted and understood. Taking the oxides as an example, phosphorus has five electrons available for bonding, so five bonds to phosphorus are possible, while oxygen is normally divalent and double bonds are allowed. Hence, *if we ignore the octet rule*, there is no problem in predicting the correct structure: phosphorus will have four ligands via three single bonds and one double bond to oxygen, with all electrons used. From the recently rehabilitated[2] valence shell electron pair repulsion (VSEPR) theory, the four ligands are expected to have tetrahedral geometry with the bond to oxygen being stronger than the others and rather polar because of the difference in electronegativity between oxygen and phosphorus. These predictions are borne out completely by measurement of the bond lengths and angles (detailed in Section III), vibration frequencies and dipole moment (Section IV.A). The strength of the PO bond is illustrated by the experience of practical chemists that its formation drives the very useful Wittig and Arbusov reactions and the reactions of life itself.

Of course, it is not that simple. First, there is the problem of the octet rule, and second, on the LCAO–MO model there are, at first sight, not enough orbitals on phosphorus. Indeed, much of the previous discussion of the bonding in phosphine oxides, (and sulphides and selenides) has centred on how to overcome these difficulties, in particular with respect to the nature of the PO bond. Thus the standard discussion of the PO bond in previous reviews of this topic[3–13] has been in terms of a combination of two different descriptions, often *via* a resonance between structures **1A** and **1B**:

$$\underset{\textbf{1A}}{P^{+}{-}O^{-}} \longleftrightarrow \underset{\textbf{1B}}{P{=}O}$$

Structure **1A** avoids the problem of violation of the octet rule, but there is evidence (Section IV.A) that there is not a full positive charge on phosphorus or negative charge on oxygen, so structure **1B** is allowed to contribute. In this case the number-of-orbitals problem is overcome by invoking a suitable virtual d orbital on phosphorus in an overlap scheme such as that in Figure 1. The conventional phrase is often used[3–13] that 'there is expansion of the octet on phosphorus to allow backbonding from oxygen lone pairs into low-lying empty d orbitals'. In turn, this explains the difference between phosphine oxides and amine oxides in that the first-row element does not have easily accessible d

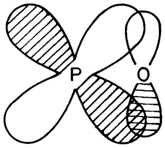


FIGURE 1. The now outdated and misleading view of the π-type orbital overlap in phosphine oxides

orbitals. Hence a discussion of the bonding in phosphine oxides leads on to the differences between the first and subsequent rows of the Periodic Table.

It is shown below that work over the last 10–15 years has rendered this description untenable[14]. First the d-orbitals concept is now redundant at best, and inaccurate and misleading at worst, because d orbitals are not required for there to be backbonding. As described in Section II, it has recently been confirmed beyond doubt by Magnusson[15] that the importance of d functions in *ab initio* calculations on these systems does not mean that they have a valence role. Second, at a deeper level, doubt has been cast on the description of the PO bond as a single bond with some backbonding, the rival description being a formal triple bond. As we shall see in Section IV, this latter issue is not yet settled and is part of a developing general controversy about the nature of multiple bonding.

Hence the investigation of the bonding in phosphine oxides (and sulphides and selenides) calls for an examination of some the most basic concepts in valency and bonding theory in the context of one of the most important bonds in practical chemistry and the processes of life. The following quotations are from two recent papers which are discussed in Section IV.D.3 and illustrate the controversial nature of the subject:

> 'These studies emphasize the importance of partial ionic bonding in second row hypervalent species... Due to the ionic character of the bonding, the *electronic* octet rule is far from being violated. This emphasizes the robustness of the Lewis octet concept'.
>
> A. E. Reed and P. v. R. Schleyer[16]

> 'Contrary to much previous experience based on molecular orbital calculations, generalized valence bond calculations exhibit six bonds to P and S atoms in the presence of electronegative ligands. One must conclude that this is strong evidence that such molecules violate the Lewis–Langmuir octet rule'.
>
> R. Messmer[17]

Even the representation of the bond from oxygen to phosphorus in tertiary phosphine oxides is contentious. Practical chemists usually just write a double bond, $R_3P{=}O$, but a number of other descriptions and representations have been advocated as the following chronological list illustrates: 'somewhere between a single and triple and only by chance it happens to be a double bond'[18]; 'a partial triple bond'[19]; 'a resonance between single and triple bond structures, the double bond being rejected on symmetry grounds'[20]; 'the dipolar structure dominates and the double bond structure contributes but little'[21]; 'a formal triple bond'[17]. In Section IV.F, we discuss the representation of the PO bond and argue that the continued use of the double bond formula is perfectly reasonable and unrelated to the controversy as to where exactly the bonding electrons are.

II. NON-INVOLVEMENT OF d ORBITALS

The description of the structure and bonding in phosphine oxides has been connected intimately with the concept of virtual d-orbital involvement in bonding in the Main

Group of the Periodic Table. Since, as we shall see, it is only recently that this concept has been discredited, a short overview of the subject is warranted.

The elegance, economy and widespread applicability of the valence bond (VB) and molecular orbital (MO) methods have made them nearly universal in both the qualitative and quantitative discussion of bonding and other molecular properties[22]. In particular, a version of the MO method, the linear combination of atomic orbitals (LCAO) scheme[22], provides the most commonly used framework for the discussion and interpretation of the bonding. In these methods atoms are considered to offer, for bond formation, the outermost valence orbitals (those which are occupied in the atom). Thus hydrogen has one atomic orbital (AO) available for bonding, the first-row elements boron to neon have four, the transition metals six, and so on. In this way, early explanations were provided for s and p bonds in the first row of the Periodic Table from lithium to fluorine. In 1931 Pauling[23] showed how, by introducing appropriate hybrids of s and p orbitals, the characteristic valence angles and bond lengths in compounds of carbon, oxygen and nitrogen could be explained. Although the rough qualitative picture obtained by bonding with these orbitals was satisfactory in most cases, some important difficulties arose.

A particular qualitative difficulty concerned the existence of the so-called 'hypervalent molecules'. In these there seem to be more bonds from the central atom than would be permitted on the basis of Langmuir's octet rule. Thus, in the valence bond picture of, for example, the SF_6 molecule, sulphur forms six σ bonds using six equivalent d^2sp^3 hybrids[24]. However, the d functions used are virtual, not being occupied in the aufbau description of the ground-state sulphur atom. It is then said[5] that SF_6 is characterized by 'outer d-orbital participation in the bond' or that there is an 'expansion of the valence shell of sulphur by promotion of an electron(s) into a low-lying vacant d orbital(s)'. Similar considerations applied to PF_5. The concept of d orbitals was then found convenient to describe two other π-type phenomena exemplified in phosphorus chemistry[3] by (i) the structure and stability of phosphine oxides and ylides (especially compared with their nitrogen analogues) and (ii) the shortening of formally single bonds such as the PO bonds in phosphates. These latter two phenomena involve d orbitals in π-type overlap with adjacent p orbitals[5].

In this way, the possession of 'low-lying' d-orbitals came to be seen as a fundamental difference between first- and second-row elements of the Periodic Table, explaining, for example, why silicon tetrafluoride hydrolyses readily whereas carbon tetrafluoride does not[25]. Since the work of Pauling[23], there have been many papers dealing with the participation of d-orbital basis functions in molecular orbitals for systems containing non-transition elements. Because of their more elaborate symmetry, d orbitals may form more kinds of bonds than can s and p orbitals and detailed and elaborate schemes were built up to use d orbitals to explain the various phenomena[26–30]. This early work is well summarized in a number of reviews[5,31–33], the most useful of which is that of Mitchell[5].

At the outset, a distinction has to be made between inner and outer d orbitals[34]. This refers to the principal quantum number of the d orbital in relation to that of the other valence electrons. *Inner* d orbitals have a principal quantum number one less than that of the other valence electrons. Thus, in the first transition metal series it is the 3d, 4s and 4p orbitals that are involved and the charge cloud for these d electrons lies mostly within that of the s and p electrons. Since these d orbitals are occupied in the ground-state atom, they are clearly required for description of the molecular wavefunction, and the question of their inclusion does not arise. This is the case for bonding in the transition metals[35] and will not be discussed further. *Outer* d orbitals, on the other hand, have the same principal quantum number as that of the other valence shell electrons. The question of their involvement in bonding is much more problematic since they are not occupied in the ground state of the atom under consideration. Indeed, the concept was never fully accepted by the chemical community, including Pauling[24], and, from an initially small group of dissenters[36–43] among whom it is probably fair to single out Rundle[39], the concept has now become redundant, at least among theoretical chemists. Its popularity probably peaked around about 1970 with the review by Mitchell[5] and the advent of the first *ab initio* calculations on these systems (see Section II.B).

A. Alternative Models

The first reservation that has to be entered about virtual d-orbital involvement in bonding is that there are alternative explanations of all the phenomena involved. One of the initial successes of the hybridization theory of bonding as proposed by Pauling[23,24] was the prediction of molecular stereochemistry in that bond directions are determined by the relative orientations of a set of hybrid orbitals on the central atom which are used to form bonds to the ligand atoms and to hold unshared electron pairs. However, during the 1950s it was shown by Gillespie that the successful prediction of molecular geometry does not require explicit reference to the bonding involved because the well known and useful VSEPR model[35,44] explains the geometry of most molecules. Also, at about the same time, a simple and reasonably easily understood model was developed which explains the bonding in non-octet (hypervalent) compounds and which does not require the use of d orbitals. This is the three-centre bond model proposed at various times by Pimental[36,37], Rundle[38,39], Havinga and Wiebenga[40,41], Pitzer[42] and Musher[43] and their coworkers and developed in detail by Rundle[39] and Musher[43]. Bonding is envisaged as partly ionic, which removes the need to involve the d orbitals and explains why fluorine is a crucial ligand in hypervalence. Better still, this model explains well the bonding in other systems where the d orbital concept is lacking, e.g. noble gas derivatives[45,46] and the interhalogen compounds[41]. As we shall see in Section IV, there is also a simple alternative to the d orbital concept as applied to $d\pi$–$p\pi$ systems.

Second, from the 1950s to 1970s there were a multitude of experimental and theoretical investigations, none of which confirmed unequivocally the validity of the concept of d-orbital involvement. This is well documented in the book by Kwart and King[47], the problem being that no study could distinguish d-orbital involvement from an alternative explanation. Indeed, it appeared that the d orbital theory might fit into Popper's category of an unfalsifiable theory[48]. Examples of phenomena which were investigated without definitive results are (i) bond length data in the series of ions XO_4^{n-} (X = Si, P, S and Cl), which are all short relative to values reasonably expected for single bonds[30,35,49], and (ii) the planarity of trisilylamines[50–53]. Probably the last example where a determined effort was made to prove d orbital involvement is the detailed study of a cyclic conjugated sulphone by Fraenkel and coworkers[54]. Even in 1986, after all the work that had gone before[47], these workers felt able to claim that their study implicated p–d bonding 'unequivocally and for the first time'[54]. However, in the light of the results discussed below, it seems likely that all they did, which was still significant, was to show that cyclic conjugation occurred in their system.

B. Theoretical Studies

Since the experimental work had been so very contradictory, it was hoped that calculations might lead to a more definitive answer. Indeed, the early theoretical work was encouraging because it had concentrated on certain issues concerning the suitability of the valence atomic d orbitals for their task[55–63]. Two issues of concern were the size and energy of the d orbitals. First, the d orbitals are too large to overlap effectively with their potential s and p partners[34,56]. By consideration of the factors affecting the size[57], namely unpaired electron spin assignments[34,58,59], the number of promoted electrons[34,59,60] and the formal charge on the central atom[59], it was shown that this objection could be overcome. In particular, the contraction of the d orbitals in a field of strongly electronegative ligands provided a neat explanation of why fluorine is able to induce the largest valence of a central atom. As regards the energies of the d orbitals, which are too high in the isolated atom for effective hybridization with s and p orbitals[5], it was also shown that a field of electronegative ligands could reduce the energies to reasonable values[57,62,63].

In about 1970, with the advent of full *ab initio* calculations on these molecular systems, more detailed investigation of the bonding became possible. For example, early descriptions of the bonding in phosphine oxides (see Section I) involved either semipolar bonds without reference to d orbitals or ordinary covalent bonds constructed from appropriate hybrids that involve d orbitals. Since the former corresponds to a zero population of d orbitals and the latter to a population of unity, it was expected that an analysis of the d populations of the calculated wavefunctions would indicate which was correct. Indeed, the first calculations appeared to confirm the importance of d orbitals because, when d functions were left out, very inaccurate results were obtained and also their addition caused very large energy decreases. Certain calculations in particular had a very strong influence, at least on the community of practical phosphorus chemists[64], e.g. the extended Huckel studies of ylides and phosphoranes by Hoffmann and coworkers[65–67] and the *ab initio* STO-3G studies by Van Wazer and coworkers on ylides and phosphine oxides[68,69]. This despite the specific warning of Hoffmann and coworkers[67] on the *deus ex machina* aspect of d orbitals.

However, there were two problems which confused the theoretical analysis of these systems, namely the incompleteness of most of the basis sets used and the requirement for polarization functions. Initially it was not well recognized that if the s and p basis sets used in the calculations were not saturated, that is, addition of further s and p basis functions still gave energy lowering, then the added d functions would make up the difference and lead to an overestimation of the importance of d orbitals. Differences in the basis set then lead to large differences in the importance of d orbitals from populations of 0.3 to greater than 1. Although the evidence for this was present from the start (see Section IV.D.2), it was only later that it was stated explicitly[19]. The difficulties were further compounded by the well known dependence of population analysis on basis set[19].

However, even if the sp basis is saturated and the population analysis is foolproof, there is still a crucial role for d functions in the calculation of molecular properties and most calculations, especially on second-row elements, will require their inclusion[1,15,70–73]. This is because they act as polarization functions [15,34,71]. Early in the development of quantum chemistry it was known[74] that a proper description of the σ bond in H_2 requires the use of a $p\sigma$ basis function on the proton. The purpose of this function is to polarize the wavefunction (see below) and thus permit the charge distribution to change shape, becoming more localized along the bond axis. This requirement is now routine[75] and for first-and second-row elements the polarization functions needed are d functions. To illustrate the effect of these polarisation functions, consider an electron in a 2p state of a fixed hydrogen atom[34] (Figure 2a). Application of a steady fixed electric field in the z-direction would polarize the charge and pull it in the z-direction. The final perturbed shape is shown in Figure 2c. It can be seen that the charge cloud, and hence the wavefunction, of the perturbed state can be approximated by a superposition (Figure 2b), of some amount, λ of d orbital character on the original p orbital[34]. Hybrids of this kind, involving a small amount of d character, will often be the easiest way of expressing perturbations or polarizations of p orbitals, for example in molecules containing a large dipole moment or in strained-ring compounds[71]. The d orbitals mixed in by this process are not suggested to have any independent existence. In fact, it can be shown[15,34] that the d contribution which expresses the polarization of a 2p orbital

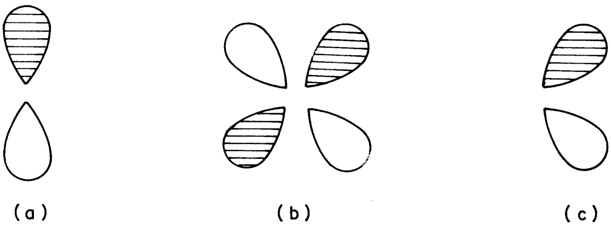


FIGURE 2. Polarization of a p orbital. (a) + λ(b) = (c)

is a 2d orbital and its function is merely to be of about the same size as the orbital it perturbs and to have the appropriate symmetry to provide the angular flexibility needed to direct the electron density efficiently into regions between bonded atoms.[15,71].

Needless to say, many theoretical workers were uneasy about ascribing a valence role to such polarization functions. During the 1970s there were a number of attempts to define circumstances in which one could say which role was taken by the d functions. For example, Coulson[34] distinguished between *polarisation* (d population < 0.1) and *participation* of d orbitals in bonding, where one or more complete d orbitals are used, and Ratner and coworkers[76,77] drew a similar distinction between the *qualitative* and *quantitative* necessity for d orbital inclusion in a basis set, while noting that the whole question is to some extent an artifact of the very convenient atom-centred LCAO method. Then, during the 1980s, it gradually became clear to the majority of theoretical workers that the maximum d population was about 0.3 in most cases and that it has no valence role. Examples of this conclusion are in calculations on, among many others, oxy- and thio-carbanions[78,79], sulphur tetrafluoride[80,81] and, especially significant, the volte-face of Cruickshank[49] on the oxyanions of second-row atoms. There was a minor renaissance[82–84], but it is now clear beyond doubt through the very recent work of Magnusson, discussed below, that the d orbital concept is redundant. Good recent leading references to this literature are the paper by Magnusson[15], that of Reed and Schleyer[16] which, since they treat phosphine oxides, is discussed in detail in Section IV.D.3.a, and the general review by Kutzelnigg[14] on bonding in Main Group compounds, which is indispensable.

C. Calculations by Magnusson

Many workers have studied the variation of the use of d functions in a calculation in order to determine their valence role and concluded that it was not large[85]. For example, Grein and Lawlor[86] showed that the use of bond functions[87] replicated the beneficial effect of d functions in calculations on H_3NO. However, the recent study by Magnusson[15] is so comprehensive and gives such an unequivocal conclusion that it surely must be the final word on the subject. Therefore, we reproduce below the main conclusions in some detail.

Magnusson[15] reported calculations for a very large number of compounds of first- and second-row elements, both normal valent and hypervalent, all at a comparable level. The basis set was of double zeta quality and the experimental geometries were used. Single and multiple sets of five Gaussian d functions were added to the basis sets of all atoms except hydrogen (p function). The exponents of the d functions on the central atom were optimized in all cases, as were those on selected peripheral atoms. The possibility of basis set superposition error was checked and avoided and also the results were compared with those obtained by adding Slater-type functions. The results are given below.

i. The most important observation is that the optimum d function exponent for any element changes very little from one compound to another, even those as different as H_2S and SF_6. Hence there is no support for the view that diffuse d orbitals on the central atom take part in bonding after being contracted by an electronegative ligand field; for example, there is no sign of any progressive contraction across the SF_2, SF_4, SF_6 sequence[15].

ii. There are large energy depressions for many other types of molecule than the allegedly hypervalent species and there is no clear demarcation between them and the normal-valent compounds. In fact, when the energy depressions are measured *per bond* they show only limited variation. This suggests that the involvement of d functions is characteristic of the bond rather than the compound that contains it, and that the extra involvement of d functions in hypervalent molecules is because they have more bonds[15].

iii. There are also energy depressions on the addition of d functions to the basis sets of peripheral atoms. The energy increment per added function is much greater for the central atom but *per bond* there is no difference[15].

iv. There are also energy depressions in compounds of first-row elements and when the results are obtained at the same basis set level the contrast between second- and third-shell behaviour is less spectacular than usually reported[15].

v. There is a strong response in the optimum exponent and d function energy increment to change in bond length. The optimum d function exponent on the peripheral atom also changes[15].

vi. Finally, there is no difference in the role of d functions between normal-valent and hypervalent compounds. They facilitate the transfer of electronic charge into the internuclear bonding region at the expense of the outer parts of the valence wavefunction. Hence the occupations of the higher order functions are strongly dependent on the degree of charge transfer from the central atom and the number of electron pairs formally arranged around the central atom. In short, their purpose is to respond to the rapidly varying molecular potential in the space between the nuclei[15].

We also leave the final word on this with Magnusson[15]: ‘accordingly, any resemblance between d functions in molecular wavefunctions and the valence d orbitals of excited second-row atoms is an artifact of the electronic structure model; they should not be called d orbitals’.

III. STRUCTURE

Structure in organophosphorus chemistry was last reviewed comprehensively in 1974 by Corbridge[9], but work on tertiary (and other) phosphine chalcogenides was not well developed at that time. Thus the material presented below is mostly from the intervening period. The usual general publications[88–91] also give some relevant data but, again, the coverage is not complete. The structures of tertiary phosphine oxides, sulphides, selenides and the few tellurides are first discussed using the data in Tables 1–3. Then these compounds are compared and contrasted with other phosphorus derivatives and non-phosphorus compounds not strictly relevant to this chapter, in particular the parent tertiary phosphines, halogenophosphoryl derivatives and amine and arsine chalcogenides using the data in Tables 4 and 5.

Although a high proportion of available structures are included in Tables 1–3, they are not comprehensive and readers requiring data on particular compounds should also refer to *Chemical Abstracts*. Readers should also refer to the original publications for detail of the structural determinations, error limits and the other molecular dimensions of the compounds quoted.

A. Bond Length–Bond Angle Relationships

The idea that bond length and bond angle are related can be helpful in the analysis of trends in the structures of molecules. It is especially useful in the case of a tetrahedral disposition of ligands around a central atom where most of the space around that atom is occupied. Then the introduction of either bulky or more electronegative groups will lead to a change in both bond angle and bond length. Thus, for example, the bond angle between bulky groups will have to be larger, so all ligand(s) will not be able to approach as close to the central atom and their bond length will be larger. On the other hand, a more electronegative group will require a shorter bond length to the central atom, forcing the other ligand(s) closer together and reducing their bond angle. The structure of the molecule then reflects the balance between these two effects.

Used carefully, the concept can reduce the number of experimental correlations that have to be explained. Obviously there are limitations on its use, e.g. (i) if the space around the central atom is not fully occupied, then bond angle can increase while maintaining bond lengths, for example in the tricoordinate phosphines[1] and perhaps in the later rows of the Periodic Table where the central atom is relatively large, and (ii) if the space around the central atom is already very crowded, as in tetrahedral derivatives of the small first-row atoms, then the size effect may be more dominant.

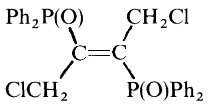
B. Phosphine Oxides

Table 1 gives some structural data for tertiary phosphine oxides, mostly determined using X-ray diffraction. As befits such an easily crystallized and thereby useful[148] compound, there are no less than eight reported X-ray crystal structure determinations on triphenylphosphine oxide[96–99,149], most of which are detailed in Table 1. This is because there are at least two crystal modifications and there have been temperature variation studies. Note the fairly large changes in structural parameters as the *R* value falls from 7.8 to 3.5. Only in one case, trimethylphosphine oxide, were both X-ray and electron diffraction used, with only moderate agreement between the methods (the difference was not caused by intermolecular contacts in the crystal[93]). A number of useful generalizations may be made from Table 1.

The PO bond length is usually in the range 147.5–149.0 pm (the figure of 146 pm, derived from the first study[98] on triphenylphosphine oxide, which was widely quoted[92,94] into the mid-1980s, is clearly in error). This PO distance is almost insensitive to molecular environment. It increases by only 1 pm on metal complexation of the triphenyl derivative[100] (Table 1) or on hydrogen bonding[9,150], although the trialkyl derivatives are affected by a larger amount by the latter change[9]. Similarly, the PO length is little changed by electronegative substituents, α,β-unsaturation or inclusion in a tricyclic ring structure (Table 1). It is possible that alkyl-substituted phosphine oxides have a PO bond length marginally shorter than aryl analogues, which could be due to a bond length–bond angle relationship, but there are not enough data to be sure. This PO bond length may be compared with those in HPO[91] (151.2 pm), diatomic PO[91] (147.6 pm) and a typical PO single bond (160 pm; bridging bond in P_4O_{10}[89]). Clearly the PO bond has high multiple character.

The PC bond length is normally in the range 179–181 pm. From the limited data available, there is a strong effect of electronegative substituents to increase the PC distance, the extreme example being the tris(trifluoromethyl)-substituted case. Also, it is possible that P—C(alkyl) is less than P—C(aryl) by about 1 pm but, again, there are

TABLE 1. Structural data[a] for some tertiary phosphine oxides

Molecule	Method[b]	r(P=O)	r(P—C)	∠OPC	∠CPC	R[c]	Ref.
$Me_3P{=}O$	E	147.6	180.9	114.4	104.1	5.2	92
	X	148.9	177.1	113.1	105.9	6.5	93
$Bu^t_3P{=}O$	E	159.0	188.8	106.1	112.9	9.7	94
$(CF_3)_3P{=}O$	E	147.6	189.7	114.2	104.3	—	95
$Ph_3P{=}O$	X[d]	148.3	179.2	112.3	106.5	6.0	96
	X[e]	148.4	180.3	112.3	106.6	4.5	97
	X[f]	146	176	111.7	107.1	7.8	98
	X[f,g]	149.1	180.3	112.4	—	3.5	99
	X[e,g]	149.4	180.0	112.4	—	3.6	99
$Ph_3P{=}O$ complexes	X[h]	150	179	111	—	—	100
$(2\text{-}MeC_6H_4)_3P{=}O$	X	147.4	181.0	112.9	106.0	7.5	101
$(4\text{-}ClC_6H_4)Ph_2P{=}O$	X	148.5	180.5	111.9	107.0	4.7	102
$(4\text{-}BrC_6H_4)Ph_2P{=}O$	X	149.7	180.8	112.0	106.9	6.4	103
$(C_6F_5)Ph_2P{=}O$	X	147.4	179.6	—	—	—	104
$Me_2PhP{=}O$	X	147.4	178.9 181.5[i]	113.9 111.9[j]	105.5	4.3	105
$ClCH_2Ph_2P{=}O$	X	149.3	183.2 180.4[i]	113.9 112.6[j]	105.6	5.3	106
$Ph_2P(O)CH_2P(O)Ph_2$	X	149.1	181.9 179.4[i]	112.0	106.8	6.3	107
$Ph_2P(O)C{\equiv}CP(O)Ph_2$	X	148.1	179.4 180.8[i]	114.4 112.9[j]	103.7 108.5[k]	3.9	108
	X	148.5	184.3 180.0[i]	112.5	106.3	3.3	109
7-Phosphanorbornene derivative[l]	X	148	186.7 181.1[i]	116.8 111.1[j]	84.3 112.9[m]	7.0	110
1-Phosphanorbornane derivative[n]	X	148.7	178.3	—	96.2	5.4	111

[a] r(P—X) = bond length in pm; ∠XPY = bond angle in degrees; mean values are quoted, unless indicated otherwise.

[b] E = electron diffraction; X = X-ray crystallography at room temperature, unless indicated otherwise.

[c] Reliability index = 100 × conventional R for both X and E, except where indicated otherwise; see original papers for definitions.

[d] Monoclinic, space group $P2_1/a$.

[e] Monoclinic, space group $P2_1/c$.

[f] Orthorhombic, space group *Pbca*.

[g] Performed at 100 K.

[h] .Average of 62 fragments from the Cambridge Crystallography Database.

[i] $P—C_{Ph}$.

[j] $O—P—C_{Ph}$.

[k] $C_{Ph}—P—C_{Ph}$.

[l] 5-Cyano-1,4,7-triphenyl-7-phosphabicyclo[2,2.1]hept-2-ene-7-oxide.

[m] $C_{Ph}—P—C_{ring}$.

[n] 1-Phosphabicyclo[2.2.1]heptane-1-oxide.

not enough data to be sure. There is a small but definite decrease in PC length (1 pm) on metal complexation at oxygen. There is a consistent deviation of the bond angles from the tetrahedral values with CPO higher (112–114°) and CPC lower (104–107°). This is consistent with the shorter PO distance relative to the PC distance.

Note the totally anomalous nature of the structure of tri(*tert*-butyl)phosphine oxide.

The remarkable features of the structure of Bu^t_3PO are (i) the much greater length of the PO bond (159.0 pm) compared with all other oxides, making it essentially a single bond length, (ii) the greater length of the PC bond (188.8pm) and (iii) the reversal of the angle deviation from tetrahedral (CPC is greater). Obviously the great bulk of the *tert*-butyl groups must be at least partly responsible for this anomalous structure. For example, the CPC angles in the parent phosphine[136] (109.9°) are already one of the highest known and could hardly be expected to decrease on oxidation. However, it should be pointed out that there is no steric requirement for the PO bond to be so long because the oxygen atom is well separated from its neighbouring carbon atoms and from the methyl group atoms[94]. The long PO bond length has therefore also been attributed[94] partly to the electron-releasing properties of the *tert*-butyl groups. In any event, it seems reasonable to regard the bonding in the molecule as purely $Bu^t_3P^+—O^-$.

Brock and coworkers[99] made a very careful study of both forms (monoclinic and orthorhombic) of triphenylphosphine oxide at low temperature. They found that there do not appear to be any important differences between the molecular dimensions in the two crystals. Even some small structural trends are shared by the two molecules; for example, of the three PC distances, 179.8, 180.3, 180.8 pm in the orthorhombic and 179.7, 180.2, 180.2 pm in the monoclinic structure, the smallest is to the phenyl ring whose plane is most nearly perpendicular to the PO bond (see also Section V).

C. Phosphine Sulphides

Table 2 gives some structural data for tertiary phosphine sulphides. Only in the case of trimethylphosphine sulphide was more than one method used to study the structure

TABLE 2. Structural data[a] for some tertiary phosphine sulphides

Molecule	Method[b]	r(P=S)	r(P—C)	∠ SPC	∠ CPC	R^c	Ref.
$Me_3P=S$	M	193.6	181.4	114.4	—	< 0.2	112
	E	194.0	181.8	114.1	104.5	4.8	92
	X	195.9	179.8	113.2	—	5.0	113
$[(Me_3P=S)_3Cu]ClO_4$	X	199.4	179.3	111.6	—	11	113
$(Me_3P=S)Cr(CO)_5$	X	199.0	179.2	112.4	106.4	6.5	114
$(cyclohexyl)_3P=S$	X	196.6	183.9	110.9	108.0	5.8	115
$(cyclopropyl)_3P=S$	X	193.9	178.5	113.4	104.9	6.0	116
$Ph_3P=S$	X	195.0	181.7	113.1	105.7	4.6	117
$(2\text{-}MeC_6H_4)_3P=S$	X	194.8	181.9[d]	112.6	106.1[e]	9.0	101
$(3\text{-}MeC_6H_4)_3P=S$	X	193.6	181.5	112.3	106.5	8.0	118,119
$(4\text{-}ClC_6H_4)Ph_2P=S$	X	194.9	180.7	112.9	105.9	5.2	120
$(4\text{-}BrC_6H_4)Ph_2P=S$	X	195.0	181.6	113.1	105.7	5.1	121
$(4\text{-}CH_3C_6H_4)Ph_2P=S$	X	194.8	179.4	113.7	105.2	6.7	122
$Ph_2P(S)C\equiv CP(S)Ph_2$	X	192.3	176.3	113.8	101.8	4.0	123
			179.5[f]	114.9[g]	108.3[h]		

[a] r(P—X) = bond length in pm; ∠ XPY: bond angle in degrees, mean values are quoted, unless otherwise noted.

[b] E = electron diffraction; X = X-ray crystallography at room temperature.

[c] R = reliability index = 100 × conventional *R* for both X and E, except where indicated otherwise; see original papers for definitions; percentage error for M.

[d] d(P = C) range = 177.3–187.0 pm.

[e] ∠ CPC range = 101.5–110.6°.

[f] P—C_{Ph}.

[g] S—P—C_{Ph}.

[h] C_{Ph}—P—C_{Ph}.

and, again, agreement was only moderate, although the gas-phase methods are in good agreement.

The PS bond length is in the range 194–195 pm. However, unlike the oxide, this shows variation with environment. Metal complexation causes it to increase by about 5 pm while conjugation appears to cause a decrease of about 2 pm. Again, it may be that P—C(alkyl) is less than P—C(aryl), but there are not enough data. This PS bond length may be compared with that of a typical PS single bond of about 208–210 pm (208.5 pm for bridging bond in P_4S_{10}[89,90]). Hence the PS bond also has high multiple character.

The PC bond length in phosphine sulphides is in the range 181–182 pm, somewhat longer than in the oxides. Once again there is a more noticeable change (decrease of 2 pm) on metal complexation at oxygen. The deviation of the bond angles from the tetrahedral values is similar to that in the oxides (CPS, 112–114°; CPC, 104–107°). The structure of the fairly bulky tricyclohexylphosphine sulphide shows, to a lesser extent, the same trends as tri(*tert*-butyl)phosphine oxide of longer bond lengths and equalization of bond angles.

D. Phosphine Selenides

Table 3 shows data from nearly all structural studies of tertiary phosphine selenides. Again, X-ray crystallography has been the method of choice and, again, only the trimethyl derivative has been studied by other methods with only slightly better agreement between them than for the oxides and sulphides.

The PSe bond length is normally in the range 209–211 pm. However, there is not enough variation in the groups attached to phosphorus to make generalizations on trends in the PSe bond length, although it is noticeable that, as usual, bulky groups increase it. Other discernible trends (e.g. shortening of PSe with electronegative substituents) may not be crystallographically significant. This PSe bond length may be compared with the PSe single bond length of 224 pm (bridging bond in P_4Se_3[89]) and again it is apparent that the PSe bond has high multiple character.

The PC bond length in phosphine selenides is variable, covering the range 178–185 pm with more values in the upper part of the range (181–184 pm). Comparison of the trimethyl and triphenyl derivatives strongly suggests that P—C(alkyl) is less (by 4 pm) than P—C(aryl), but other data in Table 3 contradict this. The deviation of the bond angles from the tetrahedral values is similar to that in the oxides and sulphides (CPSe, 112–114°; CPC, 104–107°). Again, the structure of the fairly bulky tris(2,4-dimethoxyphenyl)phosphine selenide shows, to a lesser extent, the same trends as tri(*tert*-butyl)phosphine oxide of longer bond lengths and equalization of bond angles. However, the tris(trimethoxyphenyl) derivative is anomalous in this respect in that crowding is avoided by a marked asymmetry of the substituents[130].

Allen and coworkers[129] advanced two arguments for the shortening of the P—C bond in the 2-furyl derivative; a π-type interaction with the substituent or the lower steric demand of the 2-furyl group. Given that the CPC angle is also narrowed (a bond length–bond angle relationship), it seems more reasonable to prefer the steric argument.

E. Phosphine Tellurides

To date there appear to be structural data for only one tertiary phosphine telluride[137]. Unfortunately, this is the tri(*tert*-butyl) case (included in Table 4). We have already noted the totally anomalous nature of the structure of tri(*tert*-butyl)phosphine oxide. Comparison of these (Table 4) shows that the same unusual structural characteristics are present in the telluride as in the oxide. Thus the CPC angle is greater than the TePC angle and the PC bond length is very long (same length as in the oxide), in contrast to all other tertiary phosphine chalcogenides. There must therefore be a strong suspicion

TABLE 3. Structural data[a] for some tertiary phosphine selenides

Molecule	Method[b]	r(P = Se)	r(P—C)	∠SePC	∠CPC	R[c]	Ref.
$Me_3P{=}Se$	E	209.1	181.6	113.8	104.8	9.1	124
	X	211.1	178.6	113.1	105.7	4.8	125
	N	—	—	—	105.0	±0.2	126
$Ph_3P{=}Se$	X	210.6	183.0	113.1	106.0	7.0[d]	127
$(2\text{-}MeC_6H_4)_3P{=}Se$	X	211.6	183.4	112.7[k]	106.4	6.7	101
$(3\text{-}MeC_6H_4)_3P{=}Se$	X	210.9	182	112.3	106.7	11	119
$(3\text{-}CF_3C_6H_4)_3P{=}Se$	X	209.4	181.5	113.1	105.6	5.4	128
$(2\text{-furyl})_3P{=}Se$	X	209.4	177.8	115.0	103.5	3.8	129
$(2,4\text{-}(MeO)_2C_6H_3)_3P{=}Se$	X	213.5	184.3	111.1[e]	107.9[f]	5.2	130
$(2,4,6\text{-}(MeO)_3C_6H_2)_3P{=}Se$	X	211.9	182.7[g]	112.8[h]	106.2[i]	6.4	130
$Ph_2P(Se)CH_2P(Se)Ph_2$	X	210.0	184.3	114.9	104.6	4.4	131
			181.1[j]	113.1[k]	105.5[l]		
$Ph_2PCH_2P(Se)Ph_2$	X	210.3	182.6	113.6	105.0	3.9	132
			181.3[j]				
$PhMePrP{=}Se$	X	211.9	182.3	113.1	105.7	4.8	133
			180.0[j]				
			185.4[m]				
$Ph_2P(Se)C{\equiv}CP(Se)Ph_2$	X	209.7[n]	178.3	112.7	102.6	6.3	134
			183.2[j]	114.5[k]	108.8[l]		

[a] r(P—X) = bond length in pm; ∠XPY = bond angle in degrees; mean values are quoted, unless indicated otherwise.

[b] E = electron diffraction; X = X-ray crystallography at room temperature; N = NMR in liquid crystal (nematic) phase.

[c] R = reliability index = 100 x conventional R for both X and E, except where indicated otherwise; see original papers for definitions.

[d] $R = R_w$.

[e] ∠SePC = average of 106.2, 110.0 and 117.0°.

[f] ∠CPC = average of 102.1, 110.5 and 111.0°.

[g] r(P—C) = average of 180, 182 and 186 pm.

[h] ∠SeCP = average of 103.6, 116.3 and 118.5°.

[i] ∠CPC = average of 97.8, 108.7 and 112.0°.

[j] P—C_{Ph}.

[k] Se—P—C_{Ph}.

[l] C_{Ph}—P—C_{Ph}.

[m] P—C_{Pr}.

[n] r(P—C) = average of 212.4 and 206.9 pm.

that the PTe bond length of 236.8 pm is not typical of tertiary phosphine tellurides. In fact, analogy with tri(*tert*-butyl)phosphine oxide suggests that it is significantly too long. If it were too long by the same percentage as in the oxide (6.7%), then the true length would be about 222 pm.

Against this it must be said that the PTe distance found in the other phosphine tellurides examined is, in some cases, of the same order of magnitude as this. There have been four other crystal structures reported, yielding five phosphine telluride PTe distance measurements[151-153] of 228.8, 232.2, 232.7, 235.4 and 235.6 pm. The 235.6 pm value is for the trismorpholino derivative, which, it could be argued, is crowded, leading to longer bond lengths. On the other hand, the trismorpholinophosphine selenide analogue had a normal PSe bond length[154]. The other reported structures all involve phosphorus with two nitrogen ligands in a four-membered ring; again, it could be argued that this is an unusual situation. It would be helpful to know if tri(*tert*-butyl)phosphine selenide has a longer than usual PSe bond. Even with this uncertainty, it should be noted that a PTe bond length of 236.8 pm corresponds to a bond order of 1.5 calculated[24,137] using the covalent radii of Schomaker and Stevenson.

TABLE 4. Comparison of structural data[a] for some tertiary phosphine chalcogenides $R_3P{=}Y$

Molecule	Method[b]	r(P=Y)	r(P—C)	∠YPC	∠CPC	R[c]	Ref.
Me_3P	E	—	184.7	—	98.6	—	135
$Me_3P{=}O$	E	147.6	180.9	114.4	104.1	5.2	92
$Me_3P{=}S$	E	194.0	181.8	114.1	104.5	4.8	92
$Me_3P{=}Se$	E	209.1	181.6	113.8	104.8	9.1	124
Bu^t_3P	X	—	191.9	—	109.9	—	136
$Bu^t_3P{=}O$	E	159.0	188.8	106.1	112.9	9.7	94
$Bu^t_3P{=}Te$	X	236.8	189.6	108.7	110.2	6.9	137
Ph_3P	X	—	182.8	—	103.0	—	138
$Ph_3P{=}O$	X	148.4	180.3	112.3	106.6	4.5	97
$Ph_3P{=}S$	X	195.0	181.7	113.1	105.7	4.6	117
$Ph_3P{=}Se$	X	210.6	183.0	113.1	106.0	7.0	127
$(2\text{-}MeC_6H_4)_3P$	X	—	183.5	—	101.7	4.5	101
$(2\text{-}MeC_6H_4)_3P{=}O$	X	147.4	181.0	112.9	106.0	7.5	101
$(2\text{-}MeC_6H_4)_3P{=}S$	X	194.8	181.9[d]	112.6	106.1[e]	9.0	101
$(2\text{-}MeC_6H_4)_3P{=}Se$	X	211.6	183.4	112.7	106.4	6.7	101
$(3\text{-}MeC_6H_4)_3P$	X	—	183.5	—	101.7	10.7	119
$(3\text{-}MeC_6H_4)_3P{=}S$	X	193.6	181.5	112.3	106.5	8.0	118, 119
$(3\text{-}MeC_6H_4)_3P{=}Se$	X	210.9	182	112.3	106.7	11	119
$(4\text{-}ClC_6H_4)Ph_2P{=}O$	X	148.5	180.5	111.9	107.0	4.7	102
$(4\text{-}ClC_6H_4)Ph_2P{=}S$	X	194.9	180.7	112.9	105.9	5.2	120
$(4\text{-}BrC_6H_4)Ph_2P{=}O$	X	149.7	180.8	112.0	106.9	6.4	103
$(4\text{-}BrC_6H_4)Ph_2P{=}S$	X	195.0	181.6	113.1	105.7	5.1	121
$Ph_2P(O)CH_2P(O)Ph_2$	X	149.1	181.9 179.4[f]	112.0	106.8	6.3	107
$Ph_2P(Se)CH_2P(Se)Ph_2$	X	210.0	184.3 181.1[f]	114.9 113.1[g]	104.6 105.5[h]	4.4	131
$Ph_2PC{\equiv}CPPh_2$	X	—	176.5 183.2[f]	—	100.2 102.8[h]	6.1	139
$Ph_2P(O)C{\equiv}CP(O)Ph_2$	X	148.1	179.4 180.8[f]	114.4 112.9[g]	103.7 108.5[h]	3.9	108
$Ph_2P(S)C{\equiv}CP(S)Ph_2$	X	192.3	176.3 179.5[f]	113.8 114.9[g]	101.8 108.3[h]	4.0	123
$Ph_2P(Se)C{\equiv}CP(Se)Ph_2$	X	209.7[i]	178.3 183.2[f]	112.7 114.5[g]	102.6 108.8[h]	6.3	134

[a] r(P—X) = bond length in pm; ∠XPY = bond angle in degrees; mean values are quoted, unless indicated otherwise.

[b] E = electron diffraction; X = X-ray crystallography at room temperature.

[c] R = reliability index = 100 x conventional R for both X and E, except where indicated otherwise; see original papers for definitions.

[d] d(P—C) range = 177.3–187.0 pm.

[e] ∠CPC range = 101.5–110.6°.

[f] $P{-}C_{Ph}$.

[g] $Y{-}P{-}C_{Ph}$.

[h] $C_{Ph}{-}P{-}C_{Ph}$.

[i] d(P—Se) = average of 212.4 and 206.9 pm.

F. Comparison of Phosphine Chalcogenides

First, from the discussions in the previous sections, the contraction in PY distance from a standard single bond to that in R_3PY is similar for oxides, sulphides and selenides, being in the range 6.5–7.5%. Within that range, the oxides have the largest contraction

(7.5%), sulphides are next (7.2%) and selenides have least (6.7%). Hence the three types of compound probably have similar PY bond orders with minor differences in the order O > S > Se.

Tables 4 and 5 show comparisons of the structures of phosphine chalcogenides with the parent phosphines and other pnictogen chalcogenides. A number of interesting trends may be gleaned from these comparisons. As mentioned in previous sections, there is little variation in either CPY or CPC angles in the chalcogenides and it can be seen from Table 4 that all are larger than in the parent phosphines. This is attributed in the valence shell electron pair repulsion (VSEPR) theory to greater repulsion from the lone pair than from the oxo, sulphido or seleno ligand.

The PC bond length calculated[24] by the Schomaker–Stevenson equation is 184 pm, which, not surprisingly, is the typical PC bond length in tertiary phosphines. Also in tertiary phosphines P—C(alkyl) is slightly larger than P—C(aryl), which is probably a bond length–bond angle relationship since alkyl CPC angles are less than aryl CPC angles[1]. The following related observations were taken from Tables 4 and 5:

(i) The PC bond length decreases on formation of the chalcogenide. However, it can also be seen that the fall is greatest for oxides (– 4 pm), is less for sulphides (– 2.5 pm) and may be less again for the selenides (– 1 pm, although this is not consistent). From Table 5, it can be seen that there are similar decreases in the PF and PCl bond lengths in the series $F_3P > F_3PS > F_3PO$ and $Cl_3P > Cl_3PS > Cl_3PO$. These decreases may attributed to the increase in the effective electronegativity of the phosphorus atom due to its extra positive charge in the chalcogenides which is in the order O > S > Se (see Section IV.A). The detailed differences in the lengths of the PA bond in A_3PY molecules

TABLE 5. Comparison of structural data[a] for some pnictogen chalcogenides $A_3Pn{=}Y$

Molecule	Method[b]	r(Pn=Y)	r(Pn—A)	∠ YPnA	∠ APnA	Ref.
$Me_3P{=}O$	E	147.6	180.9	114.4	104.1	92
$F_3P{=}O$	E	143.6	152.4	—	101.3	140
$Cl_3P{=}O$	E	144.9	199.3	—	103.3	140
$(MeO)_3P{=}O$	E	147.7	158.0	—	105	141
$Me_3P{=}S$	E	194.0	181.8	114.1	104.5	92
$F_3P{=}S$	E	186.6	153.8	117.9	99.6	142
$Cl_3P{=}S$	E	188.5	201.1	—	101.8	140
Me_3N	M		145.1		110.9	91
$Me_3N^+{-}O^-$	X	138.8	147.7			143
F_3N	M		136.5		102.4	91
$F_3N{=}O$	E/M	115.9	143.2	117.4	100.5	144
F_3P	E		157.0		97.8	145
$F_3P{=}O$	E	143.6	152.4	—	101.3	140
$F_3P{=}S$	E	186.6	153.8	117.9	99.6	142
Cl_3P	E		203.9		100.3	146
$Cl_3P{=}O$	E	144.9	199.3	—	103.3	140
$Cl_3P{=}S$	E	188.5	201.1	—	101.8	140
Me_3As	E		196.4		96.0	124, 147
$Me_3As{=}O$	E	163.1	193.7	112.6	—	92
$Me_3As{=}S$	E	205.9	194.0	113.4	—	92

[a] r(Pn—A) = bond length in pm; ∠ APnA = bond angle in degrees.

[b] E = electron diffraction; X = X-ray crystallography at room temperature; M = microwave spectroscopy.

have been interpreted as evidence of strengthening by a π-bonding component in some cases[124].

(ii) Most interestingly, the only exception to (i) (which is strongly in the other direction) is for the PC bond to an alkyne carbon. This is difficult to explain.

(iii) Also difficult to explain is that P—C(alkyl) is probably less than P—C(aryl) for all the chalcogenides although, as noted above, there are not enough data to be sure. There is no apparent bond length–bond angle relationship in this case.

(iv) There is a consistent variation in PO and PS bond lengths in that they decrease over the series $Me_3PO > Cl_3PO > F_3PO$ and $Me_3PS > Cl_3PS > F_3PS$. These shortenings again suggest a polarity effect which may be discussed in terms of the VSEPR theory; with more electronegative groups the electron pairs of the bonds are displaced away from phosphorus allowing the oxo or sulphido ligand to approach closer[140,155]. However, an exception may be trimethylphosphate, which has the same PO bond length as trimethylphosphine oxide, although this may be a steric effect since the terminal PO bond length in P_4O_{10}[88] is 139 pm.

For the nitrogen analogues the following comments and comparisons are derived from Table 5:

(i) The NO bond length in trimethylamine oxide is close to the NO single bond length in hydroxylamine (145.3 pm)[91], while the NO length in trifluoroamine oxide is very significantly shorter and must be accorded the status of a double bond.

(ii) There is a much larger decrease in the NO distance from the trimethyl to the trifluoro compound than in the analogous PO distance. Undoubtedly this is due both to the increased electronegativity and a strong steric effect at the small nitrogen atom.

(iii) There is an *increase* in both NC and NF bond lengths on formation of the oxide. This is the opposite of the trend noted above for the phosphine oxides. However, again, the extra factor is the small size of the first-row atom so that the ligands are already close together and the additional oxygen means they have to move apart.

IV. BONDING

For the reasons outlined in the Introduction (Section I), studies of the bonding in phosphine oxides, sulphides and selenides have concentrated on the nature of the PO bond, and to a lesser extent the PS and PSe bonds. Particular issues which have been of concern are (i) the great strength of the PO bond, (ii) the exact distribution of the electron density in the PO bond, (iii) the difference between the PO bond in phosphine oxides and the NO bond in amine oxides and (iv) the difference between the oxides and the sulphides and selenides.

A. Other Experimental Observations

From the bond lengths reported in Section III, it is clear that the phosphoryl (and thio- and seleno-phosphoryl) bond has high multiple character. In the case of the oxides, since the bond length is shorter than in HPO and of the same order as diatomic PO, the bond order lies between double and triple. Some other physical measurements support this conclusion and provide further insights.

1. Bond energies

Strong multiple character is also suggested by the paltry number of bond energies that are available for phosphine oxides and sulphides, a selection of which are given in Table 6. It can be seen that the PO bond dissociation energy is usually in the range 536–577 $kJ\,mol^{-1}$ (128–139 $kcal\,mol^{-1}$) with the electronegatively substituted com-

TABLE 6. Bond dissociation energies[a] and stretching frequencies[b] in some phosphine chalcogenides $A_3P{=}Y$

Molecule	D(P=O)	ν(P=O)	Molecule	D(P=S)	ν(P=S)	Molecule	ν(P=Se)
H_3PO	464[c]	1240[d]					
Me_3PO	582	1170[e,f]	Me_3PS		567[f]	Me_3PSe	441[g]
Pr_3PO	577	1166	Pr_3PS	383	550		
Ph_3PO	536	1195	Ph_3PS		637[g]	Ph_3PSe	561[g]
F_3PO	540[h]	1418[f]					
Cl_3PO	510[h]	1298[f]	Cl_3PS	293[i]			
P_4O_{10}	577	1400					
P_4O_6	360[j]						
$(EtO)_3PO$	619[h]	1272	$(EtO)_3PS$	379	608		
$(EtO)_3P$	385[j]						
PO diatomic	586[k]	1218[f]					

[a] D(P=Y) in kJ mol^{-1} (kcal mol^{-1}), from ref. 156 unless indicated otherwise.

[b] ν(P=Y) in cm^{-1}, from ref. 156 unless indicated otherwise.

[c] Calculated, from ref. 14.

[d] Matrix isolated species from ref. 157.

[e] Actually 1169–1180 cm^{-1}.

[f] From refs 158 and 159.

[g] From ref. 7.

[h] From ref. 14.

[i] Quoted in ref. 3.

[j] Dissociation energy of PO single bond.

[k] ± 84 kJ mol^{-1}.

pounds at the higher end of the range. In agreement with chemical experience, however, both methyl and halogen substituents have a higher bond energy than unsubstituted phosphine oxide.

In general, these bond energies are of the same order as that in diatomic PO while a PO single bond energy is about 360–385 kJ mol^{-1} (86–92 kcal mol^{-1}). The difference of about 200 ± 20 kJ mol^{-1} can be taken as an indication of the extra energy in the phosphoryl bond over that in a PO single bond.

In a useful exercise, Kutzelnigg[14] developed a series of σ and π 'increments' for various multiple bonds which were derived by a combination of calculation and the limited experimental results. His value for the π increment of the PO bond (155 kJ mol^{-1}) is in rough agreement with the figure of 200 ± 20 kJ mol^{-1} derived above, given the many approximations that have to be made and the limited experimental data. The σ increment for the PO bond was given as 335 kJ mol^{-1} whereas for the NO bond the σ increment was 188 kJ mol^{-1}, with a π increment of 368 kJ mol^{-1}. Note that, as expected[1], π bonds formed by the second-row element are weaker than its σ bonds whereas it is the opposite for the corresponding first-row element.

Kutzelnigg[14] also calculated the bond dissociation energy for H_3PO (464 kJ mol^{-1}), H_2FPO (531 mol^{-1}) and H_3NO (222 kJ mol^{-1}) and, while obviously subject to some calculational inaccuracy (see Section IV.C.1), they can be helpful for comparison. Unfortunately, the experimental results for amine oxides are almost non-existent with the only reasonably reliable one[14] being a bond dissociation energy of 276 kJ mol^{-1} for the NO bond in F_3NO.

Based on these limited comparisons, it can be seen that the NO bond energy in trifluoroamine oxide is larger than the corresponding single bond whereas the strength of the PO bond lies between those for a double and a triple bond. Also, the bond energy of the PS bond is noticeably less than that of the PO bond, but a suitable single PS bond energy does not appear to be in the literature. It should be noted that the PO bond energy is expected to be greater than the NO bond energy. This is because in structure **1A** (see Section I) an electron is removed from phosphorus and the ionization potentials of R_3P are lower than those of R_3N. In addition, there will be interelectronic repulsions of the valence electrons around the small first-row atom.

2. Infrared spectroscopy

The strength and polarity of the PO bond in phosphine oxides is attested to by the very strong and diagnostic PO stretching frequency which occurs in the range 1100–1400 cm^{-1}, usually near 1200 cm^{-1}, and Table 6 includes the values for some representative compounds. These frequencies and the derived force constants have been used[3,160] to derive bond orders of about two for the PO bond, although this is variable for reasons discussed below. The PS stretching frequency is much lower than that of the oxide, as are the PSe frequencies[7,161], possibly indicating lower bond orders.

Other useful information can also be derived from infrared spectroscopy[3,162]. Indeed the only experimental study of unsubstituted phosphine oxide is an infrared spectrum of the matrix isolated species[157] which is discussed in Section IV.C.2. The value found in this study for the PO stretch (1240 cm^{-1}) is included in Table 6. There is a well established[3,6,158,162], approximately linear[163], relationship between PO stretching frequency and electronegativity of substituent, which can be seen qualitatively in Table 6. The more electronegative the substituent, the higher is the wavenumber and the higher is the PO bond force constant, in qualitative agreement with the trend of the bond energies.

There is one other interesting observation in Table 6. As mentioned in the previous section the bond energies of both methyl- and halogen-substituted phosphine oxides are higher than that of the unsubstituted compound. However, the PO stretching frequencies of alkyl- and aryl-substituted phosphine oxides are *lower* than that in the unsubstituted molecule whereas the halogen- and oxygen-substituted cases are *higher*. This suggests that the methyl group stabilizes the phosphoryl bond while decreasing its force constant and leads to the difficulties in assigning bond orders from infrared spectra, referred to above. This observation is in agreement with the theoretical studies of substituted phosphine oxides and is discussed further in Section IV.D.5.

3. Dipole moments

Phosphine chalcogenides have significant dipole moments, some of which are given in Table 7. As can be seen, for the tertiary derivatives the polarity increases in the series oxide < sulphide < selenide. However, when this is converted into charge separation across the PY bond the order becomes[92,164] oxide > sulphide ≈ selenide, in line with

TABLE 7. Dipole moments[a] of some tertiary phosphine chalcogenides

Molecule	μ(P=O)	μ(P=S)	μ(P=Se)
$Me_3P{=}Y$	4.29	4.73	
$Ph_3P{=}Y$	4.51	4.88	5.17
$F_3P{=}Y$	1.74	0.63	
$Cl_3P{=}Y$	2.42	1.42	

[a] μ in D, from refs 164 and 165 and references cited therein.

electronegativity considerations. As might be expected, dipole moments show an inverse relationship with substituent electronegativity[164,166]. The reduced charge separation found for the trihalo derivatives has been taken as evidence of increased backbonding[164]. The fact that substituent electronegativity has a greater effect on the charge separation in sulphides than in oxides suggests that there is less multiple character in the PS bond[164].

It has long been argued[92,167] that the PO bond moment is smaller than expected for the purely coordinate structure **1A**. Thus, if the structure were **1A**, then the expected bond moment should be

$$\begin{aligned}\text{electronic charge} \times \text{bond length} &= (1.602 \times 10^{-19}\,\text{C}) \times (1.49 \times 10^{-10}\,\text{m})\\ &= 2.39 \times 10^{-29}\,\text{C m} = 7.15\,\text{D}\end{aligned}$$

However, the actual bond moment, derived by measurement on the triphenyl derivative at the time of the original discussion[167], was 3.5 D, only about 50% of the theory, so a full electron has not been transferred from phosphorus to oxygen. A similar calculation for the NO bond, using available data from trimethylamine oxide, gave 6.66 D as the maximum theoretical value while the actual value was 4.3 D, 65% of the theory. This was then be taken as evidence of a greater amount of backbonding of electron density from oxygen to phosphorus than from oxygen to nitrogen. However, this argument can be criticized[21,168] because any two charges as near as a bond length will be polarized towards each other and the bond moment will be less. In fact, this may well be the case for the amine oxides and it is possible that the difference between them and the phosphine oxides is just the greater polarizability of phosphorus. Indeed, the reduction in expected bond moment for phosphine sulphides is greater again (abut 30% of the theory), in line with the greater polarizability of sulphur. Recent, more sophisticated, measurements and calculations[169] gave the limits for the PO bond moment as 3.26–4.72 D and the PS moment as 3.65–4.85 D. Hence the issue remains unclear.

4. Magnetic resonance spectroscopy

Nuclear magnetic resonance (^{31}P, ^{1}H and ^{13}C) confirms that there is a high degree of positive charge at phosphorus in the tertiary chalcogenides and that there is multiple binding[161,170–173]. Thus, in the ^{31}P spectra of the oxides, the phosphorus atom is strongly deshielded relative to the parent phosphine, typically by about 30–40 ppm, but it can be much more[170]; for example, for the triphenyl case $\Delta\delta \approx 37$ ppm whereas for the trimethyl case $\Delta\delta \approx 100$ ppm. In a comparison of a number of bisphosphine chalcogenides, Grim and Walton[161] found that the charge developed at the phosphorus atom increased in the order oxide ($+0.29$) < sulphide ($+0.47$) < selenide ($+0.52$), in agreement with the dipole moments. Since this is not the order expected on the basis of the electronegativity of the chalcogens, they concluded that there was more backbonding for the oxide than the sulphide or selenide.

Other evidence for multiple bonding is provided by, among others, (i) ^{31}P chemical shift anisotropies, which show stronger shielding in the direction of the P=X bond[174–176], (ii) ^{31}P–^{77}Se coupling constants[177] and (iii) ^{17}O nuclear quadrupole double resonance[178].

5. Photoelectron spectroscopy

The core and valence ionization potentials of some phosphine chalcogenides are given in Table 8. From the core values we expect information on the degree of charge on the atom concerned[180], whereas the first ionization potential in these molecules corresponds to the loss of an electron from a chalcogenide lone pair[19,68,69,179,184,185]. For our purposes it is unfortunate that core potentials tend to be large and show only a small

TABLE 8. Core[a] and valence[b] ionization potentials[c] for some phosphine chalcogens and related molecules

Molecule	P(2p)	O(1s)	S(2p)	Se(3p)	1st IP
Me_3P	135.9				
Me_3PO	137.8	536.1			9.9
Me_3PS	137.5		166.9		8.48
F_3P	141.8				
F_3PO	143.0	539.1			13.52
F_3PS					11.05
Me_3NO		537.7			8.43
F_3NO		542.0			14.11
H_2O		539.8			12.91
Cl_3P	139.6				
Cl_3PO	140.9	537.8			11.93
Cl_3PS	140.5				
Ph_3P	131.1				
Ph_3PO	132.8	531.1			
Ph_3PS	132.6		162.0		
Ph_3PSe	132.6			160.8	
Ph_3PBF_3	132.2				
$Ph_4P^+Cl^-$	133.0				

[a] From refs 179–183; more accurate comparisons of molecules would be possible using data from one source only, but no one source covers the full range of molecules given.

[b] From refs 179 and 184.

[c] In eV; although some of these values are very precise, the accuracy is ca ± 0.3 eV.

variation with environment. Also, although there are valence ionization energies for a good number of phosphoryl derivatives in the literature[186–188], the data for tertiary phosphine oxides are sparse. However, some useful trends can be discerned from Table 8.

As expected, phosphorus core ionization energies in the chalcogenide derivatives are higher than those for the parent phosphine, reflecting a high positive charge at phosphorus[180,190]. Conversely, in most cases, the oxygen core potentials are lower than that for water, for example, with the striking exception of F_3NO. The elevation of the phosphorus value for the triphenylphosphine chalcogenides is about half that in tetraphenylphosphonium salts, indicating that there is not as great a positive charge at phosphorus in the former. In the few cases where comparison of chalcogenides is possible, the elevation for the sulphides and selenides is similar and less than that in the oxide, indicating a greater charge at phosphorus in the latter, as expected. Comparison of analogous phosphine and amine oxides shows that there is a larger negative charge on oxygen in the former, in agreement with electronegativity predictions. The same trends as these were found in the X-ray K emission spectra of triphenylphosphine and its oxide[190,191]. Finally, there is a change of about 2 eV in the P(2p) core potential on formation of phosphine oxides but the analogous change in N(1s) for amine oxides is much larger (4 eV), which could be taken to indicate backbonding in the phosphorus derivatives[181].

Similar conclusions can be drawn from the valence ionization potentials. First, although not shown in Table 8, there is an overall stabilization of orbital energies in the X_3P moiety in X_3PY compared with those in the parent X_3P species[184]. This corresponds to a charge transfer from the X_3P group to the Y atom[184]. From Table 8, the first ionization potential of tertiary phosphine oxides and amine oxides is less than that in water. This is consistent with an increased negative charge at oxygen. The exceptions are the trifluoro derivatives, which may be taken as evidence of extensive backbonding or may be solely due to electronegativity[188]. Also, the first ionization potential of trimethylphosphine oxide is greater than that in trimethylamine oxide, indicating a lesser charge at oxygen in the phosphine oxide. Finally, the first ionization potential of sulphides is less than that of the analogous oxide, in line with electronegativity.

B. Qualitative Considerations

To summarize the experimental observations so far: the phosphoryl bond is strong, short and polar and, whereas the sulphur and selenium analogues are similar, they are not quite as strong and are more polar. Most estimates of bond order give the PO bond as greater than two and the PS and PSe bonds as less than two. As mentioned in the Introduction (Section I), the standard description of the PO bond to account for these observations has been in terms of a resonance hybrid of structures **1A** and **1B**. The extra bond in the case of **1B** is formed by backbonding of lone-pair electron density from oxygen into suitable acceptor orbitals on phosphorus. Qualitatively, there are some obvious problems with this description.

First, the double bond formalism clashes with the octet rule. Until fairly recently, it was usual[3–13,192] to sidestep this issue by saying that this indicated that 'an expansion of the octet is required', which is a euphemism for saying that the octet rule is broken by these compounds. Also, until recently, there was a smoothly made connection[3–13,192] that this indicated that 'the low-lying atomic d orbitals are involved in hybridization at phosphorus'. We now know (Section II) that there is no role for valence d orbitals in bonding within the Main Group of the Periodic Table.

Second, the structures **1A** and **1B** are not mutually exclusive. For example, consider the overlap of oxygen lone pairs with suitable receiving orbitals on phosphorus. No matter what receiving orbitals are envisaged (either the d orbitals or some other combination—see below), the overlap would be highly unsymmetric with most of the electron density near oxygen[29]. Hence the double bond structure **1B** would necessarily lead to a polar molecule anyway. Alternatively, one could consider that the PO bond is a pure σ single bond formed by donation of the phosphine lone pair into a vacant p orbital on O (preserving the octet at phosphorus). Then the phosphorus carries a full positive charge and the oxygen a full negative change. The proximity of these two opposite charges must surely lead to a strengthening of the PO link via an ionic type of attraction. It has been often implied[21], but has not been shown explicity, that this does not account fully for the shortened PO distance and the increased bond strength.

A final difficulty is that there may be more than one way of having a π-type backbonding interaction from oxygen to phosphorus. In the case of d orbitals it was always recognized that this was the case[14,19,193], because there are two d orbitals of appropriate symmetry which could overlap with two oxygen lone pairs. This is obscured by the double bond formula **1B** and so a triple bond formula naturally arises[19]. An alternative description is as a resonance between structure 1A and a triple bond[20]. The description 'partial triple bond' is also reasonable[14,19] on the basis that the bond order is between two and three. This latter view involves one σ bond and two half π bonds and has become common recently[14,16]. Note that a formal triple bond from oxygen to phosphorus in these compounds would imply that phosphorus carries a negative charge and oxygen a positive charge, perhaps providing a qualitative rationalisation of the reduced PO bond moment discussed in Section IV.A.3, if indeed it really is reduced.

Of these difficulties the d orbital issue is easiest to deal with qualitatively. This is because there is available a perfectly reasonable alternative set of acceptor orbitals on phosphorus. We have already described[1] the backbonding in transition metal phosphine

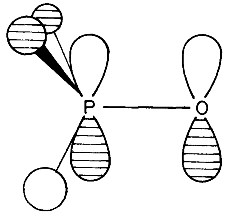


FIGURE 3. View of the bonding in phosphine oxide, showing one of the π backbonds formed by overlap of a lone pair on oxygen with an antibonding orbital of e symmetry on the H_3P moiety

complexes which is not into phosphine d orbitals but into the phosphine LUMO which is of σ^* type[194–197]. The backbonding in phosphine chalcogenides can be considered to be exactly analogous. In an AH_3 moiety there is a set of two antibonding orbitals with the e symmetry required to accept electron density from the oxygen lone pairs. These are the orbitals labelled $2e$ in Figure 3 in ref. 1 or Figure 9.6 in ref. 198. In the case of Me_3PO, H_3PO and F_3PO these are the $7e$, $3e$ and $7e$ sets, respectively (see Figure 5 in ref. 1). This alternative to d orbital involvement in the backbonding in phosphine oxides is shown in Figure 3. Some additional useful insights are provided by this analysis.

The structure of F_3NO was always very inconvenient for those who advocated the involvement of d orbitals to explain the structure of phosphine oxides. It will be recalled from Section III.F (Table 5) that the NO distance in this molecule is extremely short and must be accorded the status of a double bond and 'rightly or wrongly, few chemists would invoke the 3d-orbitals of nitrogen to explain the bonding'[199]. Thus its stability was 'somewhat surprising'[200]. Now that backbonding does not have to be into d orbitals there is no problem. Indeed, the NF bond is lengthened (see Table 5), consistent with population of the antibonding orbitals. The orbitals of F_3NO were analysed in detail by Grein and Lawlor[86], who concluded that the $3e$ orbital of NF_3 was the suitable acceptor orbital.

The energies of these antibonding acceptor orbitals are also interesting and those derived from a SCM–Xα–DV calculation[195] are detailed in ref. 1 (Figure 5 and Table 13 therein). In H_3P the $3e$ orbital is the LUMO at 0.88 eV whereas in F_3P the $7e$ orbital is the LUMO at -1.05 eV, but in Me_3P the lowest unoccupied orbital of e symmetry is the $7e$ orbital which is the NLUMO at 0.85 eV, the LUMO being $9a_1$ at 0.43 eV. Thus the appropriate acceptor orbital for the F_3P moiety of F_3PO is at significantly lower energy than that in H_3PO and Me_3PO, in agreement with greater backbonding leading to a stronger PO bond in F_3PO.

It should be noted that the idea of backbonding into antibonding orbitals to explain the bonding in phosphine oxides has been around for a long time. It is essentially the same as the concept of hyperconjugation or 'double-bond/no bond resonance'[180,199].

For the other qualitative difficulties with the description of the PO bond, we must hope that they will be answered by accurate calculation. However, as we shall see, they have not yet been satisfactorily resolved.

There is one further qualitative insight which is of value. There is a formal analogy between the semipolar bond, e.g, in H_3PO, and the bonding situation in phosphoranes such as H_3PF_2, just as H_2CO and H_2CF_2 are formally related[14,16]. In this way the PO bond can be viewed as analogous to the three-centre, two-electron bond developed by Rundle[39] to explain the bonding in phosphoranes. Note that this three-centre, two-electron bond model is not incompatible with some degree of backbonding.

C. Survey of *Ab Initio* Calculations on Phosphine Chalcogenides

At the outset, it is important to delineate what useful results should be expected from calculations on phosphine chalcogenides. Two objectives may be identified: (i) an understanding of the nature of the PO bond and (ii) predictions of the structure and properties of those members of the series which are not yet known molecules. It can be seen that these are much more ambitious objectives than in the case of, for example, calculations on the parent phosphines[1].

We have already discussed extensively[1] how calculations on phosphines have become reliable only in the last few years. The factors responsible for this (e.g. basis set inadequacy and lack of geometry optimization) apply with increased force to calculations on phosphine chalcogenides. Thus, for example, a calculation on phosphine oxide is likely to be at least 50% more difficult than phosphine owing to the increase in the number of electrons. However, an additional consideration for the chalcogenides is the increased need for polarization functions, due to the charge differences within the molecule, so that the actual increase in difficulty is even greater. Given the increased expectations for such calculations, we should not be too disappointed if they do not fulfil one or other of the objectives set out above.

1. Survey of calculations

Table 9 gives the results (total energy, geometry and dipole moment) of selected calculations on phosphine chalcogens (mainly oxides). It also includes amine oxides for comparison. The literature has been surveyed as far as the end of 1990. Owing to the extra computation required, the total number of calculations is less than for the phosphines but the quality is better. This is probably because investigators undertook studies only if they had the facilities to do so; for example, most workers took care to include polarization functions. Nevertheless, even for H_3PO, only a limited number include correlation corrections in MO treatments.

It is very difficult to assess the usefulness of the calculations whose results are reported in Table 9. In such an assessment, it is usual to examine the accuracy of predicted geometric, or other, parameters and whether the total energy has been minimized. Neither procedure is foolproof; sometimes geometry is predicted well at basis set levels which give poor results for other properties and the energy test must be carefully applied because, for example, augmenting the basis set for the inner shells has a significant effect on the total energy without improving the properties associated with the valence shell[18]. However, in this case, these difficulties are compounded by the fact that the most studied molecule, H_3PO, was unknown until recently and is very unstable. Hence its geometry is not available for comparison and the only information to date is the infrared spectrum of the matrix-isolated species[157]. This problem is discussed in detail in Section IV.C.2. It is appropriate to discuss separately the usefulness of the calculations for the two objectives mentioned above.

a. Prediction of unknown species. As regards the prediction of the structure and properties of unknown species, we may be fairly confident of reasonable accuracy in some of the latest calculations. Even so, perusal of Table 9 shows that the agreement of theory and experiment can, at best, only be described as modest. This is not surprising because it is expected[1] that basis sets of at least double zeta quality with polarization terms, full geometry optimization and some form of electron correlation will be necessary for the detailed description of compounds of third-row elements, and very few such calculations have been reported for phosphine oxides. It can be seen from Table 9 that the best split-valence and double zeta calculations are only just about adequate to describe consistently the geometric parameters of these molecules. Even then there are some worrying basis set effects; for example, the difference in predicted dipole moment for phosphine oxide between the 6–31G* and DZ + P basis sets[201] which are normally of comparable quality[22]. Basis set effects on the structure of phosphine oxide and fluorophosphine oxide have been studied in detail by two groups[201,207]. Also, there is

TABLE 9. Results of *ab initio* calculations on phosphine and amine chalcogenides $A_3E{=}Y$

Molecule	Calculation^a	Energy^b	r(E=Y)^c	r(E—A)^c	∠ YEA^d	μ^e	Ref.
$H_3P{=}O$	STO-3 G	−412.3567	165.6	138.3	118.7		201
	3–21 G	−415.0830	157.9	140.5	117.2	4.60	201
	3–21 G#	−415.2070	147.0	139.1	117.5		192
	3–21 G*	−415.2961	146.0	139.3	117.8	3.46	201
	4–31 G*	−416.8795	146.0	139.8	117.4		202
	6–31 G*	−417.3068	146.4	139.3	117.0	4.18	16, 201, 203, 204
	6–31 G**		146.5	139.6	116.9	4.19	205, 206
	DZ	−417.1831	160.5	140.5	116.0		207
	DZ + P	−417.3342	147.4	139.3	115.8	5.14	201
	TZ + P		145.6	139.2	116.0	4.22	206, 208
	> DZ + P + C^f	−417.5378					19
	TZ + P^g + C^h	−417.7140				3.87	208
$FH_2P{=}O$	STO-2 G#		142.1	139.0 H	117.2 H		209
				148.4 F	118.8 F		
	3–21 G	−513.4178	154.1	138.8 H	117.3 H	4.23	201
				161.5 F	114.5 F		
	3–21 G*	−513.7179	145.1	138.9 H	116.9 H	3.13	201
				154.2 F	115.7 F		
	> DZ + P	−515.9874	146.7	139.0 H^i	108.3 H^i	4.14	19
				157.8 F	117.3 F^i		
	6–31 G*^{j}	−516.2075					209
	6–31 G*^{j} + C^k	−516.6631					209
$MeH_2P{=}O$	STO-2 G#		141.7	138.5 H	118.2 H		209
				181.4 C	115.9 C		
	3–21 G*	−454.1131	146.5	138.1 H	116.1 H	4.28	210
				178.9 C	119.0C		

$F_3P{=}O$	STO-3G		155.7	161.2			211
	STO-2G#		140.9	149.0			209
	3–21G		150.6	157.5		1.48	212
	3–21G*	– 710.4446	142.7	152.7		1.75	212
	6–31G*		142.5	152.6	117.2		204
	> DZ + P^l	– 714.0301	145^i	157^i			213
	GVB–SOPP		147				17
	$EXPT^m$		143.6	152.4	116.8	1.74	140
$Me_3P{=}O$	STO-3G	– 528.1413	161.9	184.0	116.2		207
	3–21G		159.8	184.9		5.08	212
	3–21G*	– 531.8002	147.8	180.5		4.41	212
	6–31G*		147.4	182.0	113.8		204
	DZ	– 534.0490	159.2	182.8	113.9		207
	DZ + P^n	– 534.1679	148.0	180.0	114.4		207
	$EXPT^m$		147.6	180.9	114.4	4.29	92
$H_3P{=}S$	3–21G#	– 736.3530	192.0	138.9	117.3		20
	6–31G*		195.3	139.3	117.0	4.72^o	20, 204
$F_3P{=}S$	3–21G		204.2	158.9		1.03	212
	3–21G*	– 1031.6412	185.5	153.7		1.23	212
	6–31G*		187.4	153.5	118.1		204
	$EXPT^m$		186.6	153.8	118.1	0.63	142
$Me_3P{=}S$	6–31G*		196.5	182.4	114.0		204
	$EXPT^m$		194.0	181.8	114.1	4.73	92
H_3NO	4–31G	– 130.7596	153.1	101^i	109.5^i		214
	4–31G + P^p		145	100.1	108		215
	4–31G + BF	– 130.8057	140.0	101.0	111.0		86
	6–31G	– 130.8937	152	101^i	109.5^i	5.8	214
	6–31G*	– 130.9339	137.7	100.9	111.6	5.6	16, 214
	$GVB–SOPP^q$		142				17

(continued)

TABLE 9. (*continued*)

Molecule	Calculation[a]	Energy[b]	r(E=Y)[c]	r(E—A)[c]	∠ YEA[d]	μ[e]	Ref.
F_3NO	4–31 G	– 426.7288	118.7	141.2	117.2	0.88	215
	4–31 + BF	– 426.9059	117	136	116.6	1.20	86
	DZ + BF	– 427.4232	118	136	116.9	1.23	86
	DZ + BF + CI	– 427.7633	116	143	117.4	0.52	86
	6–31 G*		117.2	135.0	116.3		16
	GVB–SOPP		120				17
	EXPT[m]		115.8	143.1	117.1	0.04	144, 216
Me_2NO	STO – 3G	– 244.9079	158.2	147	109.5		214
	4–31 G	– 247.6864	146.6	147[i]	109.5[i]	5.2	214
	EXPT[m]		138.8	147.7		5.0	143, 217

[a] All self-consistent field, contracted Gaussian-type basis sets and geometry optimized by the gradient method unless indicated otherwise. Symbls STO-3 G, DZ, TZ, 3–21 G, 4–31 G and 6–31 G have their usual meanings[22]; * = a set of six d-type polarization functions added to basis set; # = a set of five d type functions added; P = other combinations of d functions added; BF = bond functions added as polarization functions; CI = with electron correlation by configuration interaction; C = with correlation by other methods; GVB–SOPP = generalized valence bond calculation employing the strong orthogonality and perfect pairing approximations.

[b] Total electronic energy in hartree; 1 hartree = 27.2 eV = 2625 kJ mol^{-1}.

[c] Bond length in pm; H, C or F identifies atom A.

[d] Bond angle in degrees; H, C or F identifies atom A.

[e] Dipole moment in debye.

[f] CEPA–PNO method; coupled electron pair approximation with pair natural orbitals.

[g] Two uncontracted d sets on P and one on O, one p set on H with added diffuse functions.

[h] Double substitution coupled cluster method—ACCD form.

[i] Assumed.

[j] Geometry optimized at STO-2 G# level.

[k] Correlation using Møller–Plesset perturbation theory.

[l] Two d sets on P.

[m] From Tables 1–5 and 7.

[n] Single d function on P.

[o] At STO-2 G# geometry.

[p] Single d set on N.

[q] At the geometry found for F_3NO by GVB–SOPP method.

no consistent trend in the errors in the prediction of geometric parameters, except of course the dramatic increase in bond lengths for both second- and third-row elements if polarization functions are omitted.

Notwithstanding the above comments, we may say with reasonable confidence that if the structure of phosphine oxide is determined in the future, the values will be $r(\mathrm{PO}) = 146.0 \pm 0.5$ pm, $r(\mathrm{PH}) = 139.4 \pm 0.2$ pm and $\angle \mathrm{HPO} = 116.5 \pm 0.5°$. Similar predictions can be made for other unknown species in Table 9. The bond length of 146 pm may be compared with those in HPO[91] (151.2 pm), diatomic PO[91] (147.6 pm) and a typical single PO bond (160 pm; bridging bond in P_4O_{10}[89]). Also, the PO length in H_3PO is about 2 pm shorter than in substituted phosphine oxides (Section III, Table 1) which is almost certainly a bond length–bond angle effect wherein oxygen can approach closer to phosphorus as the angle between the other ligands decreases. A similar effect is probably responsible for the shortening of the PH bond length from that in parent phosphine[1] (PH = 142 pm, HPH = 93.5°).

b. Nature of the PO bond. In this case we must be less sanguine. The results in Table 9 do not lead to total confidence in the usefulness of the calculations for the elucidation of the nature of the PO bond, a problem which has already proved intractable. They are only just about able to predict geometries with confidence, so we may feel legitimately mistrustful of their ability to describe the distribution of electron density in the region of the PO bond. More seriously, all theoretical studies so far on the nature of the PO bond have used either the 6–31G*, DZ + P or inferior levels of calculation and most have been on phosphine oxide. From Table 9 it can be seen that the lowest energy achieved so far for phosphine oxide is about 0.4 hartree below that at the 6–31G* or DZ + P levels. This is about twice the energy of the PO bond and was achieved by electron correlation. Hence, again, it is perfectly legitimate to feel uneasy as to whether the electron distribution in the PO region can be adequately described at these levels. Even with correlation, the computed PO strengths are significantly low; for example, Schmidt and Gordon[20] estimated the PO bond strength in F_3PO to be 467 kcal mol^{-1} (at the 6–31G* level with correlation by third-order Møller–Plesset theory using the 6–31G* geometry) whereas the experimental value[156] is 542 kJ mol^{-1}, an error of about 14%.

A further point is that the problem is made extra difficult by not being a comparative one. Often it is possible to obtain useful results at modest levels of calculation by comparing sets of molecules. In the determination of the PO bond, however, an absolute result is sought, namely its electron distribution. Even comparison with amine oxides may not be real since they may very well be different entities.

2. Infrared spectrum of phosphine oxide

As mentioned above, unlike the situation in the parent phosphines[1], there is a problem with comparison of theory and experiment for phosphine oxides. This is because it is only recently that good calculations could be done on anything other than $H_3P{=}O$ and, unfortunately, until recently this was an unknown molecule. Even now the only experimental study that has been reported is the infrared spectrum of the matrix-isolated species[157]. Two groups have attempted to calibrate the theory with this experimental[204–206]. However, this is more problematic than, for example, comparison of computed and measured molecular geometry data because of the extra step involved in computing the infrared spectrum.

Table 10 shows the comparison of experimental and calculated wavenumbers in the infrared spectrum of $H_3P{=}O$. Usually computed wavenumbers are considerably higher (10–15%) than experimental values and this can be seen clearly in Table 10 at all the

TABLE 10. Comparison[a] of experimental and calculated vibrational frequencies (cm^{-1}) in the infrared spectrum of $H_3P{=}O$

Mode	Experimental[b] ν_E	3–21 G#[c]		6–31 G*[d]			6–31 G**[e]			TZ + P[f]		TZ + P + A[g]	
		ν_C	Δ	ν_C	Δ	Δ_{sc}	ν_C	Δ	Δ_{sc}	ν_C	Δ	ν_C	Δ
PH a_1	2359	2687	328	2694	335	46	2647	288	23	2594	235	2500	141
PH e	2372	2644	272	2666	294	7	2618	246	−16	2573	201	2490	118
PO a_1	1240	1437	197[h]	1397	157	16	1389	149	10	1361	121	1341	101
HPH a_1	1144	1287	143[h]	1284	140	11	1282	138	10	1263	119	1245	101
HPH e	1114	1238	124	1246	132	−22	1238	124	0	1235	121	1213	99
HPO e	853	976	123	958	105	−13	959	106	7	933	80	922	69

[a] ν_E = experimental vibration frequency; ν_C = calculated harmonic vibration frequency at the indicated level of theory; $\Delta = \nu_C - \nu_E$; $\Delta_{sc} = \nu_C - \nu_E$ after scaling of the calculated value—see text.

[b] From ref. 157.

[c] From ref. 192.

[d] From ref. 204.

[e] From ref. 205.

[f] From ref. 206.

[g] A = with anharmonicity correction; from ref. 206.

[h] These frequencies interchanged from the assignment in the original work—see text.

levels of theory studied. Traditionally this difficulty has been addressed by using a scaling procedure; theoretical and experimental values are compared for related species for which data is available (e.g., PH_3 and $F_3P{=}O$ in this case) and scale factors are computed to adjust the theoretical wavenumbers for the unknown species. Scaling procedures attempt to remove systematic errors which may be due, for example, to basis set incompleteness, neglect of electron correlation or neglect of anharmonicity considerations[205,218,219]. Table 10 includes scaled values for two of the theory levels.

Returning to the question of the quality of the calculations, as can be seen from Table 10, after scaling, the predicted frequencies are accurate to about $20\,cm^{-1}$ in most cases. Schneider and coworkers[204] were non-committal about the quality of the scaled 6–31G* results, being fairly content with the PO modes but less than satisfied with the PH stretching modes (2359 and $2372\,cm^{-1}$), whereas Person and coworkers[205] considered that the scaled 6–31G** results were spectacularly good. However, it can also be seen from Table 10 that there is still a substantial difference in absolute terms between theory and experiment because, even after including a correction for anharmonicity, the calculated wavenumbers at the triple zeta plus polarization level are still approximately 5–10% higher than the experimental values. This reviewer concludes that better than TZ + P and substantial consideration of correlation effects will be necessary for satisfactory agreement between experiment and theory for the infrared spectrum of $H_3P{=}O$. This reinforces the conclusions of the previous section on the usefulness of these calculations for determining the nature of the PO bond.

A subsidiary, but significant, issue is that there is inevitable uncertainty as to the frequency of the PO stretch in H_3PO due to strong mode mixing from the H_3P bending mode[205]. For consistency because of this, in the 3–21G# column in Table 10, the values for PO stretch ($1437\,cm^{-1}$) and HPH bend ($1287\,cm^{-1}$) (both a_1 modes) are the reverse of those in the original work. Incidently, and ironically, Schmidt and coworkers[192] used this calculated value of $1287\,cm^{-1}$ to argue that the PO bond fell far short of a double bond in comparison with the calculated value of $1498\,cm^{-1}$ for the PO bond in the HPO molecule. With the revised assignments, this argument would lead to the opposite conclusion.

The PO force constant derived from the infrared spectrum[157] is $9.53 \times 10^2\,N\,m^{-1}$. This may be compared with the force constants for the PO bonds in[157] H_2POH ($4.39 \times 10^2\,N\,m^{-1}$), HPO ($8.67 \times 10^2\,N\,m^{-1}$) and diatomic PO ($9.24 \times 10^2\,N\,m^{-1}$). This confirms that the PO bond in stronger than a single or double bond and is comparable to, or greater than, the bond strength in diatomic PO.

3. *Population analyses*

A widely used device in the analysis of wavefunctions is population analysis[22]. This seeks to find, among other properties, regions of charge build-up, orbital occupancy and bond order. There are a number of methods available for this purpose[22], that of Mullikan being the most commonly used for phosphorus compounds. Others used have been that of Ahlrichs and coworkers[220,221] and the natural population analysis[222] based on the natural bond orbitals (see Section IV.D.1). A slightly different approach is the calculation of integrated spatial electron populations (ISEP) for regions bounded by minima in the projected electron density functions[21]. These methods were developed later than the Mulliken method and all claim to be better.

Table 11 gives a comparison of some results from the various population analyses which have been applied to phosphine oxides and related molecules. Population analysis, especially the Mulliken method, has been subject to much criticism[14,16,22,222] as being basis set dependent and giving unphysical results. In fact, as noted by Kutzelnigg[14], a difficulty with most population analyses of this kind (based on the LCAO method) is

TABLE 11. Population analyses[a] from *ab initio* studies of $A_3E=Y$ compounds and related molecules

Molecule	Method[b]	Calculation[c]	*q*E	*q*Y	*q*A	*p*EY	Ref.
$H_3P{=}O$	M	6-31 G*	0.92	−0.72	−0.07	0.56	203
	M	> DZ + P	1.33	−0.97		0.71	19
	M	TZ + P	0.84	−0.97	0.04		208
	M	TZ + P + C	0.72	−0.86	0.05		208
	H	> DZ + P	1.12	−0.78		1.78	19
	N	6 − 31 G*	1.51	−1.16	−0.12	0.73	16
	I	3-21 G*	1.83	−1.53	−0.10		201
	I	6-31 G*		−1.53			201
	I	DZ + P		−1.58			201
H_2POH	M	> DZ + P	0.58	−0.56		0.35	19
H_3NO	M	> DZ + P	0.39	−0.76		0.35	19
	N	6-31 G*	−0.46	−0.74	0.40	0.84	16
H_2NOH	M	> DZ + P	0.08	−0.48		0.60	19
$H_2FP{=}O$	M	STO-2 G#	1.24	−0.65	−0.40 F		209
	M	> DZ + P	1.82	−1.01		0.80	19
	H	> DZ + P	1.40	−0.77		1.94	19
	I	3-21 G		−1.23	−0.81 F		201
	I	3-21 G*		−1.51	−0.86 F		201
$MeH_2P{=}O$	M	STO-2 G#	1.03	−0.69	−0.78 C		209

[a] *q*E/Y/A = net atomic charge on E/Y/A; H, C or F identifies A atom; *p*EY = overlap population of EY bond.

[b] Type of population analysis: M = Mulliken, H = Heinzmann–Ahrichs, N = natural population, I = ISEP; see text for explanations.

[c] see footnote *a* in Table 9.

that any resolution of the charge density in a molecule into atomic contributions is not unique. Thus one seeks not to analyse the population of an individual molecule (which is not very meaningful) but to compare different molecules with the same or comparable AO basis sets and, so long as the basis sets are balanced[14], one hopes that reliable results may be obtained.

Examination of Table 11 shows the expected strong dependence on basis set of Mulliken populations. Note, for example, the variation for H_3PO even among the higher quality basis sets. Also, as expected, there is wide variation among the different methods of population analysis, both for atomic charges and overlap populations. However, it is clear that the PO bond is strongly polarized, phosphorus having a net charge near 1.0 whereas oxygen has charge of about − 1.0. It should be emphasized that the absolute values in Table 11 have no useful meaning, especially the overlap populations, but comparisons may be valid. Thus, with care, other conclusions can be drawn from Table 11 which will be discussed in the following sections.

D. Detailed *Ab Initio* Studies of the Bonding

Given the comments in Section IV.C.1 on the usefulness of the calculations reported so far, the reader will not be surprised that a single picture has not yet emerged of the nature of the PO bond. That is not to say, however, that there are no definite statements in the literature on this topic. In fact, as intimated in Section I, the debate on the nature of the PO bond has recently been vigorous with two apparently contradictory viewpoints being proposed. These may be termed the σ/π-bond description and the Ω-bond description, neither of which, of course, involves much discussion of the involvement of d orbitals. These two alternatives are described below, but first it is necessary to fill in some background for readers who are not theoreticians and to dispose of the d orbital issue.

1. Localization procedures

Before we can describe the studies which have been done on the PO bond, it is necessary to mention the concept of delocalized and localized MOs. The LCAO–MO description of chemical bonding[22] leads to a set of molecular orbitals formed by the overlap of atomic orbitals centred at different atoms. These MOs are then classified as bonding, non-bonding or antibonding, depending on whether their energy is less than, equal to or greater than that of the constituent AOs. Each of the MOs is completely delocalized about all the constituent atoms and may only be occupied by two electrons of opposite spin. To express this, the ground-state wavefunction is described by a Slater determinant of the MOs. From this wavefunction can be calculated the properties of the molecule, e.g. electron probability density, dipole moment and geometry. However, this description is significantly deficient in one very important respect: as its stands, it is inconsistent with the existence of individual bonds in the molecule. The idea of a chemical bond between a pair of atoms in a molecule, which is approximately transferable between molecules, is fundamental to chemistry, so this is a grave deficiency indeed.

However, it is possible to reconcile the MO method with reality. This is because it is possible to convert the Slater determinant of MOs, by a unitary transformation, into another Slater determinant containing a set of MOs corresponding to localized bonds. These are the *localized* MOs as opposed to the original *canonical* MOs from the LCAO–MO method. Although this transformation does not change the value of the total electronic ground-state energy, the orbital energy values are shifted. In fact, there are an infinite number of such transformations possible[22], many of them corresponding to localized MOs, so that one needs a procedure or criterion for generating them consistently. Three such procedures are:

(i) that which generates the *energy-localized* MOs, originally suggested by Lennard-Jones and Pople[223] and developed by Edmiston and Reudenberg[224]; the LMOs are defined as that set of orbitals which minimizes inter-orbital repulsion and exhange energy;

(ii) that which generates the *exclusive* MOs due to Foster and Boys[225,226], usually called the Boys LMOs, defined as that set which maximizes the sum of the squares of the distances between the orbital centroids;

(iii) a more recent method is that of the *natural localized molecular orbitals* developed by Reed and Weinhold[227], which are derived from a natural bond-orbital analysis proposed by Foster and Weinhold[228]. The natural bond orbitals correspond more closely to the picture of localized bonds and lone pairs as basic units of molecular structure, are much easier to calculate and give results usually in good agreement with the other LMO methods[229].

Of these methods, that of Boys probably has been in greater use especially for systems containing second-row atoms because of its ease of computation. All three methods have been applied to phosphine oxides, more commonly that of Boys. Normally the different localization methods give similar results but not in the case of phosphine oxide, as we shall see.

An interesting point about these localization methods is that they sometimes lead to 'banana bonds'. For example, the energy-localized MOs for N_2 are three equivalent curved bond orbitals spaced 120° apart from one another, the 'banana bonds', whereas the canonical MOs are the familiar σ bond and two π bonds[22]. A similar result may be obtained for the alkene and carbonyl groups using the Boys method[18]. Thus localization procedures tend to obscure σ/π separability, which has also been a useful concept in chemistry. This aspect is often avoided by a preliminary examination of the canonical orbitals, especially the HOMO, to see if it has π properties and is already strongly localized; if it has, it is then excluded for the localization procedure. For example, the HOMO of ethylene is excluded in the localization procedure to preserve the familiar σ/π description of the carbon—carbon double bond[22].

Note that both these difficulties (absence of identifiable bonds and then loss of σ/π separability) are artifacts of the framework chosen for solution of the Schödinger equation—the LCAO–MO method.

2. *Insignificance of d orbitals*

Phosphine oxide calculations are a very good example of the trend mentioned in Section II whereby the significance of d orbitals appeared to change during the 1970s. In 1970 three sets of calculations indicated that d orbitals were significant in the electronic description of phosphine oxide[69,185a,230]. This was on the basis that leaving out the d functions leads to large energy increases for the species. Although all groups reported that d orbitals were important there were, with hindsight, significant differences in the degree of importance. Thus, for example, Hillier and Saunders[185a] found a d population of > 1 for H_3PO at the STO-3G* level, while Demuynck and Veillard[230] found that it was 0.36 at $>$ DZ + P. Also, Marsmann and coworkers[69] noted that the d-orbital radii found, by optimization, were similar to those of the s and p orbitals but, in their opinion at that time, this merely showed that there was no problem involved in achieving good overlap of these orbitals. This bias towards one viewpoint at the time is not surprising, given the preconditioning towards it that had occurred in the previous two decades and the apparent confirmation of it in the calculations.

By 1979 the situation had changed, even though the calculations were similar. Thus, in the course of a comprehensive study, discussed further below, Wallmeier and Kutzelnigg[19] repeated the observation of Demuynck and Veillard[230] that the d population in H_3PO is 0.3 at the $>$ DZ + P level. However, they showed (convincingly by both Mulliken and Heinzmann–Ahlrichs population analysis) that the d functions used were not true valence orbitals. For example, the Mulliken d population with a saturated sp basis is 0.3, which is comparable to that found in H_3PF_2 (0.2), but the d population in H_2POH is only smaller by a factor of 2. Further, the energy lowering due to the presence of d functions is roughly proportional to the d population (in line with the considerations of Section II above). They concluded[19] that 'the traditional valence AOs of s and p type are, when appropriately deformed, able to describe the bonding in all molecules in this paper. They are slightly poorer for the electron-rich molecules but even for them there is no indication of a valence extension'.

Wallmeier and Kutzelnigg[19] also demonstrated that phosphine oxides are a good example of d functions making up any deficiencies in the s and p basis and that, to obtain consistency in d function contribution, basis sets must be used which are saturated for s and p basis functions (i.e. there should be no further energy lowering on adding more s and p basis functions). However, in retrospect, their more important finding was that the use of d functions is essential to obtain an accurate description of these molecules. For example, they found for H_3PO that, on addition of d functions, there was a strong energy lowering, amounting to 218 kJ mol^{-1} (52 kcal mol^{-1}). Also, the PO bond length optimized without d functions (160 pm) was close to that of a single bond (calculated as 167 pm in H_2POH), while the optimized bond length with d functions (147 pm) was in good agreement with experimental values[19] (see Table 9). As discussed in Section II, this need for d functions in phosphine oxide calculations is because the PO bond is very polar so that there is a rapidly varying potential between the nuclei, which cannot be described accurately by a wavefunction which includes only atom-centred s and p functions.

These early conclusions by Wallmeier and Kutzelnigg[19] have been confirmed in detail by the later studies, two of which deserve mention. Magnusson[15] included calculations on phosphine oxides in his general study of hypercoordinate molecules (described in Section II) and they followed the same general pattern whereby there is no role for valence d orbitals. Reed and Schleyer[16] addressed the same problem in their recent study of hypervalent molecules (discussed further in Section IV.D.3.a). They showed that the depletion of the Y lone-pair orbital population in A_3XY systems was not matched by a corresponding increase in the central atom d orbital population.

Finally, an interesting psychological observation can be made about the influential paper by Wallmeier and Kutzelnigg[18]. Although they demonstrated that there is no valence role for d orbitals in phosphine oxides, nevertheless they used arguments based on them, in the same paper, to explain several aspects of the bonding. This reluctance on their part to abandon the concept, even though they had disproved it, shows how convenient the idea had been up to that time.

3. *The two alternative views of the bonding in phosphine oxide*

All of the detailed theoretical studies of the PO bond to date show, in agreement with experimental observation, that the PO bond has high multiple bond character and is highly polarized[16,17,19–21,68,69,185,192,201,203,230,231]. From Table 9, the optimized PO bond length for H_3PO (146 pm) is in good agreement with the experimental value for the substituted compounds. From Section III this is less than the bond length in the PO molecule (147.6 pm) or the HPO molecule (151.2 pm), both of which must have multiple character, and is distinctly shorter than a PO single bond (160 pm).

The results of population analyses (Table 11) are consistent with the picture that about one electron is transferred from phosphorus to oxygen. The polarity of the PO bond is significantly larger in H_3PO than in H_2POH, where it is only determined by the difference in electronegativity. Also, there is significant PO overlap as measured by overlap populations. There is no problem in reconciling these population results because if there was overlap of oxygen lone pairs with suitable receiving orbitals on phosphorus it would be highly unsymmetrical with most of the electron density near oxygen, as discussed in Section IV.B. In fact, the detailed studies (see the references at the start of this section) show that the presence of backbonding does not attenuate the charge-transfer characteristic of a semipolar bond and that backbonding means that the π AOs of oxygen are strongly polarized towards the H_3P moiety[16,17,19–21,68,69,185,192,201,203,230,231].

Although we know that the PO bond is multiple and highly polar, there is still strong disagreement about the exact electron distribution in it. As mentioned above, there are two viewpoints, described below. It turns out that phosphine oxides are part of the overall dichotomy between the σ/π and bent bond descriptions of multiple bonds[22].

a. One σ bond and two half π bonds (backbonding/negative hyperconjugation). This might now be described as the traditional view, having become so over about the last 30 years with the dominance of the molecular orbital method. It has been discussed qualitatively in Section IV.B. The bond can be viewed[20,192] as a donor–acceptor or Lewis acid–base interaction with backbonding superimposed. The lone pair of electrons from phosphorus forms a σ bond to oxygen which completes its octet. Then there are two possibilities. The resulting extra charge density on oxygen may go into suitable acceptor orbitals on phosphorus, forming a double bond (or rather a partial triple bond) by a π–type interaction called backbonding[14,16,19], as shown in Figure 3. The suitable orbitals are now known[15,16,19] not to be d orbitals but a set of antibonding orbitals of *e* symmetry on the R_3P moiety (see Section IV.B). This can be viewed as a resonance between single and triply bound structures[20]. The alternative possibility[21,201] is that the two opposite charges on adjacent atoms interact in an ionic bond and strengthen the PO link so that it is multiple (essentially structure 1A with some polarization of the charges towards each other).

There has never been any doubt, from the earliest to the most recent calculations, that there is a polarization of the charge at oxygen (the lone pairs) towards phosphorus[14,16,19–21,69]. It is the interpretation of this polarization which has proved difficult because, as already pointed out, any double bond between phosphorus and oxygen must be highly polar, so that it is difficult to distinguish between ionic and covalent bonding here. Most workers have interpreted the polarization as indicating backbonding, but, for example, Streitwieser and coworkers[21,201] took the view that it is nothing more than the polarization of the charges in an ionic bond. They asserted, but did not show, that this view was consistent with the reduced dipole moment because the charges are not spherically symmetric about the nuclei[201]. Similar sentiments were raised by Wallmeier and Kutzelnigg[19] who stated at one point in their paper, but again did not show, that the polarity of the PO bond was inconsistent with double bond character. However, later in the paper, they invoked backbonding to form a partial triple bond.

Most recently, Reed and Schleyer[16] did a very useful broad general study of the bonding in A_3XY species. They used calculations at the 6–31G* level and population analyses using the natural population method. They formalized the view that the backbonding is into empty σ^* orbitals on the R_3P moiety and placed the phenomenon in the context of the more general idea of negative hyperconjugation. Hyperconjugation is the interaction of filled σ orbitals and empty π^* orbitals, e.g. the σ_{CH} bonds of the CH_2 group of cyclopentadiene with the π^* orbitals of the diene. Negative hyperconjugation is then the converse, i.e. electron donation from π to σ^* orbitals as in π_C to σ^*_{CF} donation in the $FCH_2CH_2^-$ anion[232].

There was one irritating difficulty with Reed and Schleyer's results[16]. A consequence of negative hyperconjugation in A_3XY should be relatively increased XA bond lengths. This is indeed found to be the case for, for example, F_3CO^- and in F_3NO. However, the PF bonds are shortened in F_3PO and F_3PS and in most tertiary phosphine oxides relative to the parent phosphine (see Section II). Therefore, Reed and Schleyer had to look for other factors which influence PA bond lengths and they proceeded to invoke the greater importance of d orbitals(!) for second- as opposed to first-row atoms. They then attempted to measure the relative importance of negative hyperconjugation and d orbital involvement by examining the ratio between the depletion of the lone-pair occupancy and the d orbital population on the central atom. They found that the depletion was relatively high and the d orbital population low. They therefore concluded that the bonding was a partially ionic σ bond and partial π bonding which occurs mainly through negative hyperconjugation and only secondarily through overlap with extra valence shell d orbitals.

This reviewer was surprised by the readiness of Reed and Schleyer[16] to invoke valence d orbitals as an explanation for the bond length contraction in phosphine oxides relative to the parent phosphines, especially since one of the thrusts of their paper was that the traditional dsp^3 and d^2sp^3 models are now invalid. Also, as they pointed out, d functions serve to polarize existing valence orbitals to lead to a better wavefunction for the system. This is equivalent to saying that if negative hyperconjugation occurs then d functions will be required in the LCAO–MO calculation. In fact, it is just as reasonable to argue that the need for d functions in the LCAO–MO treatment indicates that negative hyperconjugation is occurring. Hence it cannot be strictly valid to compare the amount of negative hyperconjugation with the d population since they are already related.

There are other explanations which can be resorted to before valence d orbitals need to be invoked. One such is the bond length–bond angle relationship. Thus unsubstituted and both fluoro- and methyl-substituted phosphine oxides have decreased P—ligand bond lengths compared with their parent phosphines but all also have increased bond angles, and all of the variation is of the same order (about 5 pm and 5–6°; compare Tables 4 and 5 with Tables 2–4 in ref. 1). It is commonplace to argue[1], in the case of Main Group compounds, that an increase in bond angle is related to a decrease in bond length, because as the ligands move apart from each other (bond angle increases from 90° towards 109.5°) they can approach closer to the central atom (see also Section III.A) That the first-row compounds do not follow the same pattern can be ascribed to the already crowded environment around the small central atom.

b. Three Ω *bonds* (*banana bonds/bent multiple bonds*). This might be termed the unorthodox view, the valence bond method having been somewhat in disuse until recently. There is neither a σ nor a π bond. The PO bond is a formal triple bond with the three curved regions of electron density disposed between P and O in a symmetrical fashion (at 120° to each other in Newmann projection along the PO coordinate, Figure 4A). This description arises in both the MO and VB theoretical analyses of phosphine oxides described below. In both cases the electron density of the bonds is found to be strongly displaced towards oxygen and the remaining lone pair on the oxygen atom is found to be directed away from phosphorus along the PO axis.

These curved bonds have been termed 'bent multiple' bonds[24] and 'banana' bonds[22], while more recently the terms 'τ bond' and 'Ω bond' have been coined by VB workers[233,234]. Since the term Ω bond has been used in connection with phosphine oxides already, and since the Greek letter is reminiscent of their shape, we shall use it in the following discussion. The term τ bond has been used for the specific case where the banana bonds occur in pairs, as in alkenes[22] and phosphorus ylides[234].

i. Boys localization. In SCF–HF/LCAO–MO calculations, the Boys localization procedure for phosphine oxides gives the Ω–bond description, shown as a contour plot in Figure 5, at all levels of theory studied. Guest and coworkers[231] were the first to describe banana bonds for H_3PO, Me_3PO, F_3PO, Cl_3PO and F_3PS at the STO-3G* level. Then Wallmeier and Kutzelnigg[19] found the same at the $> DZ + P$ level, after

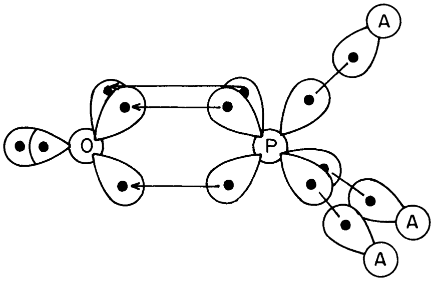


FIGURE 4A. The Ω bond model of the bonding in phosphine oxides, A_3PO. Adapted from Messmer[17]

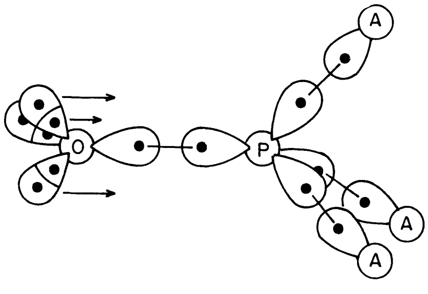


FIGURE 4B. The triple backbond model of the bonding in phosphine oxides, A_3PO. Adapted from Messmer[17]. The backbonds are shown by the arrows

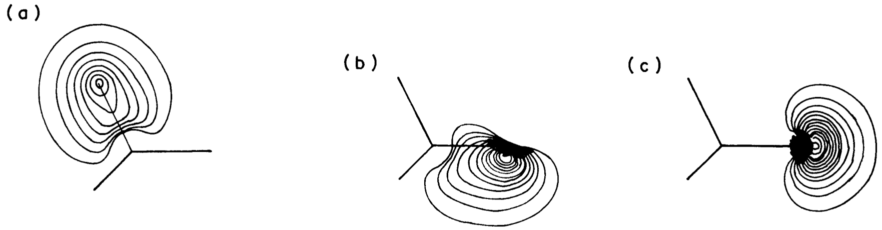


FIGURE 5. Contour plots of the Boys localized bonding orbitals of H_3PO. (a) One of three PH bonds; (b) one of three banana bonds (note that it is strongly polarized towards oxygen); and (c) the single oxygen lone pair. At the 3–21 G# level, one phase only shown, increment between all contours is 0.05 bohr$^{-3/2}$. Adapted from Schmidt and coworkers[192]

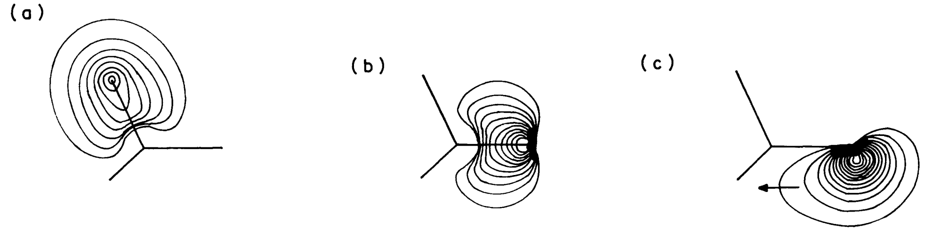


FIGURE 6. Contour plots of the energy-localized bonding orbitals of H_3PO. (a) One of three PH bonds; (b) the PO σ bond; and (c) one of three oxygen lone pairs (note the backbonding towards phosphorus, shown by the arrow). At the 3–21 G# level, one phase only shown, increment between all contours is 0.05 bohr$^{-3/2}$. Adapted from Schmidt and coworkers[192]

noting that there was no natural choice of a plane of symmetry to impose a σ/π separability. Recently, Molina and coworkers[203] found the same result at the 6–31G* level.

Schmidt and coworkers[192] found an even more interesting result. This was that, for H_3PO, the energy localization procedure gave a different result from the Boys procedure. The energy localized orbitals at the 3–21G# level for H_3PO are shown in Figures 4B and 6. They are three equivalent PH bond, one strong PO σ bond and three equivalent orbitals on oxygen whose character is principally lone pair. This is similar to a representation using structure **1A** except that each of the lone pairs possesses some tendency to back-donate electron density to phosphorus. This result is different[192] from the Boys result at the same level of theory, which is in terms of banana bonds as shown in Figures 4A and 5, whereas usually the two procedures give similar results. Even starting each procedure with the localized orbitals from other procedure gave the same end result[192]. The energy-localized result described above is in accord with the picture of the PO bond as arising from strong σ donation enhanced by some degree of π backbonding, except that the back-donating lone pairs are staggered with respect to the PH bonds, which would be inimical to negative hyperconjugation.

It is noticeable that whenever a localization procedure gives banana bonds, the result is not taken seriously[22]. This is not reasonable, since it has the same energy as a σ/π description, but it is understandable, because it is outside the familiar realm of textbook chemistry. In just the same way, those workers who obtained this result for phosphine oxide were often reluctant to take it fully on board; some comments were: 'should not be taken too literally'[19], 'overly complicated'[192], 'a very peculiar electronic distribution'[203]. Most notable was the reaction of Schmidt and coworkers[192] who had performed both localization procedures and chose to reject the banana bond description without any justification other than to say that they favoured the alternative. This was in spite of the fact that on increasing fluorine substitution the energy-localized orbitals reverted to the banana bond description (see Section IV.D.5).

ii. Generalized valence bond calculations. Very recently a new approach to the bonding in these compounds has been published[17] based on the generalized valence bond (GVB) method.

The GVB method was developed from about 1970 by Goddard and coworkers[235]. The GVB wavefunction is much simpler than a VB wavefunction and so easier to calculate. However, it is still computationally difficult and, as usual, approximations have to be made. There are two such approximations, called the strong orthogonality (SO) and the perfect pairing (PP) restrictions, first proposed by Hurley and coworkers[236] and developed by Goddard and coworkers[235]. Usually they are both applied (SOPP). The method is claimed to be a substantial improvement beyond Hartree–Fock theory in that it is the most general independent particle model and provides a unique set of localized orbitals with which to interpret the bonding[17,235]. There are very few valence bond studies of hypervalent molecules[61,81,234].

During the late 1980s Messmer and coworkers[233,237–239] started to explore the utility of GVB methods on simple systems, both with and without the SOPP restrictions. In most cases they found that the description of multiple bonds is in terms of Ω bonds. For example, in the description of difluoroacetylene the three Ω bonds may be thought of as the overlap of three sp^3 hybrids on each of the carbons[237]. These Ω bonds are very similar to the banana bonds often given by localization procedures in MO theory, except that in this case they are the only result which minimises the energy of the system. One interesting aspect of these studies was that the GVB–SOPP results may give different results from the full GVB method. For example, tetrafluoroethylene is described by the traditional σ/π representation in GVB–SOPP but by a two Ω-bond representation (τ bond) in the full GVB treatment[239]. Schulz and Messmer[239] have tried to develop guidelines on when the full GVB will give the same results as GVB–SOPP.

Very recently, these studies using the GVB–SOPP method have been applied to Main Group (N, S, and P) oxides[17,240]. It is found that in F_3PO the oxygen forms a triple bond to the phosphorus atom using three Ω bonds, very similar to the Boys localization results from MO theory shown in Figures 4A and 5. The phosphorus atom assumes a pseudo-octahedral distribution of orbitals about its core and the orbitals are strongly polarized towards the surrounding atoms.

It should be noted that, although the idea of Ω bonds now appears unorthodox, it is not at all new. In fact, Pauling introduced it in 1931[23] to explain *E*/*Z* isomerism in alkenes in the same paper which developed the sp^3 model and it is discussed at length in the third edition[24] of *The Nature of the Chemical Bond*, where he notes that the description was used by nineteenth century chemists to explain why the carbon—carbon double bond is not fully twice the energy of the single bond. However, the σ/π representation predominated later because it could be quantified fairly easily through MO theory[22].

Although this reviewer finds the triple bond description for the PO bond to be fairly convincing and appealing, some reservations do have to be entered about the GVB–SOPP results reported above. First, full GVB gives Ω bonds for $F_2C{=}CF_2$ whereas GVB–SOPP gives a σ/π description, so it is just conceivable that it could be other way around for F_3PO. Messmer[17] has argued against this possibility but he cannot yet rule it out completely. Also, many of the systems reported so far have fluorine as ligands (e.g. $FC{\equiv}CF$, $F_2C{=}CF_2$, F_3NO, F_3PO) and in the case of the amine oxides the result was different with hydrogen ligands (see Section IV.D.4). Hence there is the possibility that the result will be different for phosphine oxide or tertiary phosphine oxides. Again Schulz and Messmer[239] have indicated that change in ligand is not important, but only in references to unpublished material. More seriously, an examination of Table 9 shows that the few results available from GVB–SOPP calculations do not compare favourably with those from other calculational methods. For example, for F_3PO, the predicted PO bond length is 147 pm compared with the experimental result of 143.6 pm while the 6–31G* value was 142.5 pm.

A final point is that both the Boys localization results and the GVB–SOPP results for F_3PO are inconsistent with negative hyperconjugation. Examination of Figure 5 shows that the three Ω bonds are staggered with respect to the other phosphorus—ligand bonds, giving an octahedral disposition of electron pairs around phosphorus. This is the arrangement expected on the basis of the Pauli exclusion principle, but it would minimize the overlap of the orbital interaction required for negative hyperconjugation.

4. Comparison of phosphine oxides and amine oxides

Tables 9 and 11 also include for comparison results from calculations on ammonia oxide and other amine oxides. It is to be expected that differences between these results and those for phosphine oxides should reflect fundamental differences between first- and second-row elements. There are some anomalous results reported in Table 9. Note, for example, that most of the calculations on F_3NO are hopelessly inaccurate with the single GVB–SOPP result being particularly bad. The worst predictions are for the NF bond length and the dipole moment and only when correlation is included are the results reasonable, although the NO bond length is still overestimated. Indeed, we can be much less confident in predicting the geometry of ammonia oxide than we were above for phosphine oxide.

The observations to be explained, which may or may not be related, include:

(i) the lower dipole moment of phosphine oxides compared with amine oxides;

(ii) the PO bond in H_3PO and R_3PO is stronger and shorter than a PO single bond whereas in H_3NO and R_3NO the NO bond (length ca. 140 pm) is like an NO single bond[241];

(iii) the PO bond in F_3PO is qualitatively similar to that in H_3PO whereas the NO bond in F_3NO is a double bond on the criteria of length and strength;

(iv) the PA bond lengths in A_3PO are all shorter than those in A_3P whereas the NA lengths in A_3NO are longer than in A_3N, with the contrast being especially marked for the fluoro derivatives (compare Tables 4 and 5 with Tables 2–4 in ref. 1).

Many of the theoretical studies of phosphine oxides also include comparison with amine oxides[16,17,19,203,242] and there is greater unanimity about the bonding in amine oxides. All find that the NO bond in amine oxides is weaker than in phosphine oxides, in agreement with the chemical experience that amine oxides are oxidizing agents and phosphines are reducing agents. There is a general picture from population analyses[14,19,242] (Table 11) that ammonia oxide and tertiary amine oxides are singly bound with a semipolar bond and no backbonding, equivalent to the representation $R_3N^+{-}O^-$. The presence of backbonding in the phosphine oxides and its absence in the amine oxides then explains the lower than expected dipole moment in phosphine oxides.

The difference between R_3NO and F_3NO is also explained because it is found that there is backbonding in the fluorine derivative. As observed in Section IV.B, now that backbonding does not have to be into d orbitals there is no problem about it for nitrogen compounds. The likely acceptor orbitals for back-donation in F_3NO were analysed by Grein and Lawlor[86], who concluded that the 3e orbital of NF_3 was the most suitable. A similar picture was found in the Boys localized molecular orbitals of H_3NO at the 6–31 G* level[203], which were found to be composed of one centroid along the NO bond with the remaining ones around oxygen, in contrast to the result found by the same workers[203] for phosphine oxide outlined in the previous section.

Also similar were the GVB–SOPP calculations[17] on F_3NO and H_3NO, which gave results different from each other and from F_3PO. We have seen in Section IV.D.3.b that the result for F_3PO was three Ω bonds. The result for F_3NO was different. In this case there is a σ bond from nitrogen to oxygen and the three lone-pair orbitals on oxygen are strongly polarized towards nitrogen as in Figures 4B and 6, yielding three equivalent backbonds, amounting overall to a second bond between oxygen and nitrogen in accord with the short length (116 pm) of the NO bond in F_3NO. The result for H_3NO was different again. This time there is again a σ bond but the lone pairs on oxygen are not polarized towards nitrogen; there is no backbonding, in agreement with the longer bond lengths in substituted amine oxides. It should be mentioned that the concept of backbonding used here is different from the same idea in MO theory, because it is not based on atomic orbitals. Therefore, in order for electrons on one atom to backbond to another atom there is no need to invoke vacant atomic orbitals on the acceptor atom. The only reguirement, for example for the oxygen lone pairs in F_3NO to backbond to nitrogen, is that there be sufficient space for them, provided by the polarization of the NF bond orbitals towards fluorine. In the case of H_3NO the NH bond orbitals are not polarized towards the ligands as in F_3NO and so there is no room for backbonding electron density.

Messmer[17] contended that the fundamental difference between first- and second-row atoms is reflected in these different results from the GVB–SOPP calculations on F_3PO and F_3NO, described above. The nitrogen atom in F_3NO prefers to form four primary bonds (the backbonding is regarded as secondary) whereas the phosphorus atom in F_3PO forms six. This is a direct consequence of the greater core size in the second row.

There is one point where the unanimity breaks down, namely on the issue of where the backbonding is directed in F_3NO. What we have referred to as the traditional view would see it as going into suitable acceptor orbitals on nitrogen, the most likely being the σ^* NF antibonding orbitals. This is negative hyperconjugation and is consistent with the increased length of the NF bonds relative to F_3N. However, this agreement with the NF bond length may be coincidental, as pointed out in Section IV.D.3.a, because there is not a similar lengthening in F_3PO relative to F_3P. On the other hand, examination of the GVB–SOPP version of the backbonding in F_3NO, shown in Figures 4B and 6, shows that it is inconsistent with negative hyperconjugation. This is for just the same reasons as in F_3PO discussed in the previous section; the donating oxygen lone pairs are staggered with respect to the NF bonds.

In addition, Messmer[17] offered a simple and reasonable explanation of the trends in bond lengths found to the other ligand, i.e. the lengthening of the NF bonds in F_3NO relative to F_3N and the shortening of the PF bonds in F_3PO relative to F_3P. This is based on the bond length–bond angle relationship referred to in the previous section and on the small size of first-row elements. Thus, in going from F_3N to F_3NO the added oxygen contributes polarizable lone pairs which may contribute electron density to screen the nitrogen core. When the lone pairs approach closer to the small core, the resulting increased Pauli repulsions with the NF bonds produce a lengthening in these bonds. In the case of F_3P and F_3PO, the difference lies in the larger size of the phosphorus core, which means that it can form more bonds because there is more room. Then, because the oxygen polarizes orbitals away from P there is a reduction in Pauli repulsions with the PF bonds resulting in the shortening of these bonds.

5. *Bonding in substituted phosphine oxides*

Parent phosphine oxide is known only in matrix isolation experiments[157] and yet the formation of the PO bond drives the synthetically useful Wittig and Arbusov reactions and some of the processes of life itself. The most obvious question to be answered here then is why carbon, oxygen and fluorine substituents all stabilize phosphine oxide. The obvious answer is that decomposition by tautomerism of a hydrogen atom is prevented by any substitution. However, calculations have shown that the answer is more subtle than that, because there is a general effect of substitution to increase the PO bond strength[14,19,20,204,210,213].

Schmidt and Gordon[20] quantified this effect in detail in a comparison of substituent effects on the PO bond and some of their results are given in Table 12. They found both an increase in bond strength and a decrease in bond length on substitution (except for an Si substituent) at all levels of theory studied, including calculations with electron correlation. The effect increases with increasing electronegativity of the substituent but there is a limit to the ability of increasing electronegativity to increase bond strength. For example, from Table 12 it can be seen that in the series H, CH_3, NH_2 the bond strength increases significantly but remains nearly constant for OH and falls off slightly for F. There is a similar pattern with multiple substitution. Note that the experimental bond energy of F_3PO is 542 kJ mol^{-1}, so these computed bond strengths are too low; however, it is assumed that the calculated values are internally consistent.

Schmidt and Gordon[20] also compared the effect of substitution on H_3PO with respect to a Mulliken population analysis. They found that the substituents withdrew electron density from phosphorus, the amount of the withdrawal being consistent with electronegativity ($F > OH > NH_2 > CH_3$). The charge at oxygen was also reduced by a smaller amount. Even so, there was still a large positive charge on phosphorus and negative on oxygen. They also derived the PO bond order by Mulliken population analysis for some of the substituted phosphine oxides given in Table 12. It can be seen that the bond orders increase roughly as the computed bond strengths, i.e. with increasing

TABLE 12. Effect of substitution on PO bond lengths and strengths and orders at various basis set levels[a]

Molecule	*d*(P=O)[b]	Bond strength[c]			Bond order[d]
		3–21 G#	6–31 G*	MP3/6–31 G*	
H_3PO	142.3	377	423	531	1.58
$H_2(CH_3)PO$	141.7	423	460	565	1.66
$H_2(NH_2)PO$	142.0	494	519	628	
$H_2(OH)PO$	141.8	485	527	640	1.69
H_2FPO	141.1	481	515	628	1.74
HF_2PO	141.0	540	565	686	
F_3PO	140.9	523	540	657	

[a] All at STO-2 G# geometry from ref. 20; see Table 9, footnote *a*, for terminology.

[b] STO-2 G# computed bond lengths in pm.

[c] Energy for the dissociation of the phosphine oxide to phosphine and ^{1}D oxygen in kJ mol^{-1} using the indicated calculation; ^{1}D oxygen is about 190 kJ mol^{-1} above the triplet ground state.

[d] Derived from a Mulliken population analysis at the 3–21 G# level.

electronegativity of the substituent. This was found to be due to an increased amount of backbonding[20].

Two groups have argued that the stabilizations by fluoro and methyl substituents are caused by different mechanisms. Schneider and coworkers[204] studied a series of $A_3P{=}Y$ molecules ($A = H, CH_3, F; Y = O, S$) at the 6–31 G* level, the results of which are shown in Table 13. It can be seen that the substitution of H by both F and Me causes an increase in the P=Y bond energy but only F substitution causes an increase in stretching force constant. As noted in Section IV.A.2, this is confirmed by experimental observations. They say that this shows that methyl stabilization is by a different mechanism, because the higher P=O and P=S bond strengths in the trimethyl compounds are shown by this to be not directly related to inherent properties of the PO and PS bonds, but must rather be caused by changes in the R_3P moiety. Wallmeier and Kutzelnigg[19] studied fluorine substitution in detail, using the population analyses shown in Table 11. They found that the binding energy of the PO bond in $H_2P(O)F$ is larger than that in H_3PO. Also, the overlap population or bond order is significantly (25%) larger in $H_2P(O)F$ than in H_3PO, which confirms that fluorine substitution stabilizes the PO bond. A similar result was found for double fluorine substitution and they noted that both were in line with the results for the triply substituted compound reported by Serafini and coworkers[213].

Both Schneider and coworkers[204] and Wallmeier and Kutzelnigg[19] advanced the same mechanisms for the different ways that fluorine and methyl substituents stabilize the PO bond. Thus fluorine increases π backbonding by electron withdrawal from phosphorus, which becomes more positive, giving more opportunity for electron donation from oxygen lone pairs. On the other hand, methyl groups stabilize the partial positive charge on phosphorus in R_3PY so we must look for another effect. A possibility is that steric hindrance destabilizes Me_3P relative to H_3P to a greater extent than Me_3PY relative to H_3PY, because of the change in the angles at phosphorus (see Table 4 and Table 2 in ref. 1). Hence, since PO bond dissociation in R_3PO leads to R_3P, this gives a higher bond dissociation energy for the methyl-substituted compound.

Von Carlowitz and coworkers[210] compared bond lengths in methylphosphine and methylphosphine oxide and the effect of fluoro substitution thereupon, and some of the results are shown in Table 14. They found that there was a remarkably large variation (decrease of 10 pm) in PC bond length from methylphosphine to difluoromethylphosphine

TABLE 13. Calculated and experimental bond energies and calculated force constants for $P = Y$ in $A_3P{=}Y$ compounds

Molecule	$D_0(P{=}Y)^a$	$D_0(P{=}Y)^b$	f^c
$H_3P{=}O$	426		9.423
$F_3P{=}O$	539	540	11.812
$Me_3P{=}O$	537	582	9.144
$H_3P{=}S$	226		4.210^d
$F_3P{=}S$	269	293^e	6.093^d
$Me_3P{=}S$	324	383^f	3.917^d

[a] In kJ mol^{-1} at 6–31 G*, from ref. 204.

[b] Best available experimental comparison from Table 6.

[c] Scaled stretching force constant in mdyn Å^{-1}, using scale factors optimized for PH_3 and $F_3P{=}O$.

[d] These are not directly comparable, see ref. 204.

[e] $D_0(P{=}S)$ in $Cl_3P{=}S$.

[f] $D_0(P{=}S)$ in $(C_3H_7)_3P{=}S$.

TABLE 14. Effect of fluoro substitution on calculated bond lengths in methylphosphine and methylphosphine oxide[a]

Bond length[b]	CH_3PH_2	CH_3PF_2	CH_3POH_2	CH_3POF_2
P—C	185.3	179.9	178.9	175.3
P=O			146.5	143.1
P—F		157.8		153.9

[a] From ref. 210.
[b] In pm, using 3–21 G* basis set.

oxide. This was made up from two increments. There was the fall (5 pm) in PC on change from phosphine to the oxide explained by the bond length–bond angle relationship (see Section III.A), but there was also a decrease of about 5 pm on substitution of two fluorines for two hydrogens. They commented[210] that 'these extremely large structural variations are presumably due to the withdrawal of negative charge from the phosphorus atom and the consequent shrinkage of bonds to other electronegative substituents'. Thus, in all cases, replacement of one substituent by a more electronegative one results in a shortening of all of the other P—X bonds.

Finally, Schmidt and Gordon[20] found a very interesting result of substitution on the derived energy-localized orbitals. Methyl and silyl phosphine oxides still have the three lone-pair orbitals on oxygen and one PO σ bonding orbital as described in Section IV.D.3.b for parent phosphine oxide, Figures 4B and 6. For hydroxy and fluoro phosphine oxides, the lone-pair orbital *trans* to the substituent becomes so involved in backbonding that it tips inward and the localization procedure leads to the formation of two banana bonds from it and the σ bond. For the trifluoro compound two lone pairs tip in, leading to three banana bonds, Figures 4A and 5.

6. *Bonding in phosphine sulphides*

Some of the studies of phosphine oxides have included phosphine sulphides for comparison[16,20,231]. It is found that the sulphides are qualitatively similar to the oxides, except that they have a relatively weaker PS bond and are less polar. Schmidt and Gordon[20] studied H_3PS and derived a bond order (from Mulliken population analysis) of 1.32 for H_3PS compared with 1.58 for H_3PO. As in the oxide, electronegative substituents act to increase the PS bond strength. One additional result was that the weakness of the thiphosphoryl bond was also due to a weakening of the PS σ bond. This was derived from Mulliken population analysis of atomic charges, $P = 0.481$ and $S = -0.457$, compared with $P = -0.922$ and $O = -0.719$. They commented[20] that 'sulphur's diminished ability relative to oxygen to hold a large negative charge has decreased the charge separation in the PX bond considerably and thus weakened the formally ionic donor σ bond'.

Guest and coworkers[231] did an STO-3G* calculation at assumed geometry on F_3PS with Boys transformation of the resulting canonical orbitals. They found essentially the same features for the PS bond as for the PO bond, including banana bonds. The PS bond polarity was slightly less and the phosphorus component to the bond involved slightly smaller 3d and 3p contributions.

E. Empirical Calculations

Since the initial study of Wagner[162] there have been only a few empirical or semi-empirical studies of phosphine oxides. The earlier ones reported detailed examinations of the bonding[162,199,243–245] and concluded that the PO bond is multiple and polar, but were much taken with the influence (or lack thereof) of d orbitals. Later studies[246–252], mainly by Soviet workers, used these methods (HMO, CNDO) to predict atomic charges and dipole moments, in some cases to explain or predict extractive capability or donation ability. The SINDO method was applied to phosphine oxide by Jug and Schulz[253] in their general study but gave poor results (PO = 149 pm, PH = 142 pm).

F. Summary of Bonding and Comments on the Formula of Phosphine Oxides

Previous general discussions[3–13] of the bonding in phosphine oxides have been couched in terms of a resonance between two possible limiting structures $\mathrm{H_3P{=}O}$ and $\mathrm{H_3P^+{-}O^-}$. This view will have to be given up. It is too simplistic because, as we have seen, the presence of a multiple bond between phosphorus and oxygen is not inconsistent with a high degree of polarity. More important, this view reduces the significance of the $\mathrm{P{=}O}$ formulation without conveying in return the true complexity of the bonding. A subsidiary point is that if the Ω bond description (Section IV.D.3.b) turns out to be the correct one, the formula $\mathrm{R_3P^+{-}O^-}$ would be misleading because it implies that there is a σ bond between P and O.

The satisfactory formulation of the PO bond is difficult because we are accustomed to formulae from the first row of the Periodic Table. In the first row there is a fortuitous correspondence between bond strength, number of electron pairs and valence. This is one of the indirect consequences of the small size of these elements. Thus, for the common multiple bonds of organic chemistry, $\mathrm{C{=}C}$, $\mathrm{C{\equiv}C}$ and $\mathrm{C{=}O}$, the two (or three) lines carry three different implications at the same time: (i) that the bond is twice (or three times) the strength of a single bond between the elements concerned, (ii) that there are two (or three) electron pairs in the region between the elements and (iii) that it is possible to have an addition reaction wherein one (or two) ligand(s) is (are) added to each of the atoms involved in the bond.

This all breaks down in the second and higher rows. In the case of PO, we have a double-strength, highly polar bond composed of three (or more) electron pairs (by both of the descriptions in Section IV.D.3). Hence the PO bond can be viewed as either a double bond $\mathrm{P{=}O}$ or a triple bond $\mathrm{P{\equiv}O}$. If we wish to have one formula to represent the PO bond, we must choose which information is the most important to convey. If we consider that it is more important to convey the information that the PO bond contains three electron pairs then we should use the $\mathrm{P{\equiv}O}$ formula, but if we consider that it is more important that the strength of the bond be specified then we should use the $\mathrm{P{=}O}$ formula.

This reviewer proposes that a utilitarian view be taken. Strength and, especially, valence are the things that matter in practical chemistry (i.e. how much energy will be required for the bond to react and how many things can be attached to it in an addition reaction). Hence the formula $\mathrm{X_3P{=}O}$ is the most useful. In addition, it also has the merit that it is currently in common use. However, until now, practical chemists have been made to feel uneasy about its correctness. The above analysis shows that their instincts were correct.

Sometime in the future, better calculations will determine the electronic distribution in the PO bond. For now, the best we can say is that the nature of the PO bond will probably be one of the following:

either

'The PO bond is a double strength bond, formulated as $\mathrm{P{=}O}$. This representation also implies (i) that there are three electron pairs between P and O composed of a σ bond between P and O and two π backbonds between lone pairs on O and acceptor orbitals on P which are antibonding in character with respect to the other ligands on P as shown in Figure 3 and (ii) that the electron density of the bonds is strongly skewed towards O so that there is a high degree of positive charge on P and negative on O'.

or

'The PO bond is a double strength bond, formulated as P=O. This representation also implies (i) that there are three electron pairs between P and O composed of three Ω bonds from P to O as shown in Figure 4A and (ii) that the electron density of the bonds is strongly skewed towards O so that there is a high degree of positive charge on P and negative on O'.

or

'The PO bond is a double strength bond, formulated as P=O. This representation also implies (i) that there are four electron pairs between P and O composed of a σ bond between P and O and three backbonds from lone pairs on O to the P atom as shown in Figure 4B and (ii) that the electron density of the bonds is strongly skewed towards O so that there is a high degree of positive charge on P and negative on O'.

Finally, is the octet rule broken by phosphine oxides? As the quotations in the Introduction imply, the answer is yes and no. This reviewer would argue that it may not be broken technically because the electron density is skewed towards O so that P is not receiving a full half share of each electron pair. Reed and Schleyer[16], for example, are careful to say that the *electronic* octet rule is not broken. However, there is a strong case that it is broken in spirit because phosphorus is participating in more than four electron pair bonds.

V. CONFORMATION

There have been a number of studies, both experimental and theoretical, on the conformations of tertiary phosphine oxides. Of particular concern have been the *trans/gauche* ratio (see Figure 7) about the PC bond and the orientation of the aromatic rings in the triaryl derivatives.

A number of workers have examined the conformations about the PC bond of trialkylphosphine chalcogenides using various physical techniques, including infrared spectroscopy, dipole moments, Kerr effects and NMR[254–259]. The conclusion is that in solution there is a mixture of the *trans* and *gauche* forms with the *gauche* form usually preferred, the ratio depending on the substituents and the solvent, while only the *gauche* form remains in the solid state, at least in the case of ethyldimethylphosphine sulphide[254].

For the triaryl derivatives, the most detailed study was that of Brock and coworkers[99] at low temperatures on both forms of triphenylphosphine oxide (monoclinic and

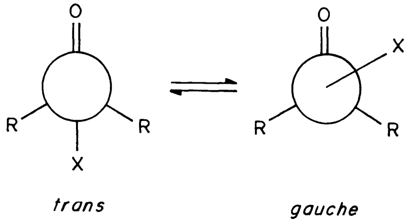


FIGURE 7. The *trans* and *gauche* conformers of a tertiary phosphine oxide

orthorhombic). In both structures the normal to one phenyl ring (A) is roughly (within 30°) parallel to the PO bond while the other two ring normals (B and C) are roughly perpendicular to this bond. A similar observation was made for triphenylphosphine sulphide[117]. As already noted in Section III.B, the smallest PC bond in both structures is the one to ring A, perhaps an indication of delocalization of the aromatic π system into the PO π^* orbital[99,260]. In solution, however, no difference has been found in the orientation of the phenyl rings by a variety of methods, including infrared and ultraviolet spectroscopy, dipole moment and Kerr constant[261–265]. The introduction of *ortho*-substituents on the aryl rings causes some minor changes in conformation[101,266–268] and, as expected, rotation of the rings is slowed on the nmr time scale[267,268].

In a particularly careful and interesting study of a very large number of published X-ray crystal structures, Bye and coworkers[100] mapped the reaction path for stereoisomerization of triphenylphosphine oxide derivatives. Their description of the interconversion is repeated here. The equilibrium structure of an isolated Ph_3PO—X fragment is close to a symmetric propeller shape with all three phenyl rings rotated from the respective CPX planes in the same sense and by approximately the same amount, about 40°. Then, starting with a molecule with positive torsion angles, the stereoisomerization path begins by rotation of one ring, say A, toward 90° (perpendicular to its CPX plane) coupled with a rotation of the other two rings in the opposite sense (toward 0°) and by half the amount of ring A. As the reaction proceeds, the rotation of the other two rings B and C becomes out of step, with one, say B, rotating less, leading to a mirror-symmetric structure with torsion angles of ca 90°, 10° and $-10°$. At this point ring A has rotated by $+50°$, ring B by $-30°$ and ring C by $-50°$. In the second part of the path, the roles of rings B and C are interchanged, so the path ends at the enantiomorphic structure with torsion angles of 140°, $-40°$ and $-40°$ equivalent to $-40°$, 40° and 40°.

The more complicated cases of mixed alkyl and aryl phosphine chalcogenides have also been studied by many workers. The orientation of the aryl ring(s) follows the same trends as in the triaryl compounds mentioned above. In the solid phase one aryl ring is usually roughly parallel with the PO bond[105,106,122] whereas in solution the non-coplanarity increases[269,270]. As regards the *trans/gauche* ratio, the same results were found as above, namely that the *gauche* conformer is the preferred form in solution, the preference increasing with increasing size of the substituent groups, and the preference becomes total in the solid state[106,271–274].

Theoretical methods have also been applied in the study of the conformations of phosphine oxides, mainly of the molecular mechanics type[209,275–278]. The results generally agree with the experimental work and there have been a number of predictions of a similar nature for species previously not studied experimentally. It is considered that in the *gauche/trans* equilibrium (Figure 7), the *trans* form is favoured by dipole–dipole interactions and the *gauche* form by steric considerations[255,272,278].

In studies of the conformations of 2-(diphenylphosphinoyl)-[1,3]-dithiane, Juaristi and coworkers[279–281] discovered the existence of a strong S—C—P anomeric effect. This is shown by the predominance of the conformer of the dithiane ring, which places the phosphinoyl group in the axial orientation. The analogous diphenylthiophosphinoyl derivative also shows the same effect to a lesser extent[282]. Similar observations on this system and on the 1,3,5-trithiane derivatives were made by Mikolajczyk and coworkers[283–287].

VI. REFERENCES

1. D. G. Gilheany, in *The Chemistry of Organophosphorus Compounds* (Ed. F. R. Hartley), Vol. 1, Wiley–Interscience, Chichester, 1990, Chapter 2, pp. 9–49.

2. R. F. W. Bader, R. J. Gillespie and P. J. MacDougall, *J. Am. Chem. Soc.*, **110**, 7329 (1988).
3. R. F. Hudson, *Structure and Mechanism in Organophosphorus Chemistry*, Academic Press, 1965.
4. A. J. Kirby and S. G. Warren, *The Organic Chemistry of Phosphorus*, Elsevier, Amsterdam, 1967.
5. K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).
6. H. R. Hays and D. J. Peterson, in *Organic Phosphorus compounds* (Eds G. M. Kosolapoff and L. Maier), Vol. 3, Wiley-Interscience, Chichester, 1972, Chapter 6, pp. 341–500.
7. L. Maier, in *Organic Phosphorus Compounds* (Eds G. M. Kosolapoff and L. Maier), Vol. 4, Wiley-Interscience, Chichester, 1972, Chapter 7, pp. 1–73.
8. B. J. Walker, *Organophosphorus Chemistry*, Penguin, Harmondsworth, 1972.
9. D. E. C. Corbridge, *The Structural Chemistry of Phosphorus*, Elsevier, Amsterdam, 1974.
10. J. Emsley and D. Hall, *The Chemistry of Phosphorus*, Wiley, New York, 1976.
11. H. Goldwhite, *Introduction to Phosphorus Chemistry*, Cambridge University Press, Cambridge, 1981.
12. D. J. H. Smith, in *Comprehensive Organic Chemistry* (Eds D. Barton and W. D. Ollis), Vol. 2 (Ed. I. O. Sutherland), Pergamon Press, Oxford, 1979, pp. 1121–1122.
13. D. E. C. Corbridge, *Phosphorus, an Outline of its Chemistry, Biochemistry and Technology*, 3rd ed., Elsevier, Amsterdam, 1985.
14. W. Kutzelnigg, *Angew. Chem., Int. Ed. Engl.*, **23**, 272 (1984).
15. E. Magnusson, *J. Am. Chem. Soc.*, **112**, 7940 (1990).
16. A. E. Reed and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **112**, 1434 (1990).
17. R. P. Messmer, *J. Am. Chem. Soc.*, **113**, 433 (1991).
18. W. Kutzelnigg, *Pure Appl. Chem.*, **49**, 981 (1977).
19. H. Wallmeier and W. Kutzelnigg, *J. Am. Chem. Soc.*, **101**, 2804 (1979).
20. M. W. Schmidt and M. S. Gordon, *J. Am. Chem. Soc.*, **107**, 1922 (1985).
21. A. Streitwieser. A. Rajca, R. S. McDowell and R. Glaser, *J. Am. Chem. Soc.*, **109**, 4184 (1987).
22. I. N. Levine, *Quantum Chemistry*, 3rd ed., Allyn and Bacon, Boston, 1983.
23. L. Pauling, *J. Am. Chem. Soc.*, **53**, 1367 (1931).
24. L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, 1960.
25. M. J. S. Dewar and E. Healy, *Organometallicas*, **1**, 1705 (1982).
26. G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).
27. R. J. Gillespie, *J. Chem. Soc.*, 1002 (1952).
28. H. H. Jaffé, *J. Phys. Chem.*, **58**, 185 (1954).
29. D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).
30. D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).
31. D. P. Craig and N. L. Paddock, in *Non-benzenoid Aromatics* (Ed. J. P. Synder), Vol. 2, Academic Press, New York, 1971, Chapter 5, pp. 273–357.
32. G. Häfelinger, *Fortschr. Chem. Forsch.*, **28**, 1 (1972).
33. M. E. Dyatkina and N. M. Klimenko, *Zh. Strukt. Khim.*, **14**, 173 (1973); Engl. Transl., *J. Struct. Chem.*, **14**, 157 (1973).
34. C. A. Coulson, *Nature* (*London*), **221**, 1106 (1969).
35. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley–Interscience, New York, 1988.
36. G. C. Pimental, *J. Chem. Phys.*, **19**, 446 (1951).
37. G. C. Pimental and R. D. Spratley, *J. Am. Chem. Soc.*, **85**, 826 (1963).
38. R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4321 (1951).
39. R. E. Rundle, *Surv. Prog. Chem.*, **1**, 81 (1963).
40. E. E. Havinga and E. H. Wiebenga, *Recl. Trav. Chim. Pays-Bas*, **78**, 724 (1959).
41. E. H. Wiebenga, E. E. Havinga and K. H. Boswijk, *Adv. Inorg. Chem. Radiochem.*, **3**, 133 (1961).
42. K. S. Pitzer, *Science*, **139**, 414 (1963).
43. J. I. Musher, *Science*, **141**, 736 (1963); *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969); *J. Am. Chem. Soc.*, **94**, 1370 (1972); *Tetrahedron*, **30**, 1747 (1974).
44. R. J. Gillespie, *Molecular Geometry*, Van Nostran Rheinhold, London, 1972.
45. R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963).
46. C. A. Coulson, *J. Chem. Soc.*, 1442 (1964).
47. H. Kwart and K. G. King, *d-Orbitals in the Chemistry of Silicon, Phosphorus and Sulphur*, Springer, Berlin, 1977.

48. K. R. Popper, *The Logic of Scientific Discovery*, Hutchinson, London, 1959.
49. D. W. J. Crickshank, *J. Mol. Struct.*, **130**, 177 (1985).
50. K. Hedberg, *J. Am. Chem. Soc.*, **77**, 6491 (1955).
51. C. Glidewell, *Inorg. Chim. Acta*, **12**, 219 (1975).
52. L. Noodleman and N. L. Paddock, *Inorg. Chem.*, **18**, 354 (1979).
53. D. B. Beach and W. L. Jolly, *Inorg. Chem.*, **23**, 4774 (1984).
54. G. Fraenkel, A. Chow, J. Gallucci, S. Q. A. Rizvi, S. C. Wong and H. Finkelstein, *J. Am. Chem. Soc.*, **108**, 5339 (1986).
55. D. G. Gilheany, *PhD Thesis*, Queen's University, Belfast, 1983.
56. G. S. Chandler and T. Thirunamachandran, *J. Chem. Phys.*, **47**, 1192 (1967).
57. D. P. Craig and C. Zauli, *J. Chem. Phys.*, **37**, 601, 609 (1962).
58. D. P. Craig and T. Thirunamachandran, *J. Chem. Phys.*, **43**, 4183 (1965).
59. C. A. Coulson and F. A. Gianturco, *J. Chem. Soc. A*, 1618 (1968).
60. D. W. J. Cruickshank, B. C. Webster and D. F. Mayers, *J. Chem. Phys.*, **40**, 3733 (1964).
61. D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, 4895 (1956).
62. G. L. Bendazzoli and C. Zauli, *J. Chem. Soc.*, 6827 (1965).
63. K. A. R. Mitchell, *J. Chem. Soc. A*, 2676, 2683 (1968); *Can. J. Chem.*, **46**, 3499 (1968).
64. S. Trippett, personal communication, 1983.
65. R. Hoffmann, D. B. Boyd and S. Z. Goldberg, *J. Am. Chem. Soc.*, **92**, 3929 (1970).
66. D. B. Boyd and R. Hoffmann, *J. Am. Chem. Soc.*, **93**, 1064 (1971).
67. R. Hoffmann, J. M. Howell and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 3047 (1972).
68. I. Absar and J. R. Van Wazer, *J. Am. Chem. Soc.*, **94**, 2382, 6284 (1972).
69. H. Marsmann, L. C. D. Groenweghe, L. J. Schaad and J. R. Van Wazer, *J. Am. Chem. Soc.*, **92**, 6108 (1970).
70. W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. DeFrees, J. A. Pople and J. S. Binkley, *J. Am. Chem. Soc.*, **104**, 5039 (1982).
71. J. Simon, *J. Phys. Chem.*, **95**, 1017 (1991).
72. C. J. Marsden and B. J. Smith, *J. Mol. Struct. THEOCHEM*, **105**, 385 (1983).
73. A. Yadav, P. R. Surján and R. A. Poirier, *J. Mol. Struct. THEOCHEM*, **165**, 297 (1988).
74. N. Rosen, *Phys. Rev.*, **38**, 2039 (1931).
75. An example of a modern calculation on H_2 including polarization functions is in R. D. Harcourt, *Theor. Chim. Acta*, **78**, 267 (1991).
76. M. A. Ratner and J. R. Sabin, *J. Am. Chem. Soc.*, **99**, 3954 (1977).
77. E. E. Ball, M. A. Ratner and J. R. Sabin, *Chem. Scr.*, **12**, 128 (1977).
78. F. Bernardi, A. Bottoni, A. Venturini and A. Mangini, *J. Am. Chem. Soc.*, **108**, 8171 (1986).
79. D. A. Bors and A. Streitwieser, *J. Am. Chem. Soc.*, **108**, 1397 (1986).
80. A. E. Reed and F. Weinhold, *J. Am. Chem. Soc.*, **108**, 3586 (1986).
81. P. J. Hay, *J. Am. Chem. Soc.*, **99**, 1003 (1977).
82. I. Mayer, *J. Mol. Struct.*, **149**, 81 (1987).
83. J. G. Angyán, R. A. Poirier, A. Kucsman and I. G. Csizmadia, *J. Am. Chem. Soc.*, **109**, 2237 (1987).
84. R. C. Haddon, *Chem. Phys. Lett.*, **120**, 372 (1985).
85. Ref. 16, footnotes 10–15.
86. F. Grein and L. J. Lawlor, *Theor. Chim. Acta*, **63**, 161 (1983).
87. Bond functions are located in the bond region rather than on the nuclei. Commonly one uses a set of s and p orbitals per bond.
88. L. E. Sutton (Ed.), *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Special Publication No. 11, Chemical Society, London, 1958.
89. L. E. Sutton (Ed.), *Tables of Interatomic Distances and configuration in Molecules and Ions—Supplement*, Special Publication No. 16, Chemical Society, London, 1965.
90. J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki and C. S. Pote, *Structure Data on Free Polyatomic Molecules*, Landolt–Börnstein, New Series, Group II, Vol. 7, Eds. K. H. Hellwege and A. M. Hellwege), Springer, Berlin, 1976.
91. M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwendemann, D. A. Ramsay, F. J. Lovas, W. J. Lafferty and A. G. Maki, *J. Phys. Chem. Ref. Data*, **8**, 619, (1979).
92. C. J. Wilkins, K. Hagen, L. Hedberg, Q. Shen and K. Hedberg, *J. Am. Chem. Soc.*, **97**, 6352 (1975).

93. L. M. Englelhardt, C. L. Raston, C. R. Whitaker and A. H. White, *Aust. J. Chem.*, **39**, 2151 (1986).
94. D. W. H. Rankin, H. E. Robertson, R. Seip, H. Schmidbauer and G. Blaschke, *J. Chem. Soc., Dalton Trans.*, 827 (1985).
95. C. J. Marsden, *Inorg. Chem.*, **23**, 1703 (1984).
96. G. Ruban and V. Zabel, *Cryst. Struct. Commun.*, **5**, 671 (1976).
97. A. L. Spek, *Acta Crystallogr., Sect. C.*, **43**, 1233 (1987).
98. G. Bandoli, G. Bortolozzo, D. A. Clemente, U. Croatto and G. Panattoni, *J. Chem. Soc. A*, 2778 (1970).
99. C. P. Brock, W. B. Schweizer and J. D. Dunitz, *J. Am. Chem. Soc.*, **107**, 6964 (1985).
100. E. Bye, W. B. Schweizer and J. D. Dunitz, *J. Am. Chem. Soc.*, **104**, 5893 (1982).
101. T. S. Cameron and B. Dahlèn, *J. Chem. Soc., Perkin Trans. 2*, 1737 (1975).
102. W. Dreissig and K. Pleith, *Acta Crystallogr., Sect. B.*, **27**, 1146 (1971).
103. W. Dreissig and K. Pleith, *Acta Crystallogr., Sect. B.*, **27**, 1140 (1971).
104. D. G. Naare and T.-W. Lin, *J. Fluorine Chem.*, **13**, 473 (1979).
105. V. V. Tkachev, L. O. Atovmyan, L. V. Goncharova, A. A. Shvets and O. A. Osipov, *Zh. Strukt. khim.*, **23**, 168 (1982); Engl. Transl., *J. Struct. Chem.*, **23**, 640 (1982).
106. G. Bernardinelli and R. Gerdil, *Cryst. Struct. Commun.*, **8**, 921 (1979).
107. M. Yu. Antipin, Yu. T. Struchkov, S. A. Pisareva, T. Ya. Medved' and M. I. Kabachnik, *Zh. Strukt. Khim.*, **21**, 101 (1980); Engl. Transl., *J. Struct. Chem.*, **21**, 644 (1980).
108. O. Orama, M. Karthu, M. Näsäkkälä, M. Sundberg and R. Uggla, *Cryst. Struct. Commun.*, **8**, 409 (1979).
109. H. Schmidbaur, K. Dziwok, G. Reber and G. Müller, *Helv. Chim. Acta*, **70**, 1905 (1987).
110. M. B. Hocking and G. W. Bushnell, *Can. J. Chem.*, **68**, 1020 (1990).
111. D. S. Milbrath, J. G. Verkade, G. L. Kenyon and D. H. Eargle, *J. Am. Chem. Soc.*,**100**, 3167 (1978).
112. J. R. Durig and K. K. Chatterjee, *Inorg. Chem.*, **28**, 298 (1989).
113. P. G. Eller and P. W. R. Corfield, *J. Chem. Soc., Chem. Commun.*, 105 (1971).
114. E. N. Baker and B. R. Reay, *J. Chem. Soc., Dalton Trans.*, 2205 (1973).
115. K. A. Kerr, P. M. Boorman, B. S. Misener and J. G. H. van Roode, *Can. J. Chem.*, **55**, 3081 (1977).
116. B. J. Bowen, *Diss. Abstr. Int. B*, **30**, 1627 (1969).
117. P. W. Codding and K. A. Kerr, *Acta Crystallogr., Sect. B*, **34**, 3785 (1978).
118. T. S. Cameron, K. D. Howlett, R. A. Shaw and M. Woods, *Phosphorus*, **3**, 71 (1973).
119. T. S. Cameron, K. D. Howlett and K. Millar, *Acta Crystallogr., Sect. B*, **34**, 1639 (1978).
120. W. Dreissig and K. Pleith, *Acta Crystallogr., Sect. B*, **28**, 3478 (1972).
121. W. Dreissig and K. Pleith, *Acta Crystallogr., Sect. B*, **28**, 3473 (1972).
122. V. V. Tkachev, A. A. Shvets, L. M. Tokina and O. A. Osipov, *Zh. Strukt. Khim.*, **28**, 149 (1987); Engl. Transl, *J. Struct. Chem.*, **28**, 948 (1987).
123. O. Orama, M. Karhu and R. Uggla, *Cryst. Struct. Commun.*, **8**, 905 (1979).
124. E. J. Jacob and S. Samdal, *J. Am. Chem. Soc.*, **99**, 5656 (1977).
125. A. Cogne, A. Grand, J. Laugier, J. B. Robert and L. Wisenfeld, *J. Am. Chem. Soc.*, **102**, 2238 (1980).
126. J. P. Allbrand, A. Cogne and J. B. Robert, *Chem. Phys. Lett.*, **48**, 524 (1977).
127. P. W. Codding and K. A. Kerr, *Acta Crystallogr., Sect. B*, **35**, 1261 (1979).
128. D. W. Allen, L. A. March and I. W. Nowell, *J. Chem. Soc., Dalton Trans.*, 483 (1984).
129. D. W. Allen, I. W. Nowell and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 2505 (1985).
130. D. W. Allen, N. A. Bell, L. A. March and I. W. Nowell, *Polyhedron*, **9**, 681 (1990).
131. P. J. Carroll and D. D. Titus, *J. Chem. Soc., Dalton Trans.*, 824 (1977); *Cryst. Struct. Commun.*, **5**, 363 (1976).
132. R. Colton, B. F. Hoskins and P. Panagiotidou, *Aust. J. Chem.*, **40**, 1909 (1987).
133. Z. Galdecki, M. L. Glòwka, J. Michalski, A. Okruszek and W. J. Stec, *Acta Crystallogr., Sect. B*, **33**, 2322 (1977).
134. O. Orama, K. Nieminen, M. Karhu and R. Uggla, *Cryst. Struct. Commun.*, **8**, 909 (1979).
135. L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, **32**, 512 (1960).
136. H. Oberhammer, R. Schmutzler and O. Stelzer, *Inorg. Chem.*, **17**, 1254 (1978).
137. N. Kuhn, H. Schumann and G. Wolmershäuser, *Z. Naturforsch., Teil B*, **42**, 674 (1987).
138. J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

139. J. C. J. Bart, *Acta Crystallogr., Sect. B*, **25**, 489 (1969).
140. T. Moritani, K. Kuchitsu and Y. Morino, *Inorg. Chem.*, **10**, 344 (1971).
141. H. Oberhammer, *Z. Naturforsch., Teil A*, **28**, 1140 (1973).
142. K. Karakida amd K. Kuchitsu, *Inorg. Chim. Acta*, **16**, 29 (1976).
143. A. Caron, G. J. Palenik, E. Goldish and J. Donohue, *Acta Crystallogr.*, **17**, 102 (1964).
144. V. Plato, W. D. Hartford and K. Hedberg, *J. Chem. Phys.*, **53**, 3488 (1970).
145. Y. Morino, K. Kuchitsu and T. Moritani, *Inorg. Chem.*, **8**, 867 (1969).
146. M. Iwasaki and K. Hedberg, *J. Chem. Phys.*, **36**, 589 (1962).
147. D. R. Lide, *Spectrochim. Acta*, **15**, 473 (1959).
148. M. C. Etter and P. W. Baures, *J. Am. Chem. Soc.*, **110**, 639 (1988).
149. A. I. Gusev, N. G. Bokii, N. N. Afonina, T. V. Timofeeva, A. E. Kalinin and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **14**, 115 (1973); *Engl. Transl. J. Struct. Chem.*, **14**, 101 (1973).
150. G. Ferguson and C. Glidewell, *J. Chem. Soc., Perkin Trans. 2*, 2129 (1988).
151. S. Pohl, *Z. Naturforsch., Teil B*, **34**, 256 (1979).
152. S. Pohl, *Z. Naturforsch., Teil B*, **34**, 610 (1979).
153. C. Rϕmming, A. J. Iversen and J. Songstad, *Acta Chem. Scand., Ser. A*, **34**, 333 (1980).
154. K. Maartmann-Moe, C. Rϕmming and J. Songstad, *Acta Chem. Scand., Ser. A*, **36**, 757 (1982).
155. S. Konaka and M. Kimura, *Bull. Chem. Soc. Jpn.*, **46**, 413 (1973).
156. S. B. Hartley, W. S. Holmes, J. K. Jacques, M. F. Mole and J. C. McCoubrey, *Q. Rev. Chem. Soc.*, **17**, 204 (1963).
157. R. Withnall and L. Andrews, *J. Phys. Chem.*, **91**, 784 (1987).
158. R. Panzer, W. D. Burkhardt, E. Walter and J. Goubeau, *Z. Anorg. Allg. Chem.*, **416**, 297 (1975).
159. J. Goubeau and A. Lenz, *Spectrochim. Acta, Part A*, **27**, 1703 (1971).
160. F. Choplin and G. Kaufmann, *Spectrochim. Acta, Part A*, **26**, 2113 (1970).
161. S. O. Grim and E.D. Walton, *Inorg. Chem.*, **19**, 1982 (1980).
162. E. L. Wagner, *J. Am. Chem. Soc.*, **85**, 161 (1963).
163. L. I. Katzin, G. W. Mason and D. F. Peppard, *Spectrochim. Acta, Part A*, **34**, 57 (1978).
164. R. R. Carlson and D. W. Meek, *Inorg. Chem.*, **13**, 1741 (1974).
165. R. S. Armstrong, M. J. Aroney, R. J. W. LeFèvre, R. K. Pierens, J. D. Saxby and C. J. Wilkins, *J. Chem. Soc. A*, 2735 (1969).
166. S. I. Vdovenko, V. Ya. Semenii, Yu. P. Egorov, Yu. Ya. Borovikov and V. N. Zavatskii, *Zh. Obshch. Khim.*, **46**, 2613 (1976); Engl. Transl., *J. Gen. Chem. USSR*, **46**, 2491 (1976).
167. G. M. Phillips, J. S. Hunter and L. E. Sutton, *J. Chem. Soc.*, 146 (1945).
168. A. F. Wells, *J. Chem. Soc.*, 55 (1949).
169. E. G. Claeys and G. P. Van der Kelen, *J. Mol. Struct.*, **40**, 97 (1977).
170. J. G. Verkade and L. D. Quin (Eds), *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH, Weinheim, 1987.
171. T. A. Albright, W. J. Freeman and E. E. Schweizer, *J. Org. Chem.*, **40**, 3437 (1975).
172. S. R. Postle, *Phosphorus Sulphur*, **3**, 269 (1977).
173. A. I. Rezvukhin, G. N. Dolenko and S. A. Krupoder, *Magn. Reson. Chem.*, **23**, 221 (1985).
174. A. J. Montana, N. Zumbulyadis and B. P. Dailey, *J. Am. Chem. Soc.*, **99**, 4290 (1977).
175. J. B. Robert and L. Wiesenfeld, *Mol. Phys.*, **44**, 319 (1981).
176. R. Radeglia and R. Wolff, *Z. Naturforsch., Teil A*, **36**, 1177 (1981).
177. W. McFarlane and D. S. Rycroft, *J. Chem. Soc., Dalton Trans.*, 2162 (1973).
178. C. P. Cheng and T. L. Brown, *J. Am. Chem. Soc.*, **102**, 6418 (1980).
179. C. J. Eyerman, W. L. Jolly, S. F. Xiang, J. M. Shreeve and S.A. Kinkead, *J. Fluorine Chem.*, **23**, 389 (1983).
180. W. B. Perry, T. F. Schaaf and W. L. Jolly, *J. Am. Chem. Soc.*, **97**, 4899 (1975).
181. S. Hoste, D. F. Van de Vondel and G. P. Van der Kelen, *J. Electron Spectrosc. Relat. Phenom.*, **17**, 191 (1979).
182. W. E. Morgan, W. J. Stec, R. G. Albridge and J. R. Van Wazer, *Inorg. Chem.*, **10**, 926 (1971).
183. T. H. Gan, J. B. Peel and G. D. Willett, *Chem. Phys. Lett.*, **48**, 483 (1977).
184. S. Elbel and H. tom Dieck, *J. Chem. Soc., Dalton Trans.*, 1757 (1976).
185. (a) I. H. Hillier and V. R. Saunders, *J. Chem. Soc. A*, 2475 (1970); (b) *J. Chem. Soc. A*, 664 (1971); (c) *J. Chem. Soc., Dalton Trans.*, 21 (1972).
186. E. Fluck and D. Weber, *Pure Appl. Chem.*, **44**, 373 (1975).
187. V. V. Zverev and Ya. Ya. Villem, *Zh. Strukt. Khim.*, **21**, 30 (1980); Engl. Transl., *J. Struct. Chem.*, **21**, 22 (1980).

188. V. V. Zverev, *Zh. Obshch. Khim.*, **54**, 1265 (1984); Engl. Transl., *J. Gen. Chem. USSR*, **54**, 1131 (1984), and references cited therein.
189. V. I. Vovna, V. V. Gorchakov, A. I. Cherednichenko and S.N. Slabzhennikov, *Zh. Strukt. Khim.*, **29**, 32 (1988); Engl. Transl., *J. Struct. Chem.*, **29**, 27 (1988).
190. S. Yasuda, *Bull. Chem. Soc. Jpn.*, **57**, 3122 (1984).
191. V. D. Yumatov, L. N. Mazalov and E. A. Il'inchik, *Zh. Strukt. Khim.*, **21**, 24 (1980); Engl. Transl., *J. Struct. Chem.*, **21**, 583 (1980).
192. M. W. Schmidt, S. Yabushita and M.S. Gordon, *J. Phys. Chem.*, **88**, 382 (1984).
193. E. A. C. Lucken and M. A. Whitehead, *J. Chem. Soc.*, 2459 (1961).
194. A. G. Orpen and N. G. Connelly, *J. Chem. Soc. Chem. Commun.*, 1310 (1985); *Organometallics*, **9**, 1206 (1990).
195. S.-X. Xiao, W. C. Trogler, D. E. Ellis and Z. Berkovitch-Yellin, *J. Am. Chem. Soc.*, **105**, 7033 (1983).
196. D. S. Marynick, *J. Am. Chem. Soc.*, **106**, 4064 (1984).
197. M. Braga, *Inorg. Chem.*, **24**, 2702 (1985).
198. T. A. Albright, J. K. Burdett and M. H. Whangbo, *Orbital Interactions in Chemistry*, Wiley–Interscience, New York, 1985.
199. L. S. Bartell, L. S. Su and H. Yow, *Inorg. Chem.*, **9**, 1903 (1970).
200. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley–Interscience, New York, 1980.
201. A. Streitwieser, R. S. McDowell and R. Glaser, *J. Comput. Chem.*, **8**, 788 (1987).
202. F. Volatron and O. Eisenstein, *J. Am. Chem. Soc.*, **109**, 1 (1987); **106**, 6117 (1984).
203. P. Molina, M. Alajarín, C. L. Leonardo, R.M. Claramunt, M. C. Foces-Foces, F. Hernández Cano, J. Catalán, J. L. G. de Paz and J. Elguero, *J. Am. Chem. Soc.*, **111**, 355 (1989).
204. W. Schneider, W. Thiel and A. Komornicki, *J. Phys. Chem.*, **92**, 5611 (1988).
205. W. B. Person, J. S. Kwiatkowski and R. J. Bartlett, *J. Mol. Struct.*, **157**, 237 (1987).
206. J. Breidung, W. Schneider, W. Thiel and H. F. Schaefer, *J. Mol. Spectrosc.*, **140**, 226 (1990).
207. J. C. Bollinger, R. Houriet, C. W. Kern, D. Perret, J. Weber and T. Yvernault, *J. Am. Chem. Soc.*, **107**, 5352 (1985).
208. C. J. Cramer, C. E. Dykstra and S. C. Denmark, *Chem. Phys. Lett.*, **136**, 17 (1987).
209. M. S. Gordon, J. A. Boatz and M. W. Schmidt, *J. Phys. Chem.*, **88**, 2998 (1984).
210. S. von Carlowitz, W. Zeil, P. Pulay and J. E. Boggs, *J. Mol. Struct. THEOCHEM*, **87**, 113 (1982).
211. M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro and W. J. Hehre, *J. Am. Chem. Soc.*, **104**, 2797 (1982).
212. W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. DeFrees, J. A. Pople and J. S. Binkley, *J. Am. Chem. Soc.*, **104**, 5039 (1982).
213. A. Serafini, J.-F. Labarre, A. Veillard and G. Vinot, *J. Chem. Soc. Chem. Commun.*, 996 (1971).
214. L. Radom, J. S. Binkley and J. A. Pople, *Aust. J. Chem.*, **30**, 699 (1977).
215. J. F. Olsen and J. M. Howell, *J. Fluorine Chem.*, **10**, 197 (1977).
216. W. H. Kirchhoff and D. R. Lide, *J. Chem. Phys.*, **51**, 467 (1969).
217. N. Hackett and R. J. W. LeFèvre, *J. Chem. Soc.*, 2612 (1961).
218. G. Fogarasi and P. Pulay, in *Vibrational Spectra and Structure* (Ed. J.R. Durig), Vol. 14, Elsevier, Amsterdam, 1985, Chapter 3.
219. P. Pulay, G. Fogarasi and J. E. Boggs, *J. Chem. Phys.*, **74**, 3999 (1981).
220. R. Heinzmann and R. Ahlrichs, *Theor. Chim. Acta*, **42**, 33 (1976).
221. C. Erhardt and R. Ahlrichs, *Theor. Chim. Acta*, **68**, 231 (1985).
222. A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, **83**, 735 (1985).
223. J. E. Lennard-Jones and J. A. Pople, *Proc. R. Soc. London, Ser. A*, **210**, 190 (1951).
224. C. Edmiston and K. Reudenberg, *Rev. Mod. Phys.*, **35**, 457 (1963); in *Quantum Theory of Atoms, Molecules and the Solid State* (Ed. P. O. Lowdin), Academic Press, New York, 1966, pp. 263–280.
225. J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 300 (1960).
226. S. F. Boys, in *Quantum Theory of Atoms, Molecules and the Solid State* (Ed. P.O. Lowdin), Academic Press, New York, 1966, p. 253.
227. A. E. Reed and F. Weinhold, *J. Chem. Phys.*, **83**, 1736 (1985).
228. J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.*, **102**, 7211 (1980).
229. A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, **88**, 899 (1988).

230. J. Demuynck and A. Veillard, *J. Chem. Soc., Chem. Commun.*, 873 (1970).
231. M. F. Guest, I. H. Hillier and V. R. Saunders, *J. Chem. Soc., Faraday Trans. 2*, 867 (1972).
232. P. von R. Schleyer and A. J. Kos, *Tetrahedron*, **39**, 1141 (1983).
233. R. P. Messmer, P. A. Schultz, R. C. Tatar and H.-J. Freund, *Chem. Phys. Lett.*, **126**, 176 (1986).
234. D. A. Dixon, T. H. Dunning, R. A. Eades and P. G. Gassman, *J. Am. Chem. Soc.*, **105**, 7011 (1983).
235. W. A. Goddard, T. H. Dunning, W. J. Hunt and P. J. Hay, *Acc. Chem. Res.*, **6**, 368 (1973).
236. A. C. Hurley, J. E. Lennard-Jones and J. A. Pople, *Proc. R. Soc. London, Ser. A*, **220**, 446 (1953).
237. R. P. Messmer and P. A. Schulz, *Phys. Rev. Lett.*, **57**, 2653 (1986).
238. P. A. Schulz and R. P. Messmer, *Phys. Rev. Lett.*, **58**, 2416 (1987).
239. P. A. Schulz and R. P. Messmer, *J. Am. Chem. Soc.*, **110**, 8258 (1988).
240. C. H. Patterson and R. P. Messmer, *J. Am. Chem. Soc.*, **111**, 8059 (1989); **112**, 4138 (1990).
241. J. E. Huheey, *Inorganic Chemistry*, 1st edn., Harper and Row, London, 1975.
242. M. W. Schmidt and M. S. Gordon, *Can. J. Chem.*, **63**, 1609 (1985).
243. F. Choplin and G. Kaufmann, *J. Mol. Struct.*, **11**, 381 (1972); *Bull. Soc. Chim. Fr.*, 387 (1971).
244. F. Acloque, O. Kahn and A. Dniestrowski, *C.R. Acad. Sci., Ser. C*, **271**, 1062 (1970).
245. R. M. Archibald and P. G. Perkins, *Rev. Rooum. Chim.*, **16**, 1137 (1971).
246. Yu. Yu. Samitov and R. K. Safiullin, *Zh. Obshch. Khim.*, **58**, 295 (1988); Engl. Transl., *J. Gen. Chem. USSR*, **58**, 258 (1988).
247. A. M. Rosen, N. M. Klimenko, B. V. Krupnov and A. S. Nikiforov, *Dokl. Akad. Nauk SSSR*, **287**, 915 (1986); Engl. Transl., **287**, 327 (1986).
248. V. V. Zverev, R. G. Islamov and Yu. P. Kitaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 496 (1979); Engl. Transl., 457 (1979).
249. C. Yuan, C. Zhou and K. Chen, *Huaxue Xuebao*, **39**, 699 (1981); *Chem. Abstr.*, **97**, 181324 (1982).
250. M. A. Landau, A. V. Fokin and A. S. Kabankin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2486 (1973); Engl. Transl., 2428 (1973).
251. O. A. Raevskii, V. E. Bel'skii and V. V. Zverev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2491 (1973); Engl. Transl., 2432 (1973).
252. O. A. Raevskii and Yu. A. Donskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2494 (1973); Engl. Transl., 2435 (1973).
253. K. Jug and J. Schulz, *J. Comput. Chem.*, **9**, 40 (1988).
254. J. R. Durig and T. J. Hizer, *J. Mol. Struct.*, **145**, 15 (1986).
255. O. A. Raevsky, *J. Mol. Struct.*, **19**, 275 (1973).
256. O. A. Raevskii, N. G. Mumzhieva, T. E. Kron and E. N. Tsvetkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1292 (1981); Engl. Transl. 1026 (1981).
257. O. A. Raevskii and N. G. Mumzhieva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1822 (1981); Engl. Transl., 1491 (1981).
258. I. I. Patsanovskii, E. N. Strelkova, É. A. Ishmaeva, A. B. Remizov, N. G. Kusainova, L. V. Naumova and A. N. Pudovik, *Zh. Obshch. Khim.*, **52**, 1045 (1982); Engl. Transl., *J. Gen. Chem. USSR*, **52**, 909 (1982).
259. B. N. Laskorin, V. V. Yakshin and L. I. Sokal'skaya, *Zn. Strukt. Khim.*, **19**, 757 (1978); Engl. Transl., *J. Struct. Chem.*, **19**, 654 (1978).
260. G. V. Ratovski, D. D. Chuvashev, L. M. Sergienko and S. L. Belaya, *Phosphorus Sulphur Silicon*, **51/52**, 242 (1990).
261. S. B. Bulgarevich, S. E. Filippov, D. Ya. Movshovich, L. V. Goncharova and A. A. Shvets, *Zh. Obshch. Khim.*, **59**, 1519 (1989); Engl. Transl., *J. Gen. Chem.* USSR, **59**, 1349 (1989).
262. S. B. Bulgarevich, L. V. Goncharova, O. A. Osipov, V. V. Kesarev and A. A. Shvets, *Zh. Obshch. Khim.*, **48**, 1331 (1978); Engl. Transl., *J. Gen. Chem. USSR*, **48**, 1219 (1978).
263. S. B. Bulgarevich, E. G. Amarskii, A. A. Shvets and O. A. Osipov, *Zh. Obshch. Khim.*, **46**, 1708 (1976); Engl. Transl., *J. Gen. Chem. USSR*, **46**, 1661 (1976).
264. É. G. Yarkova, Sh. M. Nazipov, O. B. Sobanova, A. A. Muratova and A. N. Pudovik, *Zh. Obshch. Khim.*, **48**, 749 (1978); Engl. Transl., *J. Gen. Chem. USSR*, **48**, 686 (1978).
265. G. V. Ratovskii, A. M. Panov, O. A. Yatukina, Yu. I. Sukhorukov and E.N. Tsvetkov, *Chem. Abstr.*, **90**, 143722 (1979).
266. A. P. Timosheva, G. V. Romanov, S. G. Vul'fson, A. N. Vereshchagin, T. Ya. Stepanova and A. N. Pudovik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 604 (1982); Engl. Transl., 533 (1982).

267. V. V. Negrebetskii, A. I. Bokanov, N. A. Rozanel'skaya and B. I. Stepanov, *Zh. Obshch. Khim.*, **49**, 1495 (1979); Engl. Transl., *J. Gen. Chem. USSR*, **49**, 1304 (1979).
268. V. V. Negrebetskii, L. Ya. Bogel'fer, A. I. Bokanov, N. A. Rozanel'skaya and B. I. Stepanov, *Zh. Strukt. Khim.*, **19**, 628 (1978); Engl. Transl., *J. Struct. Chem.*, **19**, 545 (1978).
269. S. B. Bulgarevich, L. V. Goncharova, P. N. Kozachenko, A. A. Shvets and O. A. Osipov, *Zh. Strukt. Khim.*, **22**, 157 (1981); Engl. Transl., *J. Struct. Chem.*, **22**, 436 (1981).
270. O. A. Raevskii, A. N. Vereshchagin, Yu. A. Donskaya, I. G. Malakhova, Yu. I. Sukhorukov, E. N. Tsvetkov and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2243 (1976); Engl. Transl., 2092 (1976).
271. I. I. Patsanovskii, É. A. Ishmaeva, E. N. Sundukova, A. N. Yarkevich and E. N. Tsvetkov, *Zh. Obshch. Khim.*, **56**, 567 (1986); Engl. Transl., *J. Gen. Chem. USSR*, **56**, 501 (1986).
272. E. N. Strelkova, I. I. Patsanovskii, É. A. Ishmaeva, E. N. Tsvetkov. É. G. Yarkova, A. N. Yarkevich, N. N. Lukovkina and T. E. Kron, *Zh. Obshch. Khim.*, **54**, 1277 (1984); Engl. Transl., *J. Gen. Chem. USSR*, **54**, 1142 (1984.)
273. A. B. Rezimov and R. K. Ismagilov, *Zh. Obshch. Khim.*, **53**, 2647 (1983); Engl. Transl., *J. Gen. Chem. USSR*, **53**, 2388 (1983).
274. É. A. Ishmaeva, E. N. Tsvetkov, E. N. Strelkova and I. I. Patsanovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1179 (1982); Engl. Transl., 1052 (1982).
275. V. G. Dashevskii, A. P. Baranov, T. Ya. Medved' and M. I. Kabachnik, *Teor. Eksp. Khim.*, **15**, 255 (1979); Engl. Transl., *Theor. Exp. Chem.*, **15**, 197 (1979).
276. O. A. Raevskii, I. O. Umarova and E. N. Tsvetkov, *Teor. Eksp. Khim.*, **19**, 87 (1983); Engl. Transl., *Theor. Exp. Chem.*, **19**, 75 (1983).
277. O. A. Raevskii and I. O. Umarova, *Teor. Eksp. Khim.*, **19**, 732 (1983); Engl. Transl., *Theor. Exp. Chem.*, **19**, 677 (1983).
278. P. Ugliengo, J. Ahmed, D. Viterbo and M. Ceruti, *Gazz. Chim. Ital.*, **119**, 493 (1989).
279. E. Juaristi, L. Valle, B. A. Valenzuela and M. A. Aguilar, *J. Am. Chem. Soc.*, **108**, 2000 (1986).
280. E. Juaristi, L. Valle, C. Mora-Uzeta, B. A. Valenzuela, P. Joseph-Nathan and M. F. Fredrich, *J. Org. Chem.*, **47**, 5038 (1982).
281. E. Juaristi, B. A. Valenzuela, L. Valle and A. T. McPhail, *J. Org. Chem.*, **49**, 3026 (1984).
282. E. Juaristi, N. A. López-Núñez, B. A. Valenzuela, L. Valle, R. A. Toscano and M. Soriano-García, *J. Org. Chem.*, **52**, 5185 (1987).
283. M. Mikolajczyk, P. Balczewski, K. Wrobelewski, J. Karolak-Wojciechowska, A. Miller, M. W. Wieczorek, M. Y. Antipin and Y. T. Struchkov, *Tetrahedron*, **23**, 4855 (1984).
284. M. Mikolajczyk, P. Graczyk and P. Balczewski, *Tetrahedron Lett.*, **28**, 573 (1987).
285. M. Mikolajczyk, P. Graczyk, M. W. Wieczorek, G. Bujacz, Y. T. Struchkov and M. Y. Antipin, *J. Org. Chem.*, **53**, 3609 (1988).
286. M. Mikolajczyk, P. Balczewski, M. W. Wieczorek, G. Bujacz, M. Y. Antipin and Y. T. Struchkov, *Phosphorus Sulphur*, **37**, 183 (1988).
287. M. Mikolajczyk, P. Graczyk, M. W. Wieczorek and G. Bujacz, *Tetrahedron Lett.*, **29**, 6801 (1988).

CHAPTER **2**

Structure and stereochemistry of secondary and tertiary phosphine chalcogenides

M. J. GALLAGHER

School of Chemistry, University of New South Wales, PO Box 1, Kensington, NSW 2033, Australia

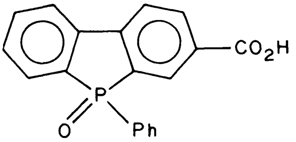
---

I. INTRODUCTION

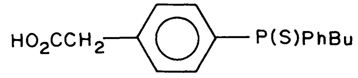
The stereochemistry of phosphorus chalcogenides, and of phosphorus compounds in general, is a subject that is essentially only 30 years old. This is despite the fact that

---

The chemistry of organophosphorus compounds, Volume 2, Phosphine oxides, sulphides, selenides and tellurides
Edited by Frank R. Hartley. ISBN: 0-471-93056-3



(1)



(2)

methylethylphenylphosphine oxide was first resolved by Meisenheimer[1] in 1911 using (+)-bromocamphorsulphonic acid as the resolving agent. He subsequently resolved benzylmethylphenylphosphine oxide in the same way in 1926[2a], but it was to be many years before another phosphine oxide, the dibenzphosphole **1** was resolved[2b]. In 1944 Davies and Mann[3] resolved the sulphide **2**. These isolated instances apart, it was generally held that the stereochemistry of phosphorus (and arsenic, antimony and bismuth) would be uninteresting, since any conversion to the trivalent form would result in racemization owing to inversion in the same way as was known to occur for nitrogen. It was further held that the equilibrium (equation 1) was a mobile one and would prevent any useful stereochemical studies of quaternary compounds. Although ample evidence to the contrary existed, the notion persisted until it was demolished entirely by Horner's isolation of stable enantiomeric phosphines by the electrolytic cleavage of resolved quaternary salts. This discovery stimulated an enormous amount of interest in the stereochemistry not only of phosphorus, but also of many other elements, and the field is now so large that it is doubtful if it could be usefully reviewed as a whole.

$$R_4P^+X^- \rightleftharpoons R_3P + RX \qquad (1)$$

This chapter is restricted to a consideration of the stereochemistry of chalcogenides of tertiary and secondary phosphines. It will be very largely concerned with oxides and sulphides, since very little work has appeared on selenides and tellurides[4a]. Indeed, simple tellurides, R_3PTe, are unstable compounds and decompose at room temperature unless kinetically stabilized by bulky groups, such as *tert*-butyl[4b].

Strictly, there are three classes of phosphine chalcogenides, primary, $RP(X)H_2$, secondary, $R_2P(X)H$, and tertiary, R_3PX, in addition to the parent compounds H_3PX. These last are unknown, although H_3PO and its tautomer H_2POH have been detected as reaction products in an argon matrix[5a]. Theoretical considerations indicate they should be stable, probably in the tautomeric form H_2PXH[5b]. Phosphine oxide has been suggested[6] to account for the formation of tertiary phosphine oxides in the attempted base-catalysed alkylation of alkyl phosphinates, $ROP(O)H_2$. Primary phosphine chalcogenides, although known, have been little studied and no stereochemical or structural information is available.

In the stereochemical discussion which follows, the terms inversion and retention of configuration refer only to the non-chalcogen atoms on phosphorus in order to avoid the confusion which may arise in discussion if the Cahn–Ingold–Prelog nomenclature is strictly adhered to. Put another way, the chalcogen atom is considered always to be the atom of lowest priority in the RS system when discussing configurational changes (or lack of them) at phosphorus.

II. SECONDARY PHOSPHINE CHALCOGENIDES $R^1R^2P(X)H$ (X = O, S, Se)

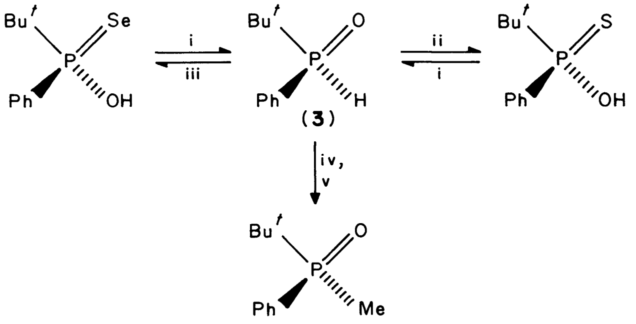
A. Preparation

Secondary phosphine chalcogenides are reasonably well known, although little structural information is available. Methods for their preparation are limited and most do not lend themselves to resolution. Nevertheless, secondary phosphine oxides and sulphides have been obtained in optically active form. The first example[7], benzylphenylphosphine oxide (**3**; $R = PhCH_2$), was obtained by lithium aluminium hydride reduction of one enantiomer of (−)-menthyl benzylphenylphosphinate (equation 2). Shortly after, β-naphthylphenylphosphine oxide (**3**, R = 2-naphthyl) was similarly obtained[8]. Both compounds had extremely low rotations ($\alpha_D - 0.52°$ and $-0.59°$, respectively) and nothing is known of the optical purity of either sample.

However, Campbell and Way[2b] and Mislow and coworkers (3)[9] had found that lithium aluminium hydride causes racemization of tertiary phosphine oxides, so it must be considered unlikely that a high degree of stereoselectivity would be obtained in the reduction of the esters. Both groups presented evidence that the observed rotation was in fact due to chiral phosphorus, but the subsequent preparation of (−)-phenyl-*tert*-butylphosphine oxide[10a] (**3**; R = *t*-Bu, $\alpha_D - 28.8$) suggests that optical purities for **1** ($R = PhCH_2$ or 2-naphthyl) were low. Michalski and Skrzypzynski[10a] obtained **3** (R = *t*-Bu) by two routes (equation 3) and assigned absolute stereochemistry on the basis of its stereospecific alkylation to give the tertiary $oxide_4$ whose absolute stereochemistry had previously been established by correlation[11].

$$(-)\text{-Ph(R)P(O)O-Menthol} \xrightarrow{\text{LiAlH}_4} \underset{(\mathbf{3})}{(-)\text{-Ph(R)P(O)H}} \qquad (2)$$

The sequence shown in equation 3 also serves to establish the stereochemistry of the addition of S and Se to secondary phosphine oxides as proceeding with retention. It is notable that the anion formed from **3** (R = *t*-Bu) retains its stereochemical integrity. This fact, together with the general observation that thiophosphinic acids are readily synthesized and usually readily resolvable, suggests that desulphurization of resolved thiophosphinates followed by base-catalysed alkylation or Michael-type addition reactions may well prove a useful general route to chiral tertiary phosphine oxides.

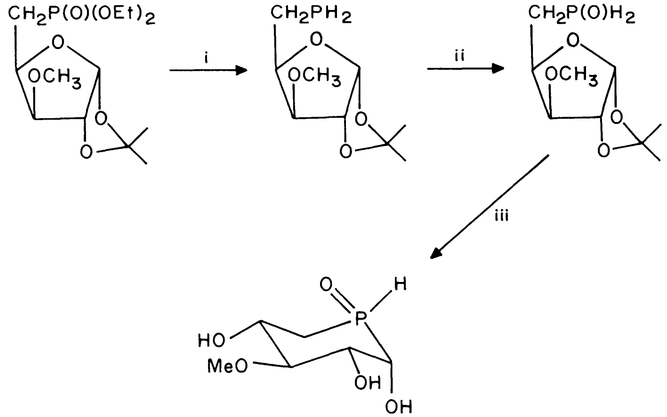


(3)

(i) Raney Ni; (ii) S_8; (iii) Se_n; (iv) NaH; (v) MeI

The same Polish workers[106] prepared the sulphur analogue, **5**, by reduction of a mixed anhydride (equation 4): Only the mixed anhydride with trifluoromethanesulphonic acid gave chiral products, presumably because the triflate anion is an excellent leaving group and substantially reduced the risk of stereomutation of the intermediate. Both

$$\underset{(+)\text{or}(-)}{\text{Bu}^t\text{PPh(S)OSO}_3\text{CF}_3} \xrightarrow{\text{NaBH}_4} \underset{\substack{(-)\text{or}(+)\\(\mathbf{5})}}{\text{Bu}^t\text{PPh(S)H}} \qquad (4)$$



(6)

(5)

(i) $NaAlH_2(OCH_2CH_2OEt)_2$; (ii) H_2O_2; (iii) H^+, H_2O

enantiomers were obtained with apparently good optical purity. There is good evidence that the reduction step proceeds with inversion in an S_N2 type of reaction. A cyclic secondary phosphine oxide, **6**, has been prepared as part of a phosphasugar study[11]. Its synthesis is shown in reaction 5. The stereochemistry at phosphorus was not assigned and some doubts have been cast on its homogeneity.

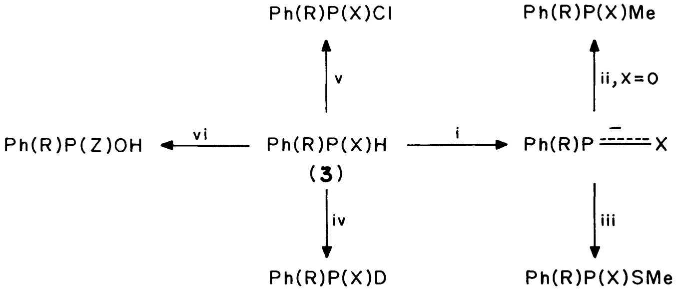
B. Reaction Stereochemistry

Like other classes of phosphorus compounds containing the structural feature P(X)H, secondary phosphine chalcogenides exist in a tautomeric equilibrium (equation 6): although, in general, evidence for the phosphorus(III) form is indirect and little is known

$$R_1R_2P(X)H \rightleftharpoons R_1R_2PXH \qquad (6)$$

of the factors influencing the equilibrium. However, the small amount of chemical evidence available suggests that the conversion does not alter the stereochemistry. Thus, deuterium exchange is rapid even with the absence of a catalyst and produces no evidence of racemization. The same behaviour has been observed[12] with isopropyl methylphosphinate, $MeP(O)(H)OPr^i$. Similarly, deprotonation of **3** ($R = t$-Bu) does not afford a racemic product although this is reported for base treatment of **3** ($R = PhCH_2$). Both **3** ($R = t$-Bu) and **5** may be converted to the corresponding halides or thiomethyl compounds with retention of stereochemistry and **3** ($R = t$-Bu) reacts with sulphur or selenium also with retention. Equation 7 summarizes the known transformations, all of which proceed with retention of configuration.

Conditions for racemization are unclear. Emmick and Letsinger[7] reported that both acids and bases racemized **1** ($R = PhCH_2$), although the related isopropyl methylphosphinate is stable to acids and not to bases[12]. Since tertiary phosphine oxides are stable to alkali and the secondary phosphine chalcogen anions retain their stereochemistry, base-catalysed inversion seems unlikely. Acids, however, do isomerize tertiary phosphine oxides, presumably via a phosphorus(v) intermediate, and this type of reaction seems more likely for the secondary analogues also, although it does not appear to have been reported, except indirectly in the preparations of **3** ($R = PhCH_2$ or



(7)

(i) NaH; (ii) MeI; (iii) MeSSMe; (iv) ROD;
(v) R_3N-CCl_4 or *N*-halosuccinimide; (vi) S_8 or Se_n.

2-naphthyl). The stereochemistry of the reversible addition of ethylphenylphosphine oxide to carbonyl compounds has been described[13], but otherwise the use of secondary phosphine chalcogenides in synthesis has been little studied.

III. TERTIARY PHOSPHINE CHALCOGENIDES, $R^1R^2R^3P(X)$ (X = O, S, Se)

A. Structure

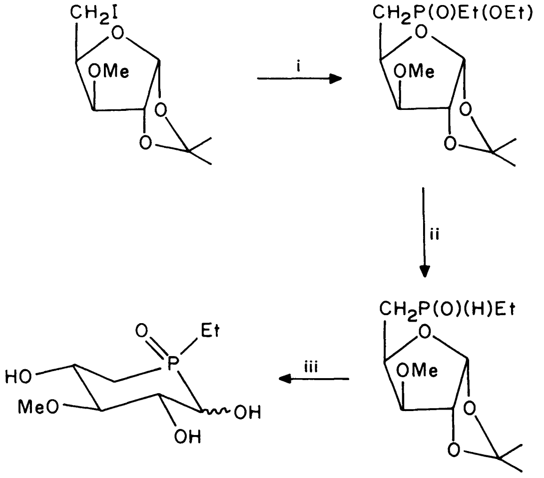
Because of their chemical stability and the fact that they are usually crystalline solids, this class of organophosphorus compounds has received much stereochemical attention. There is a wealth of structural data available, both in the solid state (in 1990 the Cambridge Crystallographic Data Base contained more than 250 structures of tertiary phosphine chalcogenides) and in solution, for oxides, sulphides and selenides, but very little for tellurides. Cyclic and acyclic compounds are well represented. Solid-state structures show a tetrahedral geometry at phosphorus with the XPC angle greater than for a regular tetrahedron, possibly owing to a repulsive interaction between the P = X and P—C bonds.

B. Preparation

1. Cyclic compounds

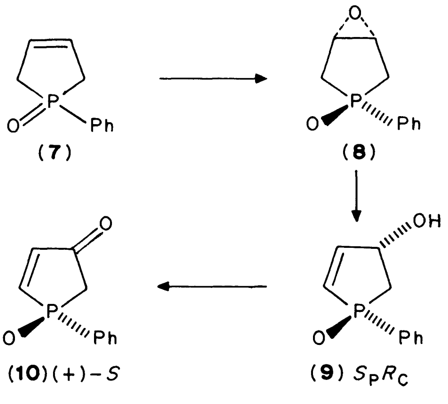
Although stereoisomerism arising from cyclic phosphine chalcogenides was not reported until the early 1960s[14], it rapidly became commonplace and *cis–trans* isomers have been observed and characterized for oxides and sulphides of cyclic phosphines of virtually every ring size that has been studied[15]. Nowadays failure to observe this type of stereoisomerism in cyclic systems would require comment. The preparative heterocyclic chemistry of tertiary phosphine chalcogenides is very extensive and cannot be surveyed here. A good book[15] is available and cyclic phosphines have been reviewed in Volume 1 of this work[16]. In general, oxidation or sulphuration of cyclic phosphines affords the corresponding chalcogenides in a stereospecific manner with retention and with the number and ratio of isomers formed being the same as are present due to the pyramidal phosphine. The diastereoisomers are usually readily separated by normal techniques. Many X-ray structures have been determined[15].

Chiral cyclic phosphine oxides are rare, the major examples being phosphinoyl sugars, which have been studied largely by Inokawa and coworkers[17]. Several X-ray structures of these have been determined[18] and, since, the absolute stereochemistry of



(8)

(i) $EtP(OEt)_2$; (ii) $NaAlH_2(OCH_2CH_2OEt)_2$; (iii) H^+, H_2O



(9)

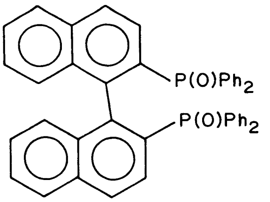
the carbocyclic portion of the ring is known, these constitute determinations of absolute stereochemistry at phosphorus, independent of correlation. Equation 8 shows one such route to this class of compounds. Another chiral cyclic phosphine oxide, 3-oxo-1-phenyl-2-phospholene-1-oxide **10**, was obtained by Bodalski and coworkers[19] from the readily accessible 1-phenyl-3-phospholene-1-oxide (**7**) (reaction 9). Stereospecific epoxidation followed by base-catalysed rearrangement gave the (±)-alcohol **9** which was resolved using camphanyl chloride to give the (+)-isomer, whose absolute configuration was determined by X-ray diffraction as S_PR_C. Oxidation afforded the chiral ketone, **10**, stable under the reaction conditions and hence probably of high optical purity.

2. *Acyclic compounds*

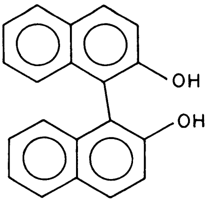
a. Resolution methods. Chiral phosphine oxides were first obtained by resolution using (+)-bromocamphorsulphonic acid[1,2], a method relying on protonation of the phosphoryl oxygen and separation of the salts by recrystallization. Tartaric acids and their derivatives have also been used[20]. The method can be, and usually is, extremely tedious and very laborious, but in Meisenheimer's hands it yielded ethylmethylphenyl- and benzylmethylphenyl-phosphine oxides of good optical purity. Part of the difficulty is that phosphines oxides are not very basic and the position of the equilibrium (equation 10) under normal circumstances would lie predominantly on the phosphine

$$R^1R^2R^3P{=}O + H^+ \rightleftharpoons R^1R^2R^3P{=}\overset{+}{O}H \leftrightarrow R^1R^2R^3\overset{+}{P}OH \qquad (10)$$

oxide side. Nevertheless, the method is occasionally useful and has been used by Nyori and coworkers[21] for the resolution of 2,2′-bisdiphenylphosphino-1,1′-dinaphthyl (**11**). The related compound, (+)- or (−)-2,2′-dihydroxy-1,1′-dinaphthyl (**12**), has been successful in the resolution of phosphine oxides by diastereoisomeric complex formation[22]. Although simple and giving excellent yields and purity, the method appears extremely sensitive to spatial factors. Thus, it resolved EtMePhP(O) but not MePrPhP(O). Tartaric acid has also been used successfully in the resolution of phosphine oxides. Very high yields and virtually complete enantiomeric separations have been obtained chromatographically for phosphine oxides using a column with a bonded stationary phase of 3,5-$(NO_2)_2C_6H_4CONHCHPhCONH(CH_2)_3$[23a], with normal stationary phases on a cyclodextrin column[23b] or using Pirkle's chiral stationary phase[23c]. A range of organophosphorus compounds can be resolved on a column of optically active poly(trityl methacrylate)[24]. In view of the present availability of very efficient chromatographic processes, the development of a range of columns would seems to be the most hopeful area for convenient resolutions in the future.



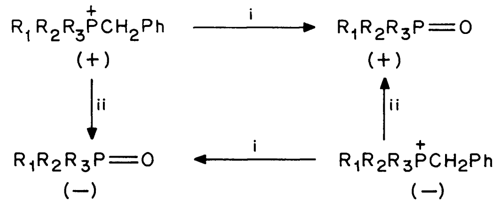
(11)



(12)

Although Davies and Mann[3] resolved the phosphine sulphide **2** nearly 50 years ago, there has been no reported interest since then. Sulphides are much weaker protic bases than oxides and the acid–base approach will not be successful here. No resolution of a selenide has been described. The sulphur chalcogenides are commonly obtained by stereospecific synthesis from the phosphine[25] using a range of reagents; selenides are similarly prepared. Sulphides may also be prepared from the oxides with predominant (acyclic) or complete (cyclic) retention of configuration using B_2S_3 as a reagent[26].

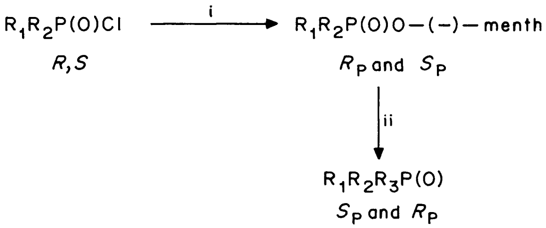
b. Synthesis. McEwen and coworkers[27] resolved the first acyclic phosphonium salt (benzylethylmethylphenyl) using the dibenzoyl hydrogentartrate anion and converted



(11)

(i) Wittig reaction; (ii) $OH^- - H_2O - ROH$

the enantiomeric salts into the corresponding oxides by either alkaline hydrolysis (inversion) or the Wittig olefination reaction (retention) (equation 11). As a general method this is restricted by the stereochemical complications which can arise in the alkaline hydrolyses of phosphonium salts[28], the fact that the benzyl group will not necessarily be the only group participating in the Wittig reaction and by difficulties in the preparation and resolution of the phosphonium salts.



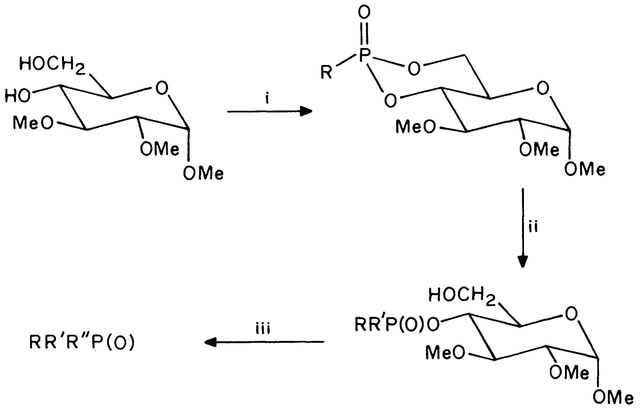
(12)

(i) (−)−menthol−R_3N; (ii) R_3MgX

Mislow and coworkers[29] separated the diastereoisomeric esters of phosphinic acids and (−)-menthol, in itself a difficult and low-yielding process, and converted them into phosphine oxides by stereospecific Grignard reactions (equation 12). The reaction is believed to proceed with inversion since Hudson and Green[30] had earlier shown that transesterification of phosphinate proceeds with inversion. Until recently, this method was the most widely used, despite the practical difficulties. (−)-Menthol is almost invariably the resolving agent, although cholesterol was briefly tried[31]. The use of organolithiums in place of Grignards does not produce any great improvement and often gives products of lower optical purity. If the chiral starting ester is a resolved cyclic phosphonate, then the reaction has the advantage that by altering the sequence of the two Grignard displacements enantiomeric phosphine oxides may be obtained from the same starting material[32] e.g. by interchanging steps ii and iii in equation 13.

Inch and coworkers[32] successfully used carbohydrate diols as the asymmetric unit (equation 13) and noted that the cyclic phosphonate was readily separated into its diastereoisomers, which is often not the case for acyclic phosphinates. Further, the assignment of absolute configuration to the starting phosphonate is more straightforward in view of the well established correlations in the carbohydrate field. However, the reaction suffers from the same disadvantages as the phosphinate method in terms of sluggish reactions and low yields.

Some variations on this theme have appeared in recent years which seek to overcome some of the problems by using other stereospecific reactions. Kato and coworkers[33] began with the isomerically pure diol **13** and prepared the cyclic phosphonates (**14**),



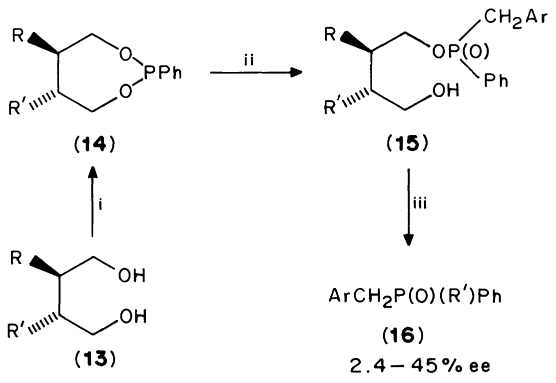
(13)

(i) $RP(O)Cl_2$—Py; (ii) R'MgX; (iii) R"MgX

which underwent the Michaelis–Arbuzov reaction (retention) to give the benzyl phosphonate (**15**), which was then subjected to a Grignard reaction (reaction 14). However, the optical purities of the products were not high. Similarly, Juge and Genet[34] opened the ring of the readily accessible chiral 1,3,2-dioxaphospholan **17** by Arbuzov alkylation and, after transesterification, Grignard reaction gave the phosphine oxides (**18**) (reaction 15). By varying the order of addition of the substituents they obtained either enantiomer with good enantiomeric excesses.

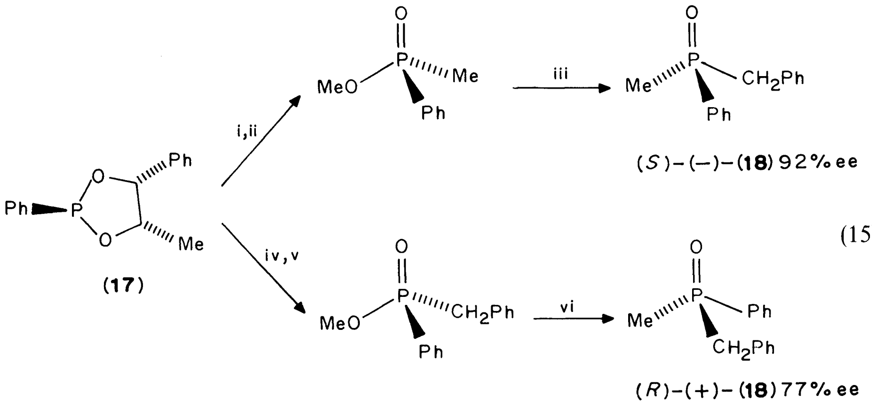
A variation of this approach (reaction 16) utilizes the readily resolvable *O*-alkyl monoesters of alkylphosphonothioic acids (**19**). The stereochemical consequences here are less certain, particularly as displacement of the thiolo group may be sensitive to subtle variations of reaction conditions and structure[35]; generally, however, displacement of a thiolate group at phosphorus proceeds with retention, not inversion as is the case for alkoxy groups.

An alternative approach avoids the often vexatious Grignard reaction altogether (reaction 17). Alkylation of the secondary phosphine oxide (**29**) with (−)-menthyl chloroacetate, separation of the diastereoisomers, hydrolysis and decarboxylation afford



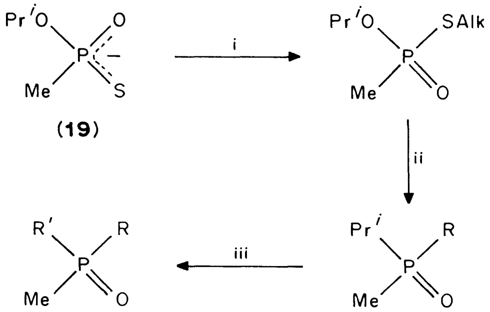
(14)

(i) $PhPCl_2$— Py; (ii) $ArCH_2Cl$; (iii) R'MgX



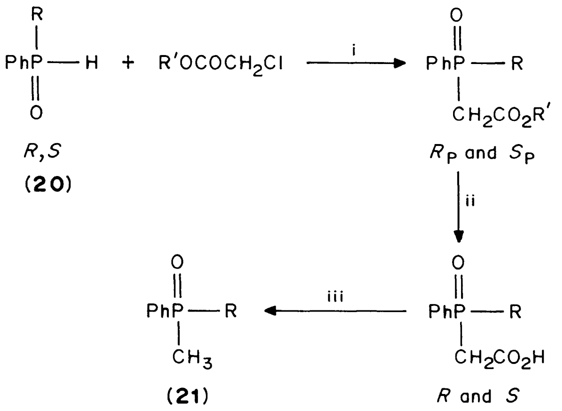
(15)

(i) MeI; (ii) MeOH — H^+; (iii) $PhCH_2MgBr$; (iv) $PhCH_2Br$;
(v) MeOH — H^+; (vi) MeMgBr



(16)

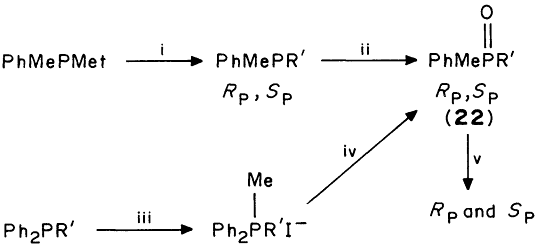
(i) Alkyl halide; (ii) RMgX; (iii) R′MgX



(17)

(i) base; (ii) hydrolysis; (iii) pyrolysis; R′ = (−)-menthol the chiral methyl oxides (**21**) with essentially 100% enantiomeric excess. Provided that the secondary phosphine oxide is available, this seems a general and useful route to a range of compounds of good chiral purity.

In an alternative approach, two groups have prepared diastereoisomeric phosphines by the reaction of alkali metal phosphides with optically active halides (reaction 18) followed by oxidation and separation of the mixtures[36,37]. Elimination was a serious side reaction with the substitution procedure. A variant is to prepare the phosphines from diphenyl phosphide and then to quaternize and hydrolyse the salts with alkali[38]. Crystal structures have established the absolute stereochemistry at phosphorus in the menthylmethylphenylphosphine oxides (**22**)[37,38].

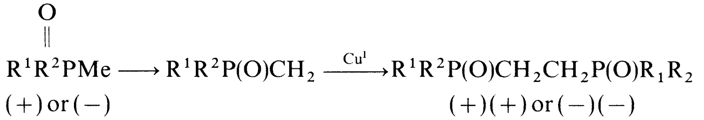


(18)

(i) (−)-menthyl chloride; (ii) H_2O_2; (iii) MeI

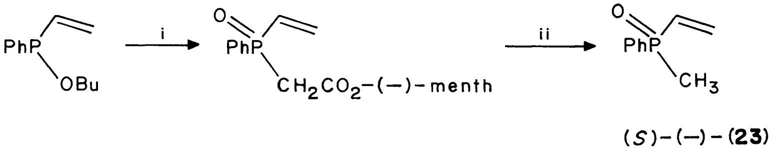
(iv) HO^- — H_2O — MeOH; (v) recrystallization

All the foregoing syntheses involve a separation of diastereoisomers, and this is very often tedious, difficult and, worse still, unpredictable. An alternative approach is to start from a phosphine oxide already resolved and to elaborate it further using reactions which do not affect the stereochemistry at phosphorus. An initial step in this direction was taken by Mislow and coworkers[39], who showed first that deprotonation of carbon attached to chiral phosphorus left the stereochemistry there unaffected and used this reaction to prepare and oxidatively couple the anions to make chiral diphosphine dioxides (reaction 19). This reaction is important since it provides a route to chiral diphosphines[40], which are very valuable as chelating agents in homogeneous transition metal catalysis.



$$\underset{(+)\text{or}(-)}{R^1R^2\overset{\overset{\displaystyle O}{\|}}{P}Me} \longrightarrow R^1R^2P(O)CH_2 \xrightarrow{Cu^I} \underset{(+)(+)\text{or}(-)(-)}{R^1R^2P(O)CH_2CH_2P(O)R_1R_2} \qquad (19)$$

A much more flexible approach, however, has been developed recently by Pietrusiewicz and coworkers[41]. They have established a good preparative route (reaction 20) to (−)-(*S*)-methylphenylvinylphosphine oxide (**23**) of high optical purity. Unlike most other oxides, **23** contains a reactive site at which a great deal of chemistry can be carried out without affecting the stereochemistry at phosphorus. Vinyl phosphine oxides, particularly those unsubstituted at the β-carbon, are excellent Michael acceptors and **23** readily adds alcohols[42], amines[43,44], alkyl groups[45,46] (as the cuprates), thiols[42] and secondary phosphine oxides[47]. The alkene will undergo Diels–Alder[45] and related[48] cycloaddition reactions. By halogenation and dehydrohalogenation, **23** is converted to the α-halovinyl oxide (**24**), which will in turn undergo a number of addition–elimination

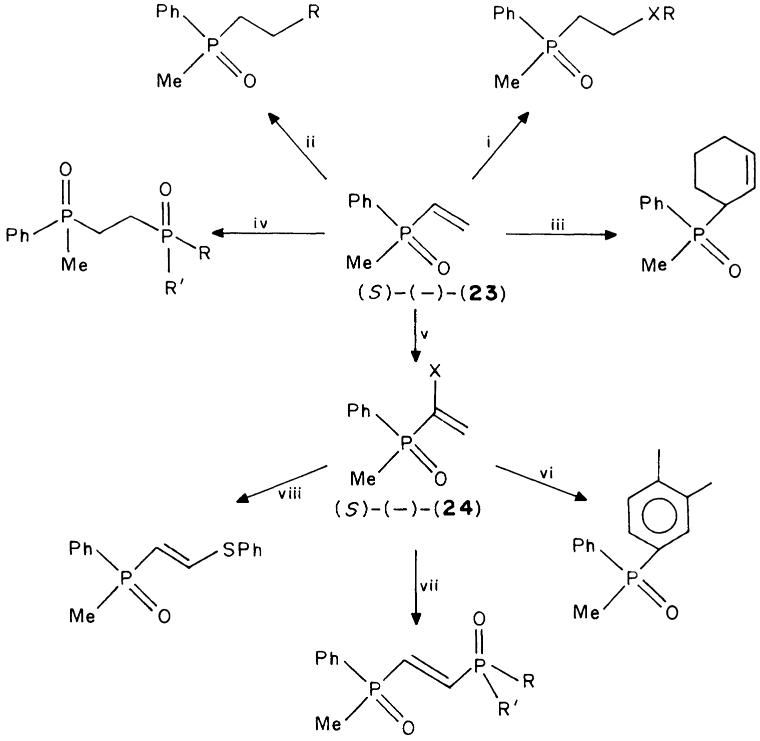


(20)

(i) $ClCH_2CO_2$-(−)-menth; (ii) LiCl, H_2O, Me_2SO

reactions as well as cycloadditions[48]; some of these transformations are summarized in equations 21. The addition of secondary phosphine oxides is of particular interest since it results in diastereoisomer formation if the secondary oxide is chiral and hence the effective resolution of another tertiary oxide. Similarly, the α-halovinylphosphine oxide **24** affords chiral *trans*-ethene-1,2-bisphosphine oxides[49]. It is clear that this approach is versatile and flexible and represents the first systematic development of an active chemistry of this class of compounds as distinct from preparing examples.

Much less work has been done with chiral sulphides and selenides. However, a method exists for converting oxides to sulphides stereoselectively with retention using boron



(21)

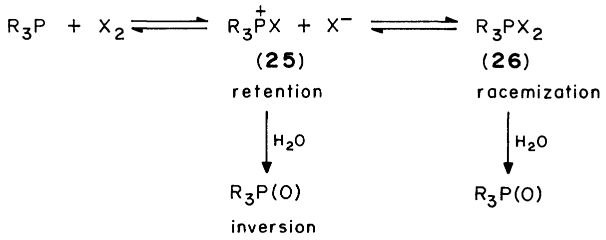
(i) RXH; (ii) Bu_2CuLi; (iii) $CH_2{=\!=}CHCH{=\!=}CH_2$; (iv) RR′P(O)H;

(v) X_2, base; (vi) 2,3-dimethylbutadiene; (vii) RR′P(O)H, base;

(viii) RSH, base

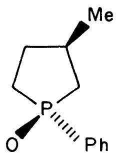
sulphide, B_2S_3[50]. The more commonly used phosphorus pentasulphide causes racemization[51].

The simplest and most straightforward method of obtaining isomerically pure chalcogenides is to treat the corresponding phosphine with an oxidising agent or with sulphur or selenium reagents. These last two methods work well, the reaction proceeding cleanly and essentially stereospecifically with retention at phosphorus. A common method of determining stereoisomer distribution in mixtures of diastereoisomeric phosphines is to convert them to their sulphides, which are air stable and usually crystalline. Oxidation, however, is not so straightforward and stereochemical integrity can easily be lost. Stereochemical results can vary with the reagent[52–55] and solvent[52,53] and may depend on whether the phosphine is cyclic or not. Retention, inversion and racemization have all been observed in the formation of phosphine oxides from phosphines. In particular, any reaction proceeding via a phosphorane can lead to partial or complete racemization because of ligand reorganization in the intermediate. This process does not require a symmetrical intermediate and is normally very rapid at ambient temperature. Halogens[55], pseudo-halogens[55], 'positive' halogen compounds[51] and mono- or dialkyl-peroxides[53] will, in general, give either racemization via a phosphorus(V) intermediate (**26**) or inversion [via displacement on an initially formed phosphorus(IV) (**25**)], depending on whether a nucleophilic solvent is absent or present. Polar solvents will usually favour polar intermediates such as **25** and hence are less likely to lead to loss of optical activity, although this can be brought about by a reversible S_N2 processes. Bistrimethylsilyl peroxide oxidizes phosphines to their oxides cleanly and with retention[56].

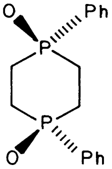


(22)

Perhaps the most general oxidant is aqueous hydrogen peroxide, which affords the oxide with retention and relatively few side-reactions[54,57]. It is occasionally difficult, however, to separate unreacted peroxide from the product. Aerial oxidation, although sometimes very clean, can result in P—C bond cleavage and should be avoided. Polish workers have used an unusual class of reagents, the selenoxides, RR'SeO, which convert phosphines, their sulphides or their selenides, into the corresponding oxides with variable stereochemical results[58]. For Me_2SeO, the reaction proceeds with inversion for acyclic compounds and retention for cyclic compounds, but other selenoxides are less specific and the steric result may also vary with the solvent. Oxides may also be obtained from the other chalcogenides by oxidation, but the stereochemical results are not promising. For example. N_2O_4, a reagent widely used for oxidizing phosphites to phosphates, converts sulphides to oxides with overall retention but partial racemization[59]. This reagent will even induce racemization in phosphine oxides, e.g., **27**, and hence its value as an oxidant in stereochemical work is dubious. Other oxidants, e.g. $KMnO_4$, do not look much more promising, retention with partial racemization being the general rule[54a]. These results presumably reflect the formation of pentacovalent species from the chalcogenide and oxidant with the degree of racemization being a function of the lifetime of the intermediate. Enantiospecific oxidation of phosphenes has been reported to be unsuccessful[36].



(27)



(28)

In general, claims in the literature for oxidation with complete retention or inversion should be treated with caution since, though this may well be the case in the quoted examples, it would be unwise to assume that the statement is generally true.

C. Determination of Stereochemistry

1. Cyclic compounds

This is a large field and a great deal of principally spectroscopic work has been done to elucidate diastereoisomerism and conformation. Much of this relates to oxa-, thia- or aza-heterocycles and is outside the scope of this chapter. Rings which are carbocyclic, except for the phosphorus atom, are less amenable to ^{1}H NMR for reasons of spectral complexity[60b]. Lanthanide shift reagents can sometimes simplify the spectra sufficiently for them to be useful, although several instances are known of conformational equilibria being disturbed by the reagent. Lanthanides complex at the phosphoryl oxygen even when alternatives sites, such as carbonyl, are available. These reagents have been used successfully for rigid systems such as phosphetane oxides[61] or bicyclic oxides[62,63]. Sulphur and selenium complex poorly with lanthanides, making the shift reagents of little use in stereochemical assignments for these chalcogenides.

The principal spectroscopic tool is ^{13}C NMR, for which well established Karplus-type angular dependencies, $^{n}J_{PC}(n = 1,2$ and $3)$ are available[15,60a]. Such relationships do not, however, establish the geometry at phosphorus and for this reliance must be placed on chemical shift trends and X-ray analysis. However, for those cyclic oxides where the proton spectra are resolved, $^{2}J_{PCH}$ is related to the dihedral angle OPCH with the *anti* orientation having a smaller magnitude than the *gauche* orientation[17]. This appears to be reliable since, although relatively few examples have been reported, they are mainly from the well established carbohydrate field. The range of values for $^{2}J_{PCH}$ is considerable and it would be unwise to make an assignment without having both isomers at hand.

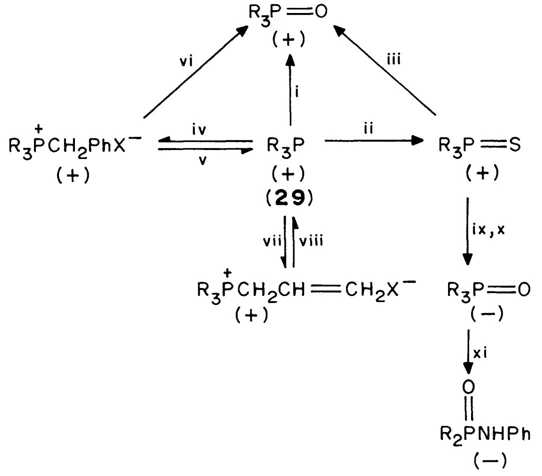
Since the steric (or volume) requirements of oxygen, sulphur, and selenium at phosphorus are not large and since the increased length of the phosphorus—carbon bonds (compared with carbon—carbon bonds) diminishes non-bonded interactions further, influences on the carbon chemical shift are usually related to the orientation of the exocyclic carbon substituent at phosphorus. In general, the carbon substituent on phosphorus of the more crowded isomer (usually the axial substituent in phosphinanes) absorbs upfield of its less crowded partner. This effect is independent of ring size, although the magnitude may vary considerably and would be expected to diminish in large rings. No consistent variation is observed in $^{1}J_{PC}$ for axial or equatorial disposition of the substituent. There is no useful correlation between ring geometry and phosphorus chemical shift, although in restricted classes of compounds a correlation may be observed. There are differences in both chemical shifts and coupling constants for axial and equatorial selenium[60c] and the developing field of ^{17}O spectroscopy appears very promising, since both chemical shift and $^{1}J_{P^{17}O}$seems very sensitive to geometry[60d].

Dipole moments have also been used, particularly for rings with more than one phosphinyl group, and the technique is one of the few methods available for isomer determination in large rings[64]. Generally, conformational bias in phosphorus heterocycles is considerably less than is found in their carbocyclic analogues, presumably because of the increased bond lengths to phosphorus in comparison with the same distances to carbon. These resulting small energy differences are reflected in at least one instance[15] of both conformers being found in the same crystal and in conformational preferences in solution varying with solvent.

In phosphinane chalcogens the chalcogen atom will normally occupy the axial position[15,65] unless steric factors elsewhere on the ring dictate otherwise. Strongly electronegative groups on phosphorus may alter this preference. There is no reason to suppose that the rings do not undergo rapid flipping, however, the *cis*-diphosphinane **28** shows only a single absorption in its ^{31}P NMR spectrum[66] and, in general, separate peaks for conformers are only seen as low temperatures. Absolute configurations at phosphorus have been assigned in the phosphasugar series and substantiated by X-ray structures[17,18]. The only other example is compound **10**, whose configuration was also established by X-ray techniques[19].

2. *Acyclic compounds*

The initial steps in this field were taken by McEwen and coworkers[27], who first resolved an acyclic phosphonium salt and, with both enantiomers available, were able to construct the simple cycle (equation 11) which established that alkaline hydrolysis and the Wittig reaction proceeded with opposite stereochemistries. Since it was very likely that the Wittig olefination proceeded with retention, they suggested that alkaline hydrolysis went with inversion. Shortly thereafter, Horner and coworkers[54] established the basic principles on which assignments of the steric consequence of reaction now depend, using resolved tertiary phosphines as the starting point. Benzylation of a phosphine and its regeneration by electrolytic cleavage proceed without affecting the stereochemistry at phosphorus; similarly, allylation of a phosphine and its regeneration by removing the allyl group with cyanide ion leave the configuration at phosphorus unaffected. Since the latter reaction, in particular, proceeds by reaction remote from phosphorus, it is overwhelmingly probable that alkylation proceeds with retention. Oxidation and sulphuration are similar to alkylation in involving the lone pair on phosphorus, and it follows that they too should proceed with retention; hence the steric course of alkaline hydrolysis and the Wittig reaction of phosphonium salts are as proposed by McEwen and coworkers. Sulphides may be converted to oxides with inversion by alkylation at sulphur, which necessarily proceeds with retention at phosphorus, followed by hydrolysis, hence adddition of sulphur to a phosphine proceeds with retention as expected. Benzylmethylphenylphosphine oxide undergoes a Wittig–Horner reaction with benzaldehyde-*N*-phenylimine to give *N*-phenylmethylphenylphosphinamide, whose optical rotatory dispersion curve had the same sign as the starting oxide, thus lending strong support to the notion that the Wittig reaction proceeds with retention. Most Wittig reactions are now believed to proceed via a phosphorane and should theoretically be capable of stereomutation at phosphorus; such a process might result in racemization, but it is difficult to see the net steric result being inversion. These reactions and a number of others shown in equations 23 (largely due to Horner and coworkers) are used to establish the stereochemistry of phosphine chalcogenides in general. It would be unwise, however, to assume that these reactions always apply, and there are many instances of reversal of the expected results. Thus the stereochemical consequence of the alkaline hydrolysis of a phosphonium salt is sensitive to the nature of the leaving group, and the size and nature of the substituents[28,67–69]. Small or strained rings may give

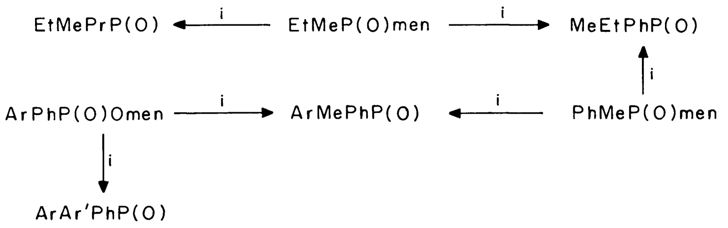


(23)

(i) H_2O_2; (ii) S_8; (iii) $KMnO_4$–Py; (iv) $PhCH_2X$;
(v) cathodic reduction; (vii) Wittig, (vii) $CH_2{=}CHCH_2X$;
(viii) CN^-; (ix) MeI; (x) aq. OH^-; (xi) Wittig

unexpected results; phosphetanes, for example, react predominantly with retention at phosphorus[70] and the 7-phosphanorbornene system undergoes a range of reactions unprecedented in less strained or acyclic systems[71]. The stereochemistry of none of these pathways can be assumed on the basis of results with unrelated systems.

The ability to determine absolute stereochemistry spectroscopically would be very desirable but has attracted relatively little attention. Small chemical shift differences have been observed for enantiomeric phosphine oxides in both ^{31}P and ^{1}H NMR spectra when they are in the presence of a chiral solvent; thus Mislow and coworkers[68] used (+)-1-phenyl-2,2,2-trifluoroethanol (Pirkle's reagent) to determine the optical purity of *tert*-butylmethylphenylphosphine oxide. The same group established the absolute configuration at phosphorus in the diastereoisomerically pure methyl phosphinates from their proton spectra[72] and hence, by inference, the configurations of the phosphine oxides prepared from them by Grignard reaction[29]. Pirkle and coworkers[73] found small differences (1.4–3.2 Hz at 100 MHz) in the chemical shift of the methyl group of the enantiomers of three phosphine oxides using (+)-1-phenyl-2,2,2-trifluoroethanol as cosolvent. With more modern higher field instruments, these differences will be amplified considerably. More recently, Moriyama and Bentrude[35] have shown that *tert*-butylphenylthiophosphinic acid gives better separation (3.0–10.6 Hz at 90 MHz) of enantiomeric groups in the proton NMR and suggest it may be generally useful for this purpose. Two groups have used chiral shift reagents, (*R*)-(−)-*N*-3,5-dinitrobenzyl-1-phenylethylamine and (+)- or (−)-1-phenylethylamino-3,5-dinitrobenzamide, to determine stereochemical purity by proton NMR on the basis of chemical shift differences, usually of a methyl group[74,75]. These differences are not large, however, typically only 0.01–0.02 ppm. It might be expected that ^{31}P NMR differences would be greater and, although they have been observed[76] with lanthanide shift reagents, no stereochemical use of them has been described, possibly because of difficulties in quantifying the peak heights.



(24)

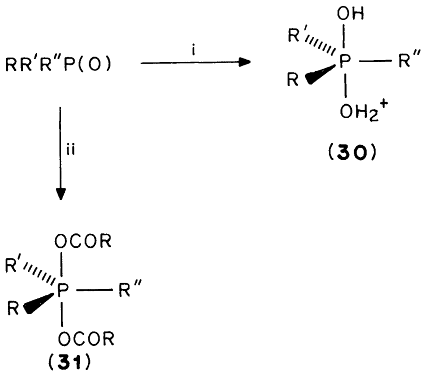
(i) RMgX or RLi; Ar = 2-MeOC$_6$H$_4$, Ar' = 2-naphthyl;
HOmen = (−)-menthol

Other physical methods have not been much used, although diarylmethylphosphine oxides have been correlated with sulphoxides by circular dichroism. The method is limited by the need for an appropriate chromophore[77]. Chemical methods of configurational correlation are uncommon, largely as a consequence of the limited chemistry that has been studied for groups attached to phosphorus. Conversion of methylphenylvinylphosphine oxide to ethylmethylphenylphosphine oxide by hydrogenation is one example[41]. By utilizing relay compounds, Lewis and Mislow[78] ingeniously correlated trialkyl- and triaryl-phosphine oxides (equation 24). Conformational analysis of acyclic compounds has received a reasonable amount of attention primarily for phosphine oxides. Normal methods for study are dipole moment variation and proton NMR spectroscopy. The subject has been reviewed[79].

D. Reaction Stereochemistry

1. Oxides

The phosphoryl group is normally regarded as being particularly stable and its formation is believed to constitute a strong driving force for a reaction. In fact, its dissociation energy does not differ all that greatly from that of a carbonyl group and its apparent lack of reactivity seems more a reflection of its reduced polarity, generally attributed to backbonding between oxygen and phosphorus, than any inherent great stability. The oxygen is sufficiently basic to allow its protonation with reasonably strong acids which, if they are chiral, will allow resolution. Whether a hydroxy phosphonium

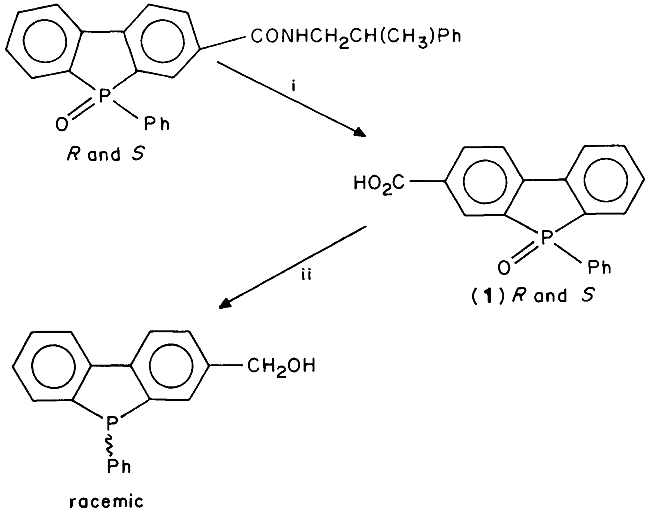


(25)

(i) H$^+$, H$_2$O; (ii) (RCO)$_2$O

salt exists under these conditions or a strongly hydrogen-bonded complex is not known. With sufficiently powerful alkylating agents, usually trialkyloxonium salts, alkoxyphosphonium salts are formed with, of course, retention of configuration at phosphorus[80]. These salts, like their sulphur analogues, undergo alkaline hydrolysis with complete inversion of configuration; attack at carbon does not seem to occur and has been excluded by isotopic experiments. Under vigorous acid conditions such as refluxing aqueous hydrochloric acid, racemization at phosphorus in phosphine oxides occurs, accompanied by ^{18}O exchange[81,82]. This suggests the formation of a pentacovalent species **30**, which is essentially symmetrical under aqueous conditions. A similar result is obtained by heating the phosphine oxide with a carboxylic acid anhydride to give, presumably, the diacycloxyphosphorane **31**. However, a symmetrical intermediate is not essential for racemization of a pentacovalent species as ligand reorganization can produce inversion without bond breaking, as is evidenced by obtaining the same result with hydrogen chloride in dry dioxane[82]. Racemization may also be brought about by N_2O_4[59], a reaction whose mechanism is not obvious but which presumably also involves reversible formation of a phosphorane.

Stereomutation also occurs with Lewis acids, e.g. phosphine oxides are racemized by lithium aluminium hydride[9], presumably via reversible formation of a phosphorus(V) species. This accounts for the failure of Campbell and Way[26] to reduce their resolved phosphine oxide (equation 26) to an optically active phosphine and the general failure of this reducing agent to give stereospecific reduction of phosphine oxides. However, like most reactions of phosphorus compounds, stereochemical generalizations are difficult to maintain. Thus, the resolution of **1** involved the preparation and separation by crystallization of the diastereoisomeric amides of the acid with (−)-phenylethylamine. The enantiomers were regenerated by vigorous acid hydrolysis, which appears to have had no effect on the optical purity since both enantiomers were obtained with equal and opposite rotations[2b]. Further, phosphine oxides with *tert*-butyl substituents have been reduced by lithium aluminium hydride with overall retention[83]. These reactions

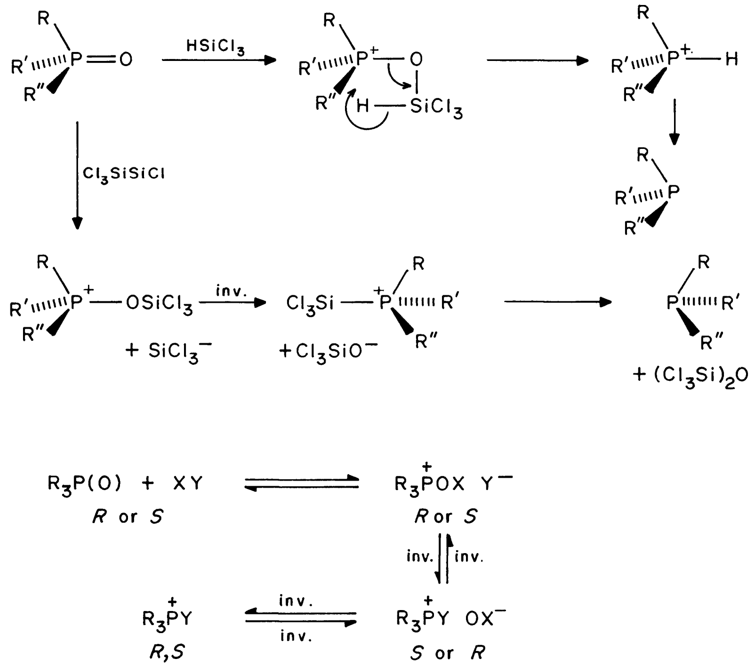


(26)

(i) H^+, H_2O; (ii) $LiAlH_4$

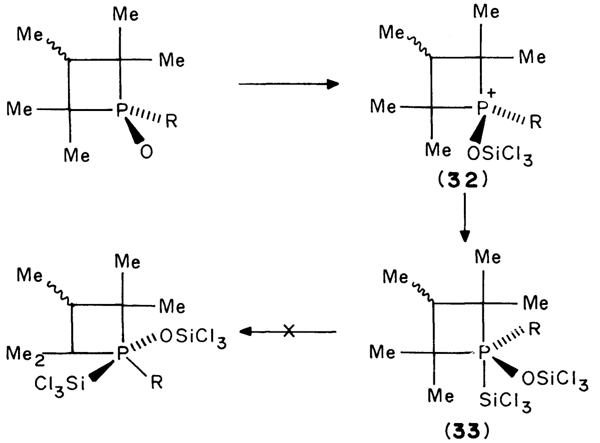
suggest that the racemization process may be subject to both ring and substituent effects. The combination of lithium aluminium hydride and cerium(III) chloride reduces phosphine oxides readily but non-stereoselectively[84].

Reduction of phosphine oxides proceeds fairly readily with a variety of silanes containing a silicon—hydrogen bond under mild conditions unlikely to produce thermal epimerization of the product phosphine. The inexpensive and readily available trichlorosilane converts phosphine oxides to phosphines with different stereochemical consequences, depending on the presence or absence of amines in the reaction mixture[85]. In the absence of an amine the reaction proceeds with predominant retention, as it does also in the presence of pyridine; in the presence of triethylamine, inversion is observed. It was soon realized[86] that the steric result was affected by the base strength of the amine used and that with strong bases reduction was being brought about by decomposition products of the trichlorosilane. This observation led to the introduction of hexachlorodisilane as a reducing agent[86] and this was found to reduce phosphine oxides to phosphines of good optical purity with inversion at phosphorus. Experimental conditions are critical with hexachlorodisilane, however, since extended reaction times beyond that necessary for reduction may result in extensive racemization of the product phosphine. Some racemization of the phosphine oxide may occur; both processes may result from the reversible formation of pentacovalent phosphorus species or alternatively via reversible substitutions on an intermediate phosphonium salt. The latter proposal is supported by the fact that phosphine oxides may be racemized by silicon tetrachloride, acetyl chloride, or phosphorus trichloride when the solvent acetonitrile is used, which should favour polar intermediates. Suggested mechanisms for silane reductions and racemizations are outlined in Scheme 1. Other silanes, such as phenyl- or diphenyl-silane,

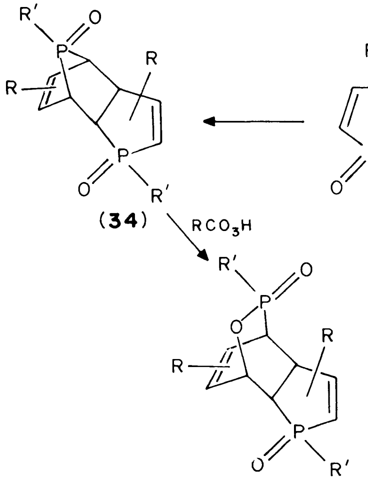


SCHEME 1

are also commonly used and, as would be expected from the initial studies on trichlorosilane, these reductions also proceed with retention. All silane reductions are frequently non-stereospecific and varying degrees of racemization are observed. It seems that a general principle where maximum stereoselectivity is important is to minimize exposure of the product phosphine to the reducing agents and their oxidation products. Phosphetane oxides are reduced with retention, regardless of the silane used, reflecting the constraints imposed by the four-membered ring on the intermediates. Initial reaction of a phosphetane oxide will give a phosphonium cation (**32**), particularly susceptible to further attack to give a phosphorane (**33**) because of the relief of the severe angular distortion at phosphorus (ca 20° from tetrahedral) in the four-membered ring when it is incorporated into trigonal bipyramidal geometry. Permutational isomerisation of such an intermediate is blocked by the inability of the four-membered ring to lie in the equatorial plane, since the four-membered ring could not accommodate a 120° angle at

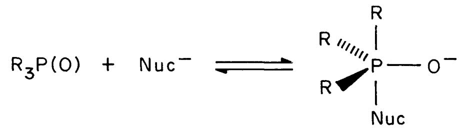


(27)



(28)

phosphorus (equation 27). Similarly, phosphetane oxides alkylated at oxygen undergo hydrolysis with retention rather than inversion and this has been shown by isotopic techniques to proceed via attack at phosphorus[87]. This type of behaviour is common with phosphetanes and reflects a generally increased reactivity of the phosphoryl group as a consequence of ring strain. All phosphetane oxides currently available have their reactivity masked by heavy substitution on the ring, a consequence of the limited methods of preparation available, and a simpler, less crowded system, should display a diverse and interesting chemistry. The bicyclic phosphine oxides, e.g. **34** (equation 28), readily available by either dimerization or Diels–Alder cycloaddition of intermediate phosphole oxides, possess a severely strained bridging phosphorus which exhibits a remarkable range of reactions many of which are often unprecedented, and usually unexpected, on the basis of less strained derivatives[71]. Angular distortion in these structures is of the same order as in phosphetanes, i.e. about 20° from the tetrahedral. Attempted oxidation of the double bond in the ring resulted in oxygen insertion in to the P—C bond[88], a reaction analogous to the Bayer–Villiger reaction, which is general for strained bicyclic systems[71] and also occurs with phosphetanes[89]. The phosphorus may be epimerized by the action of water or amines, a reaction in striking contrast to the otherwise inert behaviour of the phosphoryl group towards nucleophiles in unstrained systems. For example, prolonged refluxing with aqueous alkali or alcoholic alkoxides does not affect the stereochemistry at phosphorus[82] in acyclic systems. It does not follow, however, that nucleophilic attack has not occurred under those conditions, since in the expected intermediate (**35**, equation 29) the oxygen ligand may be effectively locked in the radial plane of the pentacovalent species.



(35)

(29)

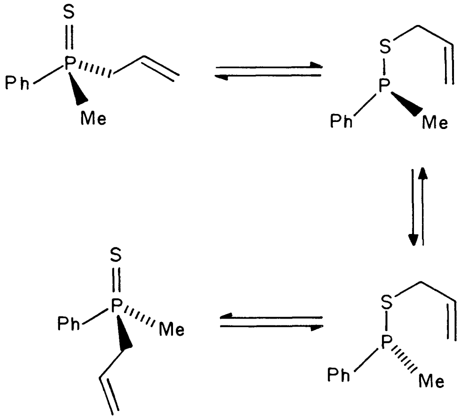
Apart from the foregoing, relatively few reactions of the phosphoryl group are known whose stereochemical consequences have been examined. Allylic optically active phosphine oxides are thermally stable, unlike the sulphides, e.g. resolved allylmethylphenylphosphine oxide showed no loss of optical activity after 12 h at 200 °C[90]. The phosphoryl group may be converted to thiophosphoryl, B_2S_3 giving retention and P_2S_5 racemization[51]; removal of proton from carbon adjacent to phosphorus does not affect the stereochemistry there[39]. When a chiral phosphinoyl group migrates in a carbonium ion rearrangement, it does so with retention of configuration at phosphorus[91].

2. Sulphides and selenides

Little chemistry has been done with selenides and even less of stereochemical interest. Like sulphides, they are converted by selenoxides into phosphine oxides with a stereochemical result depending on the selenoxide and the reaction conditions[58].

Sulphides are much less basic towards protons than oxides, but since they are softer bases they alkylate more readily and alkaline hydrolysis of the resulting thioalkylphosphonium salts affords the oxides with inversion at phosphorus[54a,79]. Reduction of sulphides with hexachlorodisilane proceeds, unexpectedly, with high retention of stereochemistry at phosphorus[79], in marked contrast to the behaviour of oxides. The reason for this difference is obscure and, as in the case of phosphine oxide reduction, a clearer understanding is hampered by difficulties in identifying the silicon by-products. Once again, in contrast to phosphine oxides, optically active sulphides are reduced to the phosphine by lithium aluminium hydride with retention of configuration[92].

Allylic phosphine sulphides may be racemized thermally, presumably via allylic rearrangement to a trivalent thiophosphinite which then undergoes thermal inversion[93] (equation 30). This is supported by the facts that the activation energy of the process is



(30)

similar to the activation energies for the thermal inversion of phosphines and also that allylic thiophosphinites are known to undergo thermal allylic rearrangement to the corresponding sulphides[93,94]. Conversion of phosphine sulphides to oxides is brought about by a range of oxidizing agents and with variable stereochemical results, but usually overall retention is observed.

IV. REFERENCES

1. J. Meisenheimer, *Chem. Ber.*, **44**, 356 (1911).
2. (a) J. Meisenheimer, J. Casper, M. Horing, W. Lauter, L. Lichtenstadt and W. Samuel, *Justus Liebigs Ann. Chem.*, **449**, 213 (1926);
   (b) I. G. M. Campbell and J. K. Way, *J. Chem. Soc.*, 2133 (1961).
3. W. C. Davies and F. G. Mann, *J. Chem. Soc.*, 276 (1944).
4. (a) W. W. du Mont, R. Hensel, S. Kubiniok and L. Lange, in *The Chemistry of Organic Selenium and Tellurium Compounds*, (Ed. S. Patai), Vol. 2, Wiley–Interscience, Chichester, 1987, p. 591;
   (b) N. Kuhn, H. Schumann and G. Wolmerhauser, *Z. Naturforsch., Teil B.*, **42**, 674 (1987).
5. (a) R. Withnall and L. Andrews, *J. Phys. Chem.*, **91**, 784 (1987);
   (b) V. N. Zemleanov, O. I. Kolodiazhnyi and V. P. Kukhar, *Phosphorus Sulfur and Silicon*, **51/52**, 182 (1990).
6. C. J. R. Fookes and M. J. Gallagher, *J. Chem. Soc., Perkin Trans. 1*, 1876 (1975).
7. J. L. Emmick and R. L. Letsinger, *J. Am. Chem. Soc.*, **90**, 3459 (1968).
8. O. Cervinka, O. Belavsky and M. Hepnerova, *Chem. Commun.*, 562 (1970).
9. P. Henson, K. Naumann and K. Mislow, *J. Am. Chem. Soc.*, **91**, 5645 (1969).
10. (a) J. Michalski and Z. Skrzypzynski, *J. Organometl. Chem.*, **97**, C31 (1975);
    (b) Z. Skrzypzynski and J. Michalski, *J. Org. Chem.*, **53**, 4549 (1988).

11. (a) R. L. Whistler and C. C. Wang, *Bull. Chem. Soc. Jpn.*, **41**, 1472 (1968);
    (b) H. Yamamoto, T. Hanaya, S. Inokawa, K. Seo, M.-A. Armour and T. T. Nakashima, *Carbohydr. Res.*, **114**, 83 (1983).
12. L. P. Reiff and H. S. Aaron, *J. Am. Chem. Soc.*, **92**, 5275 (1970).
13. S. Musserowicz and W. T. Waszkuc, *Phosphorus Sulfur*, **3**, 345 (1977).
14. (a) M. Davis and F. G. Mann, *J. Chem. Soc.*, 3770 (1964);
    (b) L. D. Quin, J. D. Gratz and R. E. Montgomery, *Tetrahedron Lett.*, 2187 (1965).
15. L. D. Quin, *The Heterocyclic Chemistry of Phosphorus*, Wiley–Interscience, New York, 1981.
16. L. D. Quin and W. Hughes, in *Organophosphorus Chemistry*, (Ed. F. R. Hartley), Vol. 1, Wiley–Interscience, Chichester, 1990.
17. H. Yamamoto and S. Inokawa, *Adv. Carbohydr. Chem.*, **42**, 135 (1984).
18. (a) S. Inokawa, K. Yamamoto, H. Kawamoto, H. Yamamoto, M. Yamashita and P. Luger, *Carbohydr. Res.*, **106**, 31 (1982);
    (b) H. Yamamoto, K. Yamamoto, S. Inokawa and P. Luger, *Carbohydr. Res.*, **110**, 187 (1982);
    (c) P. Luger, E. Muller, H. Yamamoto and S. Inokawa, *Carbohydr. Res.*, **145**, 25 (1985);
    (d) M. Namashita, Y. Nakatsuka, S. Inokawa, K. Hirotsu and J. Clardy, *Chem Lett.*, 871 (1978).
19. R. Badalski, T. Janecki, Z. Galdecki and M. Glowka, *Phosphorus Sulfur*, **14**, 15 (1982).
20. (a) H. Brunner, W. Pieronczyk, *Ger. Pat.*, 2 908 358; *Chem. Abstr.*, **94**, 103556f;
    (b) L. Horner and G. Simons, *Phosphorus Sulfur*, **19**, 77 (1984).
21. H. Takaya, S. Akutagawa, R. Noyori, *Org. Synth.*, **67**, 20 (1989).
22. F. Toda, Z. Stein, I. Goldberg and K. Mori, *J. Org. Chem.*, **53**, 308 (1988).
23. (a) A. Tambute, P. Gareil, M. Caude and R. Rosset, *J. Chromatogr.*, **363**, 81 (1980);
    (b) P. Macandiere, M. Caude, R. Rosset and A. Tambute, *J. Chromatogr.*, **405**, 135 (1987);
    (c) P. Pescher, M. Caude, R. Rosset and A. Tambute, *J. Chromatogr.*, 371, 159 (1986).
24. Y, Okamoto, S. Honda, K. Hatada, I. Okamoto, Y. Toga and S. Kobayashi, *Bull. Chem. Soc. Jpn.*, **57**, 1681 (1984).
25. L. Maier, in *Organic Phosphorus Compounds*, (Eds G. M. Kosolapoff and L. Maier), Vol. 4, Wiley–Interscience, New York, 1972, p. 1.
26. B. E. Maryanoff, R. Tang and K. Mislow, *Chem. Commun.*, 273 (1973).
27. (a) K. F. Kumli, W. E. McEwen, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **81**, 248, 3805 (1959);
    (b) H. Baldé-Font, C. A. VanderWerf and W. E. McEwen, *J. Am. Chem. Soc.*, **82**, 2396 (1960).
28. A survey of this complex area is given by R. Luckenbach, *The Dynamic Stereochemistry of Pentacoordinate Phosphorus*, Thieme, Stuttgart, 1973.
29. O. Korpiun, R. A. Lewis, J. Chickos and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4842 (1968).
30. M. Green and R. F. Hudson, *J. Chem. Soc.*, 540 (1963).
31. A. Nudelman and D. J. Cram, *J. Org. Chem.*, **36**, 335 (1971).
32. (a) D. B. Copper, T. D. Inch, and G. J. Lewis, *J. Chem. Soc., Perkin Trans. 1*, 1043 (1974);
    (b) for a review see C. R. Hall and T. D. Inch, *Phosphorus Sulfur*, **7**, 171 (1979).
33. T. Kato, K. Kobayashi, S. Masuda, M. Segi, T. Nakajima and S. Suga, *Chem. Lett.*, 1915 (1987).
34. S. Juge and J. P. Genet, *Tetrahedron Lett.*, **30**, 2783 (1989).
35. M. Moriyama and W. G. Bentrude, *J. Am. Chem. Soc.*, **105**, 4727 (1983).
36. R. A. Naylor and B. J. Walker, *Chem. Commun.*, 45 (1975).
37. C. Fisher and H. S. Mosher, *Tetrahedron Lett.*, 2487 (1977).
38. D. Valentine, J. F. Blount, and K. Toth, *J. Org. Chem.*, **45**, 3691 (1980).
39. C. A. Maryanoff, B. E. Maryanoff, R. Tang and K. Mislow, *J. Am. Chem. Soc.*, **95**, 5836 (1973).
40. B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachmann and D. J. Weinkauff, *J. Am. Chem. Soc.*, **99**, 5946 (1977).
41. R. Bodalski, E. Rutkowska-Olma and K. M. Pietrusiewicz, *Tetrahedron*, **36**, 2353 (1980).
42. K. M. Pietrusiewicz and M. Zablocka, *Phosphorus Sulfur*, **40**, 477 (1988).
43. G. Märkl and B. Merkl, *Tetrahedron Lett.*, **22**, 4459 (1981).
44. K. M. Pietrusiewicz and M. Zablocka, *Tetrahedron Lett.*, **29**, 1991 (1988).
45. K. M. Pietrusiewicz and M. Zablocka, and J. Monkiewicz, *J. Org. Chem.*, **49**, 1522 (1984).
46. K. M. Pietrusiewicz and M. Zablocka, *Tetrahedron Lett.*, **29**, 937 (1988).
47. K. M. Pietrusiewicz and M. Zablocka, *Tetrahedron Lett.*, **29**, 1987 (1988).
48. K. M. Pietrusiewicz and M. Zablocka and W. Wisniewiski, *Phosphorus Sulfur Silicon*, **49**/**50**, 263 (1990).
49. K. M. Pietrusiewicz W. Wisniewski and M. Zablocka, *Tetrahedron*, **45**, 337 (1989).
50. B. E. Maryanoff, R. Tang and K. Mislow, *Chem. Commun.*, 273 (1973).

51. J. Omelanczuk and M. Mikolajczyk, *Tetrahedron.*, **27**, 5587 (1971).
52. D. B. Denney and J. W. Hanifin, *Tetrahedron Lett.*, 2177 (1963).
53. D. B. Denney and N. G. Adin, *Tetrahedron Lett.*, 2569 (1966).
54. (a) L. Horner, *Pure Appl. Chem.*, **9**, 225 (1964);
    (b) L. Horner and R. Luckenbach, *Phosphorus*, **1**, 73 (1971).
55. L. Horner and H. Winkler, *Tetrahedron Lett.*, 455 (1964).
56. L. Wozniak, J. Kowalski and J. Chojnowski, *Tetrahedron Lett.*, **26**, 4965 (1985).
57. O. Cervinka and O. Kriz, *Collect. Czech. Chem. Commun.*, **31**, 1910 (1966).
58. (a) M. Mikolajczyk and J. Luczak, *J. Org. Chem.*, **43**, 2132 (1978);
    (b) M. Mikolajczyk and J. Luczak, *J. Gen. Chem. USSR*, **58**, 1804 (1988).
59. W. Egan, G. Chauviere, K. Mislow, R. T. Clark and K. L. Marsi, *Chem. Commun.*, 733 (1970) (footnote and ref. 8 therein).
60. J. G. Verkade and L. D. Quin (Eds), *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH, Deerfield Beach, FL, 1987;
    (a) Chapter 12;
    (b) Chapter 11;
    (c) Chapter 13;
    (d) E. L. Eliel, S. Chandrasekaran, L. E. Carpenter, and J. G. Verkade, *J. Am. Chem. Soc.*, **108**, 6651 (1986).
61. J. R. Corfield and S. Trippett, *Chem. Commun.*, 721 (1971).
62. Mazar-ul-Haque, W. Horne, S. E. Cremer and J. T. Most, *J. Chem. Soc., Perkin Trans. 2*, 1000 (1981).
63. M. Rotem and Y. Kashman, *Tetrahedron Lett.*, 63 (1978).
64. T. H. Chan and B. S. Ong, *J. Org. Chem.*, **39**, 1749 (1974).
65. I. D. Blackbourne, A. R. Katritzky, D. M. Read, R. Bodalski and K. M. Pietrusiewicz, *J. Chem. Soc., Perkin Trans. 2*, 1155 (1974).
66. P. Brookes, M. J. Gallagher, A. Sarroff and M. Bowyer, *Phosphorus Sulfur*, **44**, 235 (1989).
67. J. R. Cornfeld, J. R. Shutt and S. Trippett, *Chem. Commun.*, 789 (1969).
68. R. A. Lewis, K. Naumann, K. E. DeBruin and K. Mislow, *Chem. Commun.*, 1010 (1969).
69. (a) R. Luckenbach, *Phosphorus*, **1**, 293 (1972);
    (b) R. Luckenbach, *Phosphorus*, **3**, 177 (1973).
70. M. J. Gallagher, in *Stereochemistry of Heterocyclic Compounds, Part 2* (Ed. W. L. F. Armarego), Wiley–Interscience, New York, 1977, p. 382.
71. L. D. Quin, *Rev. Heteroatom Chem.*, **3**, 39 (1990).
72. R. A. Lewis, O. Korpiun and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4847 (1968).
73. W. H. Pirkle, S. D. Beare and R. L. Muntz, *J. Am. Chem. Soc.*, **91**, 4575 (1969).
74. E. Dunach and H. B. Kagan, *Tetrahedron Lett.*, **26**, 2659 (1985).
75. Z. Zhou, *Huaxue Shiji*, **9**, 109 (1987); *Chem Abstr.*, **107**, 108337 (1987).
76. F. Mandel, R. H. Cox and R. C. Taylor, *J. Magn. Reson.*, **14**, 235 (1974).
77. F. D. Saeva, D. R. Rayner and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4177 (1968).
78. R. A. Lewis and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7009 (1969).
79. O. Raevskii and T. I. Ignatev, *Russ. Chem. Rev.*, **52**, 1156 (1983).
80. G. Zon, K. E. DeBruin, K. Naumann and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7023 (1969).
81. L. Horner and H. Winkler, *Tetrahedron Lett.*, 3271 (1964).
82. D. B. Denney, A. K. Tsolis and K. Mislow, *J. Am. Chem. Soc.*, **86**, 4486 (1964).
83. R. Luckenbach, *Phosphorus*, **3**, 77 (1973).
84. T. Imamoto, T. T. Takeyama and T. Kusumoto, *Chem. Lett.*, 1491 (1985).
85. L. Horner and W. D. Balzer, *Tetrahedron Lett.*, 1157 (1965).
86. K. Naumann, G. Zon and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7012 (1969).
87. K. E. DeBruin, G. Zon, K. Naumann and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7027 (1969).
88. Y. Kashman and O. Awerbouch, *Tetrahedron*, **31** 53 (1975).
89. L. D. Quin, J. C. Kisalus, and K. A. Mesch, *J. Org. Chem.*, **48**, 4466 (1983).
90. A. W. Herriot and K. Mislow, *Tetrahedron Lett.*, 3013 (1968).
91. F. Allen, O. Kennard, L. Nassimbeni, R. Shepherd and S. Warren, *J. Chem. Soc., Perkin Trans.2*, 1530 (1974).
92. R. Luckenbach, *Tetrahedron Lett.*, 2177 (1971).
93. W. B. Farnham, A. W. Herriot and K. Mislow, *J. Am. Chem. Soc.*, **91**, 6878 (1969).
94. A. E. Arbuzov and K. V. Nikonorov, *Zh. Obshch. Khim.*, **18**, 2008 (1948).

CHAPTER 3

Electrochemistry of organophosphorus(V) compounds

K. S. V. SANTHANAM

Chemical Physics Group, Tata Institute of Fundamental Research, Colaba, Bombay 400005, India

---

The chemistry of organophosphorus compounds, Volume 2, Phosphine oxides, sulphides, selenides and tellurides
Edited by Frank R. Hartley. ISBN: 0-471-93056-3

I. INTRODUCTION

The pivotal role played by electrochemistry in unravelling the chemistry of reactive phosphorus intermediates of organophosphorus(V) compounds is discussed in this chapter.These intermediates are either free radical anions or cations undergoing cleavage reactions or geometrical isomerizations or biochemical energy transductions. In several ways the cleavage reactions are similar to the phosphorus(III) compounds discussed in the earlier volume of this series[1]; P—C bond cleavage is observed after adding one electron (1e) to the organophosphorus compound. By contrast, the P—O bond in phosphorus(V) compounds is remarkably stable and is useful in generating reactive species for initiating redox reactions. One example of this kind is the energy transduction in biochemical reactions occurring through the phosphate bond of adenosine triphosphate (ATP); the high-energy phosphate bond (ca 33 kJ mol^{-1})[2] usefully converts the reduced or oxidized form of 1e transducing systems. Examples of transducing systems are pyruvate–acetate, CO_2; pyruvate CoA–acetyl CoA*, CO_2; α-ketoglutarate–succinate, CO_2; and acetaldehyde–acetate. The phosphate bond has the potential to increase the concentration of the unenergized form 10^6-fold by changing the Nernstian voltage by 350 mV.

These results have led to the introduction of energy coupling schemes in biological chemistry[3]. An important transduction of the phosphate bond energy into redox energy is the ATP-dependent reduction by dihydronicotinamide adenine dinucleotide (DPNH) of 3-phosphoglycerate[3,4] via 1,3-diphosphoglycerate to glyceraldehyde-3-phosphate. By this mechanism uphill reactions proceed at the expense of the high-energy phosphate bond of ATP. Consequently, there has been growing interest in the redox reactions of organophosphorus(V) compounds in the last two decades. This quest has led to the synthesis and characterization of phosphorus(V) liganded complexes using electrochemical techniques. Of greater importance is the chemistry of the geometrical isomerization of metal–phosphido complexes[5].

The electrochemistry of diphosphonucleotides has evoked detailed investigations for more than a decade into understanding the reduction mechanisms of these compounds. Does the chemical or biochemical reduction occur through a hydride ion or an electron–proton–electron transfer scheme? This question led to analogues of phosphonucleotides being synthesized for electrochemical studies to obtain an answer.

The interfacial phenomena at the electrode/solution interface such as adsorption of organics, in general, and more specifically organophosphorus(V) compounds, has generated an interest in understanding the geometry of these molecules in the adsorbed state in addition to the adsorption kinetics. Theoretical models proposed by Frumkin[6], Langmuir[7] and others[8] have been tested by using the interfacial adsorption of phosphorus compounds.

This review discusses the mechanisms and reactivities of organophosphorus(V) compounds during and after the charge transfer at the electrode.

II. PHOSPHINE OXIDES

A. Triphenylphosphine Oxide: Ph_3PO

1. Polarographic characteristics

The electrochemistry of Ph_3PO is of interest in relation to Ph_3P for the mechanistic changes occurring in the valence transformation of phosphorus(III) to phosphorus(V)[9–14]. The polarographic characteristics have been examined in solvents such as *N*,*N*-dimethylformamide (DMF), acetonitrile (MeCN) and hexamethyl phosphoramide (HMPA); the two waves appearing for Ph_3PO in these solvents are identified as due to successive 1e additions occurring with $E^{\mathrm{I}}_{1/2} = -2.51$ V and $E^{\mathrm{II}}_{1/2} = -2.84$ V vs SCE. Figure 1 shows a typical polarogram of 1.32mM Ph_3PO. The wave nature defined by

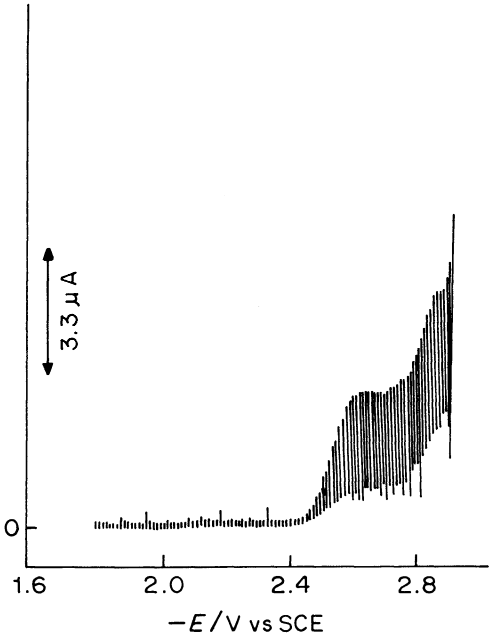


FIGURE 1. Polarogram of triphenylphosphine oxide from a solution containing 1.32 mM triphenylphosphine oxide and 0.1 M tetrabutylammonium iodide in DMF. Taken from ref. 11. Copyright (1968) American Chemical Society.

$E_{3/4} - E_{1/4}$ for the first wave has a value of 60 mV and for the second wave about 62 mV. The diffusion coefficient of $(Ph_3)_3PO$ is estimated to be $2.35 \times 10^{-5}\,cm^2\,s^{-1}$ in DMF. The polarographic wave of this compound is shifted in the positive direction with respect to Ph_3P, which shows $E_{1/2} = -2.70$ V vs SCE. Both the polarographic waves of Ph_3PO are diffusion controlled in the above solvents.

2. *Cyclic voltammetric characteristics*

Cyclic voltammetric experiments at a hanging mercury drop electrode (HMDE) also exhibit two cathodic peaks at $E^{I}_{pc} = -2.52$ V and $E^{II}_{pc} = -2.88$ V, corresponding to two successive 1e transfers; the first peak is reversible, exhibiting a complementary anodic peak. The constancy of the current function of the first peak and the peak current ratio $i_{pa}/i_{pc} \approx 1.0$ suggests high stability of the radical anion and the absence of any prior reaction of Ph_3PO and DMF[11]. However, at very low scan rates, below $0.067\,V\,s^{-1}$, the anion radical of Ph_3PO produced at -2.52 V undergoes a catalytic reaction[13] in solvents such as MeCN and HMPA; the catalytic reaction is faster in MeCN. This catalytic reaction is attributed to the electrophilic attack by the solvent on the radical anion or impurities in the solvent. This interpretation is supported by the observation of the ESR spectrum of the free radical anion of Ph_3PO in DMF by Illyasov *et al.*[14] with ^{31}P coupling to the protons of the ring. However, the radical anion decomposes during longer periods of storage.

The solvent-dependent feature of cyclic voltammetric behaviour was reported by Santhanam and Bard[11]; in DMSO containing Bu_4NI two peaks at $E_{pc} = -2.44$ V and $E_{pc} = -2.51$ V were observed at a slower scan rate of $0.15\,V\,s^{-1}$. The two peaks merged into one broad peak at higher sweep rates. Both peaks are irreversible in nature. These peaks are shifted to negative potentials in DMF.

3. *Controlled potential electrolysis*

The long-term stability of the 1e reduction product of Ph_3PO has been investigated by controlled potential electrolysis[11,13]. Exhaustive reduction in DMF at -2.60 V invariably resulted in a higher steady-state current than the background current electrolysis. The current–time decay features and cyclic voltammetric analysis after the electrolysis were indicative of a Ph_3PO radical anion reacting with the medium to regenerate Ph_3PO. Saveant and Binh[13] proposed an electrophilic addition by the supporting electrolyte.

4. *ESR features*

The electrochemically generated Ph_3PO radical anion produces an *ESR* spectrum[12,14] with fine structure arising from ^{31}P coupling with the ring protons. Chemical reduction using metallic potassium resulted in the radical anion spectrum of $Ph_3PO^{-}K^{+}$, with the spectrum containing potassium ion hyperfine splittings.

5. *Redox reaction scheme*

The first step in the electrochemical reduction of Ph_3PO produces the anion by reaction 1[11,13].

$$Ph_3PO + e \rightleftharpoons Ph_3PO^{-\bullet} \tag{1}$$

The radical anion reacts with the supporting electrolyte, Bu_4N^{+}, as indicated by reactions 2–4.

$$Ph_3PO^{-\bullet} + Bu_4N^+ \xrightarrow{k} Ph_3P\dot{O}Bu + NBu_3 \qquad (2)$$

$$Ph_3P\dot{O}Bu \xrightarrow{k_1} Ph^{\bullet} + Ph_2POBu \qquad (3)$$

$$Ph_2POBu \xrightarrow{k_2} Bu^{\bullet} + Ph_3PO \qquad (4)$$

An alternative mechanism depicted by reactions 5–7 has also been proposed[13].

$$Ph^{\bullet} + Ph_3PO^{-\bullet} \longrightarrow Ph_3PO + Ph^- \qquad (5)$$

$$Bu^{\bullet} + Ph_3PO^{-\bullet} \longrightarrow Ph_3PO + Bu^- \qquad (6)$$

$$2Bu^{\bullet} \longrightarrow C_8H_{18} \text{ or } C_4H_{10} \qquad (7)$$

The alkylation reactions in DMF and HMPA proceed with rate constants $k_1 = 0.14\,mol^{-1}\,l\,s^{-1}$ and $k_1 = 0.05\,mol^{-1}\,l\,s^{-1}$ [13], suggesting that the alkylation reaction 3 is 20 times slower in HMPA. The cleavage of the P—C bond in reaction 3 is dependent on the dielectric constant; it appears to be facilitated by the alkylation reaction 2.

III. PHOSPHATES

A. Nitrophenyl Phosphates

1. Polarographic characteristics

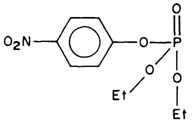
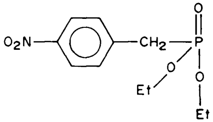
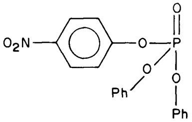
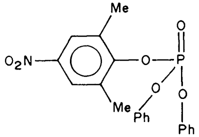
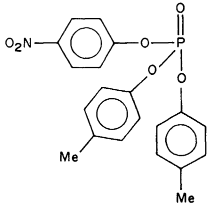
A large number of nitro-substituted phenyl phosphates have characteristic polarographic reductions[15–17]. The characteristic constants are listed in Table 1. The diffusion current constant values indicate that these nitro compounds undergo 1e reductions with the exception of multi-nitro-substituted compounds. This class of compounds show multiple reductions as each nitro group is susceptible to reduction [see tris(*p*-nitrophenyl) phosphate], provided that geometrical considerations allow sufficient electron density for the electron transfer. The 1e reduction produces a stable radical anion of nitrophenyl phosphates; these behavioural patterns are comparable to those of the well studied nitrobenzenes[18–24].

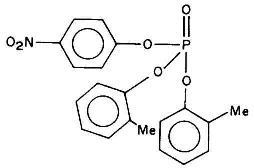
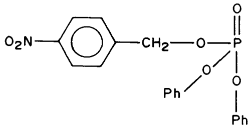
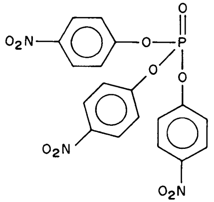
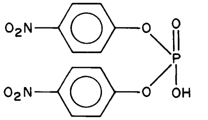
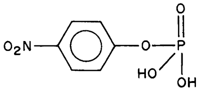
A general feature of nitro compounds is their affinity for adsorption on a mercury surface; this adsorption results in the appearance of polarographic pre-waves. In a few cases these waves have been identified and distinguished from the diffusion-limited waves. Thus *p*-nitrophenyl phosphate exhibits a well defined adsorption wave (see Table 2)[25,26]. The $E_{1/2}$ of diphenyl-4-nitrobenzyl phosphate is shifted in the positive direction owing to its adsorption on mercury; this feature is also observed with tris(*p*-nitrophenyl) phosphate[15,25]. The polarographic characteristics such as $E_{1/2}$ and $|E_{3/4} - E_{1/4}|$ are not significantly altered by the solvent; the values in MeCN and DMF are nearly the same[15].

2. Cyclic voltammetric patterns

In-depth studies of nitro-substituted phosphates have been carried out using tris(*p*-nitrophenyl) phosphate, bis(*p*-nitrophenyl) phosphate and mono(*p*-nitrophenyl) phosphate as model compounds for the phosphates[25,26]. Typical cyclic voltammetric curves of tris(*p*-nitrophenyl) phosphate and bis(*p*-nitrophenyl) phosphate are depicted in Figure 2. The five well defined peaks of tris(*p*-nitrophenyl) phosphate in the cyclic voltammogram are reduced to three for bis(*p*-nitrophenyl) phosphate. This difference

TABLE 1. Characteristic polarographic features of nitro-substituted phosphorus compounds in acetonitrile[a]

Structure	Species	$-E_{1/2}$ (V)	$i_{d/c}$ (μA l mmol^{-1}	$E_{3/4} - E_{1/4}$ (V)	I^b
	Diethyl-4-nitrophenyl phosphate	1.07	2.93	0.078	2.7
	Diethyl-4-nitrobenzyl phosphate	1.11	4.18	0.053	3.6
	Diphenyl-4-nitrophenyl phosphate	1.09	3.92	0.057	3.4
	Diphenyl-2,6-dimethyl-4-nitrophenyl phosphate	1.14	3.19	0.056	2.8
	Di(4-methylphenyl)-4-nitrophenyl phosphate	1.09	4.77	0.057	4.2

	Di(2-methylphenyl)-4-nitrophenyl phosphate	1.10	3.52	0.05	3.1
	Diphenyl-4-nitrobenzyl phosphate	0.086 1.211	4.64 3.81	0.071 0.068	4.0 3.3
	Tris(*p*-nitrophenyl) phosphate	0.83	–	0.080	3.5
	Bis(*p*-nitrophenyl) phosphate	0.94	0.80	–	
	*p*-Nitrophenyl phosphate	1.28	0.080	–	

---

[a] Taken from refs 15–17. Potentials measured with respect to the saturated calomel electrode (SCE).

[b] $I = \frac{i_d}{m^{2/3} t^{1/6} C}$, calculated from i_d/C values.

i_d = diffusion current, m = mass of mercury drop, t = seconds, C = concentration.

TABLE 2. Relative changes in the polarographic reduction of tris(*p*-nitrophenyl)phosphate[a]

Height of mercury column (cm)	Wave I, $i_{d/h}$ (μA cm^{-1})	Wave II, $i_{d/h}{}^{1/2}$ (μA cm$^{-1/2}$)
110.9	0.0139	0.86
100.9	0.0139	0.87
90.9	0.0137	0.83
70.9	0.0127	0.92

[a] Medium: DMF containing1.47 mM tris(*p*-nitrophenyl) phosphate and 0.1 M Bu_4NI. $m = 1.70\,mg\,s^{-1}$; $t = 2.4$ s. Reprinted with permission from ref. 25. Copyright (1967) American Chemical Society.

appears to arise from the complex chemical reactions that occur with the multiple charge-transfer schemes on attachment of more nitrophenyl groups to phosphate. Table 3 gives cyclic voltammetric data for the three nitro compounds; these features are indicative of chemical reactions accompanying the charge-transfer process[25]. The peak current increases directly with increasing scan rate.

3. *ESR features*

The nitrophenyl phosphates produce ESR spectra on electrochemical reduction on the first wave. Mononitrophenyl phosphates of the type listed in Table 4 show ESR spectra with characteristic coupling constants arising from nitrogen, protons and phosphorus[15]. The anion radical of diphenyl-4-nitrobenzyl phosphate is unstable and hence produces no ESR signal. An interesting feature of the ESR of nitrophenyl phosphates is their close resemblence to those of the nitrophenyl group. The nitrogen coupling constants of nitrobenzene can be matched with those of nitrophenyl phosphates; $a_{H(o)}$ and $a_{H(p)}$ are identical for the two compounds. The conclusion one can draw from the data is that the introduction of the phosphate moiety into the nitrobenzene ring does not perturb the π-electron density distribution in the ring. Further, as the phosphorus coupling to the electron is observed, there is no steric hindrance offered by the phosphate. The characteristic ESR patterns of a variety of phosphates are shown in Figure 3.

The mechanism of the spin density transmission to phosphorus in anion radicals is fascinating from a geometrical point of view. If the geometry of the neutral molecule persists even after the 1e reduction, then the P—O bond length in PO_4^{3-} will be 1.54 Å (shorter by 0.19 Å from covalent radii) with a bond order of 1.70. It is altered in esters and phosphoryl oxygens to 1.63 and 1.43 Å. As the O—P—O and P—O—C angles were determined by Davies and Stanley[27] from crystallographic data as 117° and 122°, the nitrophenyl phosphates with the above parameters have tetrahedral geometry. The situation changes with diethyl-4-nitrobenzyl phosphonate; the P—CH_2—C angle is estimated to be 109°. The spin density transmission would depend on the position of the C—Y—P plane with respect to the plane of the nitrophenyl group (C and Y refer to the ring carbon atom and oxygen or carbon atom). When a group such as —$CH_2PO(OEt)_2$ is coupled to the nitrophenyl ring, the phosphorus atom is pushed out of the plane of the aromatic ring[15]. This understanding is supported by the value of methylene proton coupling constant (2.70 G), which is far from that of the 4-nitrotoluene anion radical (3.92 G). Further, this non-planarity has reduced a_p in comparison with

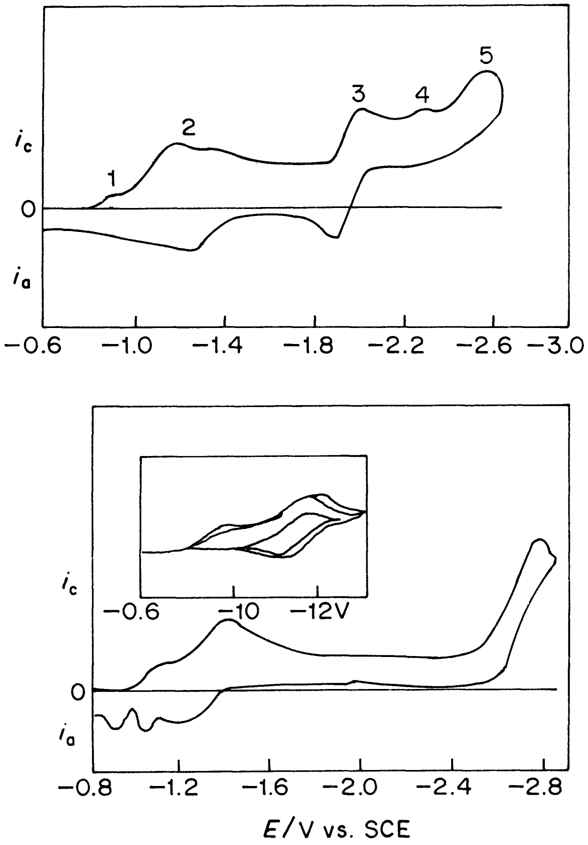


FIGURE 2. Top: cyclic voltammetric curve of tris(*p*-nitrophenyl) phosphate from a solution containing 0.1 M tetra-*n*-butylammonium iodide and 2.85 mM tris(*p*-nitrophenyl) phosphate in DMF. Numbers on the recording represent the number of peaks observed. Sweep rate, 153 m s^{-1}; working electrode, platinum (area = 0.031 cm^2). Taken from ref. 16. Bottom: cyclic voltammetric curve of bis(*p*-nitrophenyl) phosphate from a solution containing 0.1 M tetra-*n*-butylammonium iodide and 0.3 mM bis(*p*-nitrophenyl) phosphate. Sweep rate, 153 mV s^{-1}. Inset: repetitive cycling of the electrode potential between −0.83 and −1.25 V. Working electrode, hanging mercury drop electrode (area: 0.022 cm^2). The oscillations on the anodic scan are due to oscillation of the mercury drop due to the 'stirring phenomenon'. Reprinted with permission from ref. 17. Copyright (1969) American Chemical Society.

the planar structure that exists in the semiquinone phosphates[28] which have values in the range 17.2–20 G. Hence the mechanism of spin transmission appear to be based on C—P hyperconjugation.

The bis- and tris-(*p*-nitrophenyl) phosphates produce radical anions that can be

TABLE 3. Cyclic voltammetric characteristics of nitrophenyl phosphates[a]

Compound	Peak 2		Peak 3		Peak 4		Peak 5	
	E_{pc} (V)	$i_p/v^{1/2}$ (μA s$^{1/2}$ mV$^{-1/2}$)	E_{pc} (V)	$i_p/v^{1/2}$ (μAs$^{1/2}$ mV$^{-1/2}$)	E_{pc} (V)	$i_p/v^{1/2}$ (μA $^{1/2}$ mV$^{-1/2}$)	E_{pc} V	$i_p/v^{1/2}$ (μA s$^{1/2}$ mV$^{-1/2}$)
Tris(*p*-nitrophenyl)	− 1.13[b]	3.27	− 1.96	3.12	− 2.24	0.81	− 2.51	6.11
phosphate	− 1.14[c]	2.96	− 1.99	1.93	− 2.34	2.47	− 2.59	1.98
Bis(*p*-nitrophenyl)	− 1.35[d]	0.73	− 2.54	2.40	–	–	–	–
phosphate	− 1.37[e]	0.65	− 2.77	2.50				
Nitro-phenyl phosphate	− 1.28[f]	–	−2.02					

[a] Taken from refs 25 and 26. Potentials are with respect to SCE.
[b] Sweep rate for this set at 67.1 mV s^{-1}.
[c] Sweep rate for this set at 222 mV s^{-1}.
[d] Sweep rate for this set at 91.4 mV s^{-1}.
[e] Sweep rate for this set at 943 mV s^{-1}.
[f] Sweep rate of 67.1 mV s^{-1}.

TABLE 4. Electron spin resonance data for nitrophenyl phosphates[a]

Compound[b]	Parameter	Acetonitrile	DMF
1	a_{N}	10.43 ± 0.06	9.93 ± 0.03
	$a_{\text{H}(o)}$	3.64 ± 0.04	3.44 ± 0.04
	$a_{\text{H}(m)}$	1.13 ± 0.02	1.13 ± 0.02
	a_{P}	7.05 ± 0.06	7.28 ± 0.02
2	a_{N}	10.27 ± 0.04	9.71 ± 0.03
	$a_{\text{H}(o)}$	3.47 ± 0.02	3.46 ± 0.02
	$a_{\text{H}(m)}$	1.13 ± 0.02	1.12 ± 0.01
	a_{P}	10.29 ± 0.04	10.84 ± 0.02
3	a_{N}	10.26 ± 0.26	9.61 ± 0.19
	$a_{\text{H}(o)}$	3.33 ± 0.05	3.38 ± 0.02
	$a_{\text{H}(m)}$	1.10 ± 0.02	1.08 ± 0.05
	$a_{\text{H(CH}_2)}$	2.70 ± 0.02	2.81 ± 0.02
	a_{P}	13.59 ± 0.23	17.51 ± 0.24
4	a_{N}	9.96 ± 0.03	9.50 ± 0.03
	$a_{\text{H}(o)}$	3.42 ± 0.02	3.47 ± 0.02
	$a_{\text{H}(m)}$	1.12 ± 0.01	1.12 ± 0.01
	a_{P}	7.92 ± 0.02	8.35 ± 0.02
5	a_{N}	10.50 ± 0.04	9.75 ± 0.19
	$a_{\text{H}(o)}$	3.39 ± 0.01	3.40 ± 0.01
	$a_{\text{H}(m)}$	1.03 ± 0.01	1.02 ± 0.01
	a_{P}	10.50 ± 0.04	11.06 ± 0.06
6	a_{N}	10.14 ± 0.04	9.89 ± 0.03
	$a_{\text{H}(o)}$	3.46 ± 0.02	3.45 ± 0.02
	$a_{\text{H}(m)}$	1.12 ± 0.01	1.12 ± 0.01
	a_{P}	7.90 ± 0.02	8.00 ± 0.03
7	a_{N}	10.15 ± 0.06	9.87 ± 0.03
	$a_{\text{H}(o)}$	3.46 ± 0.01	3.46 ± 0.04
	$a_{\text{H}(m)}$	1.12 ± 0.02	1.12 ± 0.02
	a_{P}	8.27 ± 0.06	8.39 ± 0.03
8	a_{N}	10.32	9.83
	$a_{\text{H}(o)}$	3.39	3.32
	$a\ _{(m)}$	1.09	1.09
	$a^{\text{H}}_{\text{H}(p)}$	3.97	3.97

[a] Absolute values of coupling constants are given in gauss, and standard deviations from the mean are indicated. Proton positions are labelled with respect to the nitro group. All the radicals in both solvents had a g factor close 2. Reprinted with permission from ref. 15. Copyright (1966) American Chemical Society.

[b] 1 = Diethyl-4-nitrophenyl phosphate; 2 = *O,O*-diethyl-*O*-4-nitro- phenyl thio-phosphate; 3 = diethyl-4-nitrobenzyl phosphonate; 4 = diphenyl-4-nitrophenyl phosphonate; 5 = diphenyl-2,6-dimethyl-4-nitrophenyl phosphate; 6 = di(4-methylphenyl)4-nitrophenyl phosphate; 7 = di(2-methylphenyl)-4-nitrophenyl phosphate; 8 = nitro-benzene.

explained as being due to secondary products such as 4,4′-dinitrobiphenyl anion radical with coupling constants $a_{\text{N}} = 2.96$ G, $a_{\text{H}} = 1.21$ G and $a_{\text{H}} = 0.21$ G. The ESR spectra of these radicals are shown in Figure 4. The 4-nitrophenyl phosphate group can be identified in the spectral recordings[26].

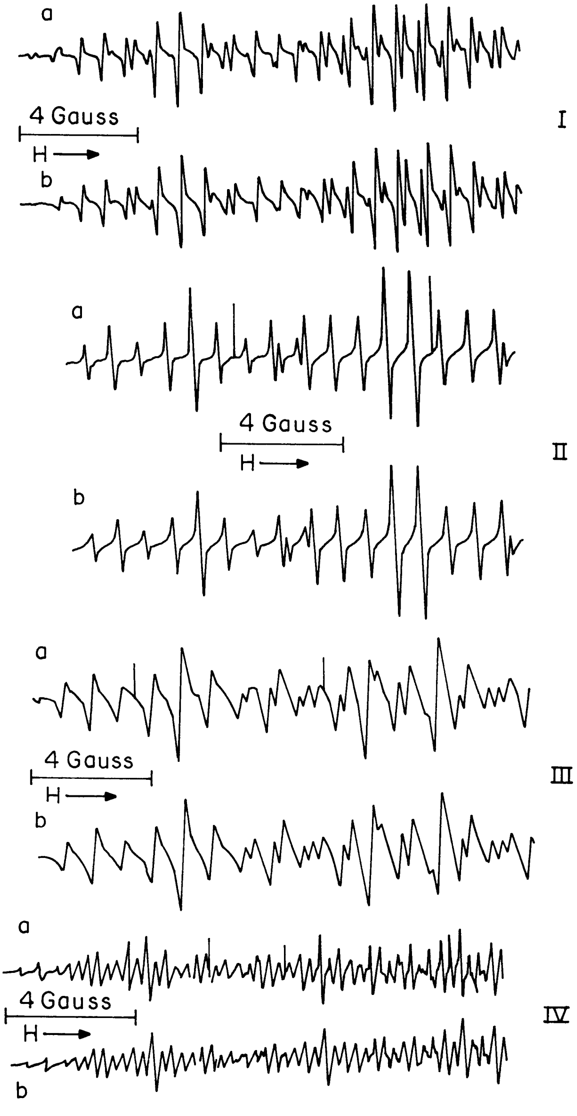


FIGURE 3. I. (a) First-derivative ESR spectrum of the anion radical of diphenyl-2,6-dimethyl-4-nitrophenyl phosphate in DMF. Low-field half of the spectrum. (b) Computed spectrum using $a_N = 9.71$ G, $a_H = 3.395$ G, $a_H = 1.02$ G and $a_P = 11.06$ G. Line width: 0.125 G. II. (a) ESR spectrum of diphenyl-4-nitrophenyl phosphate anion radical in DMF. Low-field half of the spectrum. (b) Computed spectrum using $a_N = 9.46$ G, $a_H = 3.46$ G, $a_H = 1.12$ G and $a_P = 8.31$ G. Line width, 0.125 G. III. (a) ESR spectrum of diethyl-4-nitrophenyl phosphate anion radical in DMF. Low-field half of the spectrum. (b) Computed spectrum using $a_N = 9.93$ G, $a_H = 3.47$ G and $a_P = 7.28$ G. Line width, 0.23 G. IV. (a) ESR spectrum of diethyl-4-nitrobenzyl phosphonate in DMF. Slightly more than the low-field half of the spectrum. (b) Computed spectrum using $a_N = 9.70$ G, $a_H = 3.34$ G, $a_H = 1.08$ G, $a_H = 2.79$ G and $a_P = 17.60$ G. Line width, 0.140 G. Reprinted with permission from ref. 15. Copyright (1986) American Chemical Society.

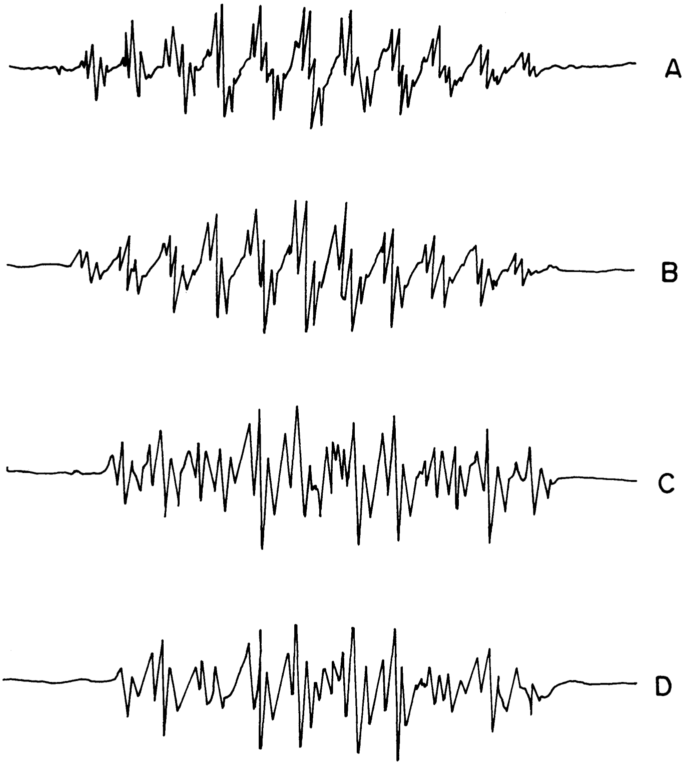
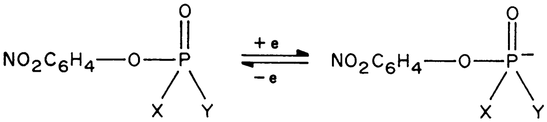


FIGURE 4. (A) Derivative ESR spectrum of 4,4′-dinitrobiphenyl anion radical obtained by electroreduction of 2.38 mM tris(p-nitrophenyl) phosphate in DMF. (B) Computed spectrum with $a_N = 2.62$ G, $a_H = 1.21$ G and $a_H = 0.21$ G. (C) Derivative ESR spectrum of nitrophenyl phosphate anion radical during reduction of tris(p-nitrophenyl) phosphate in DMF. (D) Computed spectrum with $a_N = 3.3$ G, $a_H = 0.83$ G and $a_P = 11.4$ G. Reprinted with permission from ref. 16. Copyright (1969) American Chemical Society.

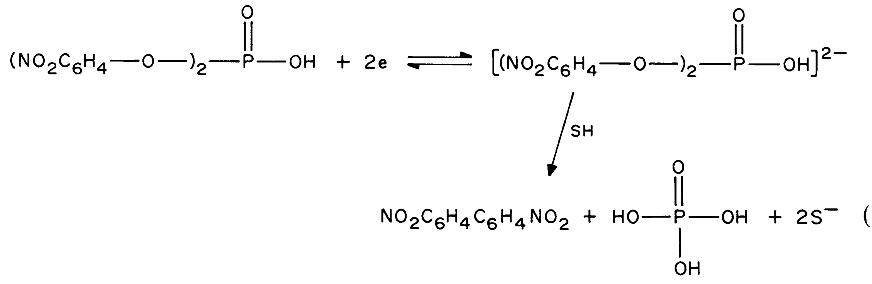
4. Redox mechanisms

A strong resonance interaction between the nitro group and other substituents has been observed in the series of compounds listed in Table 1. The half-wave potentials for compounds with reference to nitrobenzene shift in the direction predicted by Hammett's constant. σ. This shift also correlates with the observed shift in the values of a_p[15,19].

With only one p-nitrophenyl substituent attached to phosphate, the reduction proceeds as in equation 8, where X and Y represent the substituent groups listed in Table 1, such as phenyl, methyl, ethyl or benzyl. When two p-nitrophenyl substituents are attached to phosphate, the radical anion produced is unstable and decomposes by the pathway in reactions 9–11, where SH represents DMF. The 4,4′-dinitrobiphenyl is further reduced at -2.54 V and appears as the third peak in the cyclic voltammetric patterns. Cleavage of the C—O bond has been observed by Santhanam and Bard[26] followed by coupling of the radicals to produce 4,4′-dinitrobiphenyl. This molecule is easier to reduce than bis(*p*-nitrophenyl) phosphate and hence the electron spin resonance spectrum of 4,4′-dinitrobiphenyl is observed.



$$NO_2C_6H_4{-}O{-}P(=O)XY \underset{-e}{\overset{+e}{\rightleftharpoons}} NO_2C_6H_4{-}O{-}P(=O)^{-}XY \tag{8}$$

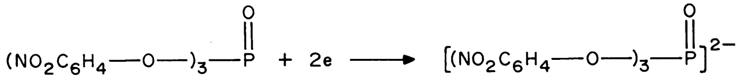


$$(NO_2C_6H_4{-}O{-})_2{-}P(=O){-}OH + 2e \rightleftharpoons [(NO_2C_6H_4{-}O{-})_2{-}P(=O){-}OH]^{2-} \tag{9}$$

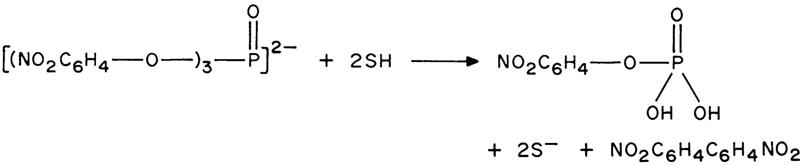
$$\xrightarrow{SH} NO_2C_6H_4C_6H_4NO_2 + HO{-}P(=O)(OH){-}OH + 2S^{-} \tag{10}$$

$$NO_2C_6H_4C_6H_4NO_2 + e \rightleftharpoons [NO_2C_6H_4C_6H_4NO_2]^{-} \tag{11}$$

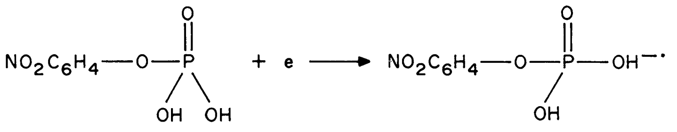
The introduction of third nitrophenyl group into phosphate produces more complexity but nevertheless cleavage of the C—O bond is observed. The reaction scheme during reduction is depicted by equations 12–15. With this series of molecules the energy-rich P—O bond remains intact; cleavage of the C—O bond takes place with ease; a similar phenomenon is observed with diphenylphosphate on reduction.



$$(NO_2C_6H_4{-}O{-})_3{-}P{=}O + 2e \longrightarrow [(NO_2C_6H_4{-}O{-})_3{-}P{=}O]^{2-} \tag{12}$$



$$[(NO_2C_6H_4{-}O{-})_3{-}P{=}O]^{2-} + 2SH \longrightarrow NO_2C_6H_4{-}O{-}P(=O)(OH)(OH) + 2S^{-} + NO_2C_6H_4C_6H_4NO_2 \tag{13}$$



$$NO_2C_6H_4{-}O{-}P(=O)(OH)(OH) + e \longrightarrow NO_2C_6H_4{-}O{-}P(=O)(OH){-}OH^{-\cdot} \tag{14}$$

$$NO_2C_6H_4C_6H_4NO_2 + e \longrightarrow NO_2C_6H_4C_6H_4NO_2^{-\cdot} \tag{15}$$

B. Nitrophenyl Thiophosphate

O,*O*-Diethyl *O*-4-nitrophenyl thiophosphate generates a polarographic wave in MeCN with a half-wave potential at $E_{1/2} = -1.16$ V vs SCE, with a wave slope of $|E_{3/4} - E_{1/4}|$

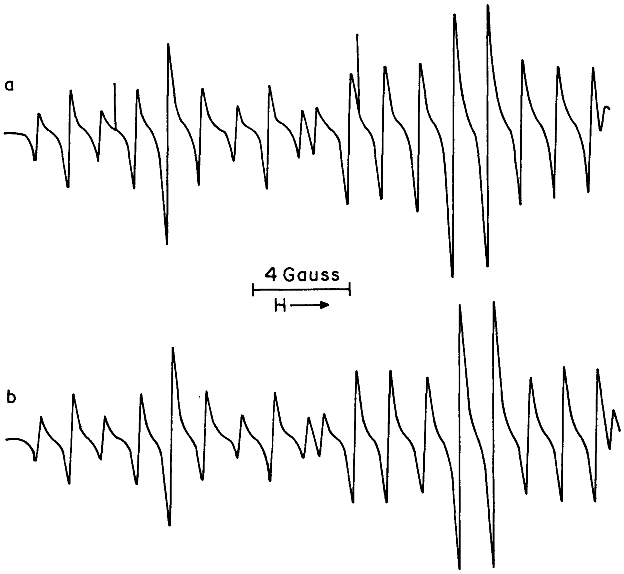


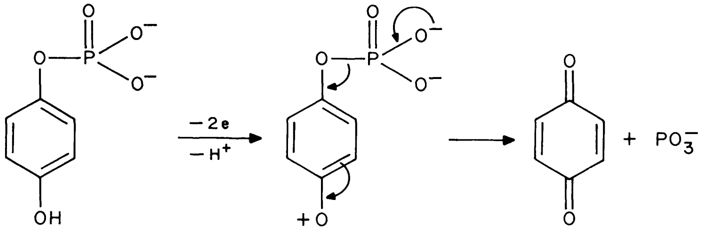
FIGURE 5. (a) Derivative ESR spectrum of the anion radical of 0,0-diethyl-0,4-nitrophenyl thiophosphate in DMF. (b) Computed spectrum using $a_N = 9.68$ G, $a_H = 3.46$ G $a_H = 1.135$ G and $a_P = 10.82$ G. Line width, 0.185 G. Reprinted with permission from ref. 15. Copyright (1966) American Chemical Society.

≈ 53 mV. This wave *is due to a 1e reduction of this molecule*[15] and the free radical anion produces an ESR spectrum as shown in Figure 5. The spectrum shows the following coupling constants in DMF: $a_N = 9.68$ G, $a_{H(O)} = 3.46\, a_{H(m)} = 1.13$ G and $a_p = 10.82$ G. The coupling constants are slightly shifted in MeCN: $a_N = 10.27$ G, $a_{H(O)} = 3.47$ G, $a_{H(m)} = 1.13$ and $a_p = 10.29$ G. Replacement of the phosphoryl oxygen by sulphur (see Section 3.) produces a_N and ring proton coupling constants that are virtually unchanged, but results in an increase in a_p by about 45%. This feature of incresing a_p has also been observed for the radical produced by dehydrogenation of diphenyl(4-hydroxy-3,5-di-*tert*-butylphenyl)phosphine oxide; a change in a_p from 14.7 to 15.4 G is observed with the analogous phosphine sulphide[30]. As oxygen is more electronegative than sulphur, it does not attract the electron towards itself.

C. Quinol Phosphates—Biological Significance

1. Oxidative phosphorylation

Oxidative phosphorylation plays a role in energy transfer schemes in biological processes. Quinol phosphates possesses the potential for understanding the energy transduction in biological mechanisms[31]. The pioneering work in understanding the phosphorylating agent stems from a series of publications by Todd and co-workers[32–35]. Phosphorylating agents such as phosphonic anhydrides on reaction with quinol phosphate expel an anion as in equation 16.

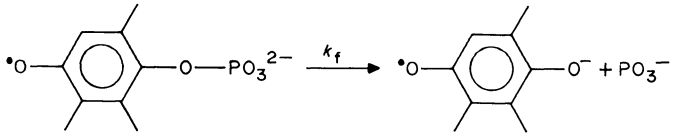


(16)

Several studies[32,33] have been carried out on the initiation of the P—O and C—O bond fission processes. Lapidot and Samuel[36,37] indicated that both fission processes operate in the oxidation schemes. The implication of this finding is that the P—O bond fission will produce a metaphosphate intermediate for the phosphorylation. Todd's group[32] has demonstrated metaphosphate generation, but could not find support for phosphoryl cation formation during the oxidation of quinol diphosphates by a number of oxidizing agents. The product of these oxidations is quinone; a qualitative correlation between the redox potential of the quinone–quinol system and the efficiency of quinone formation has been observed[32]. Further support for the finding that P—O bond fission is susceptible to metaphosphate intermediate formation during phosphorylation has been arrived at through cyclic voltammetric studies on 2-methyl-1,4-naphthoquinol 1-phosphate[38].

2. *Cyclic voltammetric pattern*

Quinol phosphate (2-methyl-1,4-naphthoquinol 1-phosphate) oxidation at an electrode takes place over a wide pH range from 2.50 to 10.39[38]. The 2e oxidation occurs in acidic solutions at $E_p = 0.60$ V vs SCE. The product undergoes fast hydrolysis to produce a semiquinone. The oxidation process occurring at different pH values is depicted in Figure 6. The anodic peak current decreases with increasing pH, which is attributed to the equilibrium that exists between the ionized and non-ionized forms. A complete reaction scheme is shown in Figure 7. The oxidized product is unstable and decomposes to form the quinone, which is easily identified by its characteristic cyclic voltammetric features. The cyclic voltammetric parameters are listed in Table 5. The $|E_p - E_{p/2}|$ value is close to the 2e irreversible peak having a transfer coefficient of 0.5[38]; the increase in the $|E_p - E_{p/2}|$ value with increasing pH is consistent with the complexity of the mechanism and changes in the transfer coefficient. The current function also decreases with increasing pH and is a characteristic feature of this oxidation.



(17)

In basic media 1e oxidation of quinol phosphate followed by further oxidation and cleavage of the P—O bond is observed. The rate constant for the process in equation 17 is controlled by the prior equilibrium that exists which depends on the hydroxide ion concentration (pH of the medium and pK_a). It is considered to be composed of

$$k_f = k_1 + k_2[OH^-] \tag{18}$$

with $k_1 = 0.2 \pm 0.1\ s^{-1}$ and $k_2 = 700 \pm 400\ l\,mol^{-1}\,s^{-1}$. Using equation 18, an estimate of k_f in any basic solution can be determined.

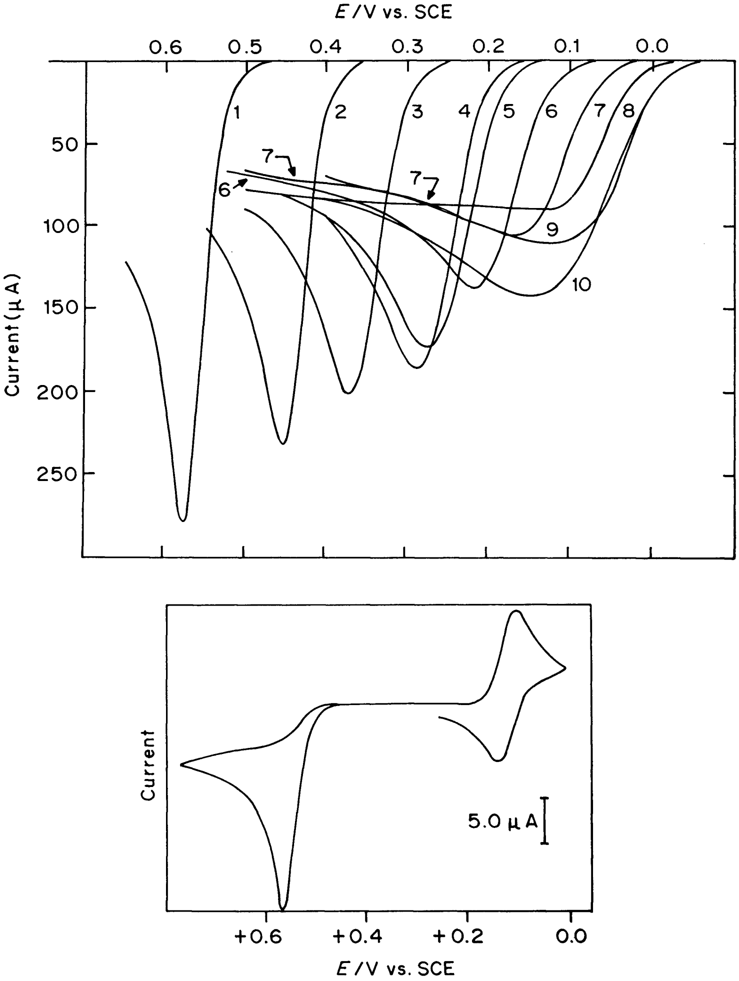


FIGURE 6. Top: current–voltage curves for 2-methyl-1,4-naphthoquinol 1-phosphate in acetate, phosphate and borate buffers. (1) 1 M H_2SO_4; (2) pH 2.50; (3) pH 4.04; (4) pH 5.63; (5) pH 6.32; (6) pH 7.44; (7) pH 8.38; (8) pH 9.27; (9) pH 11.18; (10) pH 11.87. Bottom: cyclic voltammetric curve for 0.53 mM 2-methyl-1,4-naphthoquinol 1-phosphate in 1 M H_2SO_4. Sweep rate for both recordings, 60 mV s^{-1}. The reversible couple at 0.20 V is due to the quinone formed after the electrochemical oxidation of the electroactive species at +0.58 V. Working electrode, carbon paste (Nujol). Reprinted with permission from ref. 38. Copyright (1966) American Chemical Society.

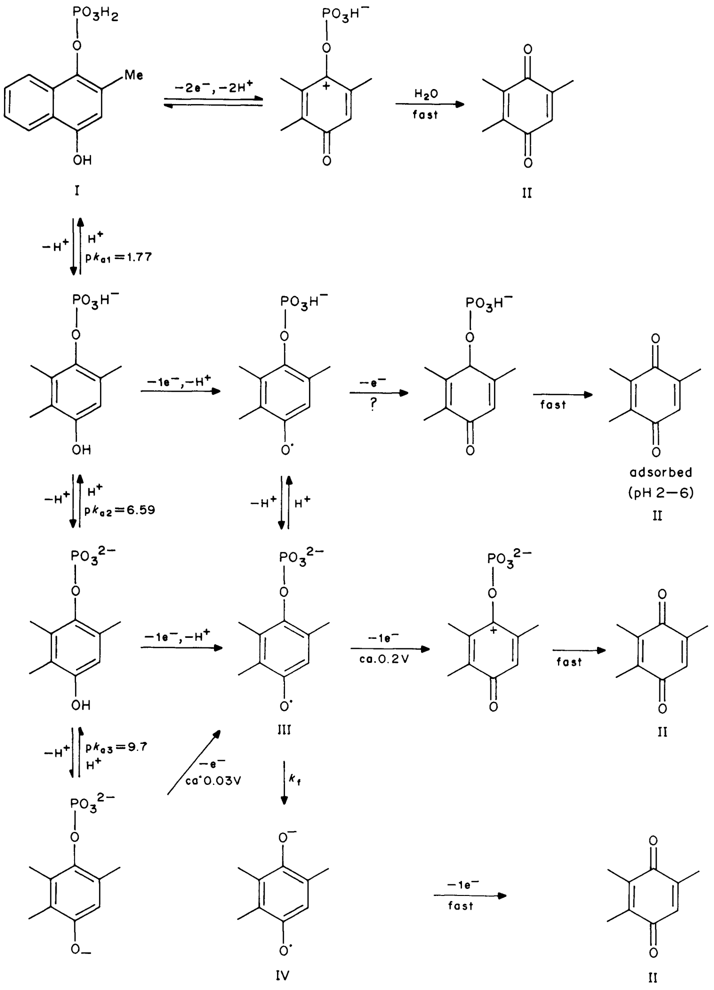


FIGURE 7. Reaction mechanism for quinol phosphate oxidation.

3. *Electron spin resonance features*

The ESR spectral features of the oxidized product of quinol phosphate (2-methyl-1,4-naphthaquinol 1-phosphate) are identified as arising from the substituted quinone (product II in Figure 7)[38]. Allen and Bond[39], however, generated the following semiquinone phosphate radical:

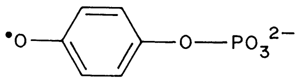


TABLE 5. Cyclic voltammetric parameters 2-methyl-1,4-naphthoquinol 1-phosphate[a]

pH	$E_p - E_{p/2}$ (mV)	$i_p/ACv^{1/2}$ ($A\,cm^{-2}\,l\,mol^{-1}\,V^{-1/2}\,s^{1/2}$)
0.59	26.5	2.18
1.44	30.5	1.89
2.50	30	1.84
3.48	36	1.86
4.04	40	1.55
4.48	46	1.38
5.63	49	1.41
6.32	55	1.35

[a] Sweep rate $0.10\,V\,s^{-1}$. Reprinted with permission from ref. 38. Copyright (1966) American Chemical Society.

by chemical oxidation using permanganate at high pH (11.7). The electrolytic oxidation of quinol phosphate at this pH value can only generate a weak, unresolved signal, indicating the instability of the radical.

The phosphorylation reaction in biological systems has been of importance in arriving at the bioenergetics. The nature of the phosphorylating agent is speculative[31,40,41]; is there a reactive intermediate in phosphorylation reactions[42,43]? The electrochemical data together with ESR results for quinol phosphate suggest that the semiquinone phosphate radical is the phosphorylating agent[38].

D. *S*-(1,2-Dicarbethoxyethyl)-*O*,*O*-dimethyl Dithiophosphate or *O*,*O*-Dimethyl *S*-(1,2-dicarbethoxyethyl Phosphorodithioate) (Malathion): $(CH_3O)_2P(S)SCH(COOC_2H_5)CH_2COOC_2H_5$

The electrochemical reduction of malathion occurs at $E_p = -0.21$ V vs SCE at a DME in ethanol–HCl medium. The second peak is observed at $E_p = -0.80$ V vs SCE. In alkaline medium (NaOH), only one reduction peak at $E_p = -0.80$ V is observed[44].

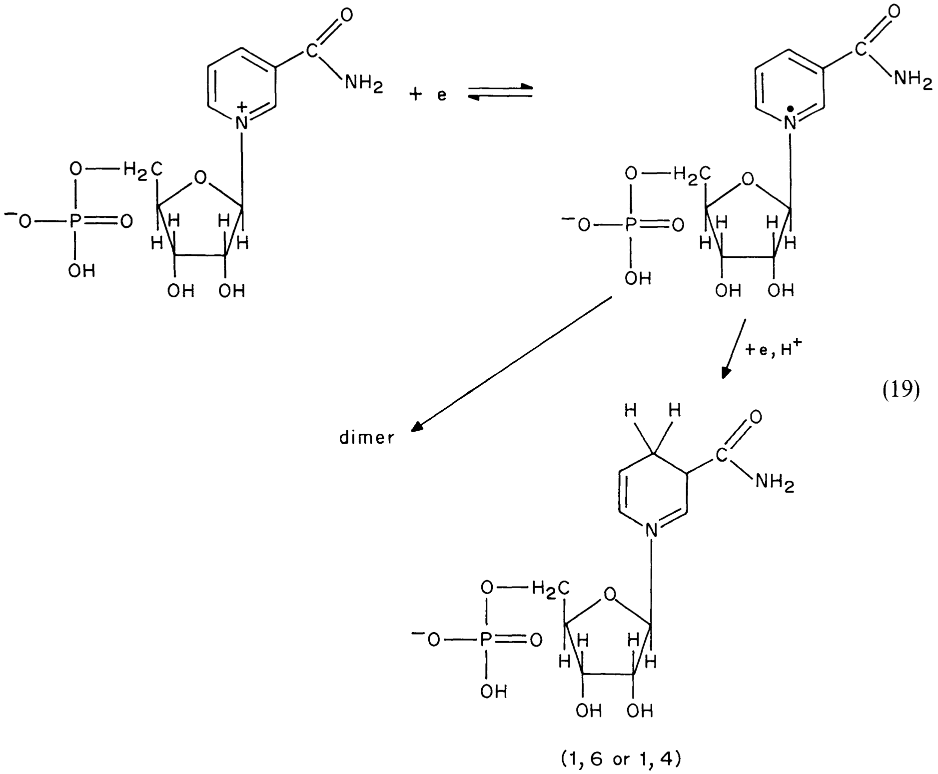
E. Nicotinamide Ribose Monophosphate

The redox chemistry of the most familiar form of β-nicotinamide ribose mono-phosphate (NMN) has been investigated extensively by Schmakel *et al.*[45], using this as a model compound to understand several nucleotides, such as nicotinamide adenine dinucloetide (NAD^+) and nicotinamide adenine dinulceotide phosphate ($NADP^+$). NMN exhibits a half-wave potential which is independent of pH up to 5, becomes more negative between pH 5.0 and 7.5 and then remains constant up to pH 12. These shifts occur as a result of secondary phosphate dissociation. While the first well defined wave of NMN^+ is observed at $E_{1/2} = -0.90$ V vs SCE, the second wave which appears at $E_{1/2} = -1.60$ V vs SCE is not visible in solutions of pH 5 owing to the background electrolysis setting in earlier. Both the waves are well defined in solutions of pH 9.6. A.c. polarographic measurements conclusively establish the first wave as being due to a reversible 1e process. The reversibility of the electron transfer reaction has been confirmed by fast-sweep cyclic voltammetric studies. Table 6 provides the data for NMN^+ at pH 5–9. The first 1e reduction produces a neutral radical which dimerizes rapidly with a rate constant of $1.5 \times 10^6\,l\,mol^{-1}\,s^{-1}$. The dimer has been identified by spectral and

TABLE 6. Dimerization rates of the free radicals derived from NMN^+, DPN^+ and TPN^{+a}

Parent compound	Solvent	pH	k_d ($l\,mol^{-1}\,s^{-1}$)	Temperature (°C)
NMN^+	H_2O	5–9	1.5×10^6	30
DPN^+	H_2O	5	2.2×10^6	30
		7	8.49×10^6	
		8	$> 10^b$	
		9	2.4×10^6	
	DMSO		9.0×10^5	40
TPN^+	H_2O	5	4.3×10^6	30
		7	$5.45 \times 10^{10\,b}$	
		9	1.6×10^6	30
	DMSO		5×10^6	40

[a] Taken from ref. 58. Measurements using peak current ratio.
[b] Cyclic voltammetric peak potential method.



(19)

NMR studies as a mixture of isomers of 4,4′-, 4,2′- and 6,6′-dimers[45–47]. The activation energy for the dimerization process has been estimated at 3.6 kcal mol^{-1}. The oxidation of the dimer at -0.28 V produces the monomer[45,46].

The second electron reduction process produces 1,6-dihydro-NMN (NMNH) as the major product; the other product is 1,4-dihydro-NMN (NMNH). The characteristic features of the absorption spectra are NMN$^+$ in unreduced form having a peak at 265 nm; in the reduced form 1,2-species, i.e. 1,2-NMNH, has a maximum at 400 nm. 1,4-NMNH has maximum at 340 nm and 1,6-NMNH shows maxima at 270 and 350 nm. The features for the dimers of NMN are that the 4,4′-dimer absorbs at 340 nm and the 6,6′-dimer at 260 and 345 nm.

The electrochemical redox pattern in DMSO for NMN$^+$ provides strong support for the mechanism postulated in aqueous media. It is reduced at $E_{1/2} = -0.99$ V with a wave slope of 45 mV. By detailed analysis of the polarographic, cyclic voltammetric and a.c. polarographic data, the reduction is attributed to the nicotinamide moiety[48]. NMN is strongly adsorbed on mercury and exhibits a pre-wave at -0.38 V. The diffusion-controlled process occurs at -0.99 V and a wave slope of 45 mV is indicative of a dimerization process accompanying the 1e reduction.

The controlled potential electrolysis of NMN$^+$ in both aqueous and non-aqueous media supports the 1e reduction process producing the dimer at the first polarographic wave. The electrolysis at the second polarographic wave results in the consumption of 2e per mole of NMN$^+$. The dihydro product has been identified by several physical techniques[45,48]. The reaction mechanism postulated for NMN$^+$ is as shown in equation 19.

1. Oxidation of NMNH

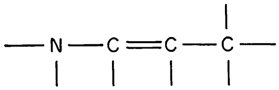
The electrochemical oxidation of NMNH in DMSO proceeds at $E_p = 0.84$ V vs SCE and based on the data obtained through cyclic voltammetry and chronoamperometry the process responsible for this wave is estimated to be 2e. The 2e oxidation produces NMN$^+$ and has been identified by the characteristic cathodic peak at -0.97 V vs SCE. Interestingly, the exhaustive electrolysis of NMNH does not produce NMN$^+$ due to the following reaction scheme[49–52]:

$$\mathrm{NMNH} \longrightarrow \mathrm{NMN}^+ + \mathrm{H}^+ + 2\mathrm{e} \tag{20}$$

$$\mathrm{NMNH} + \mathrm{H}^+ \longrightarrow \mathrm{H(NMNH)}^+ \tag{21}$$

$$\mathrm{H(NMNH)}^+ \longrightarrow \text{decomposition products absorbing at 280–290 nm} \tag{22}$$

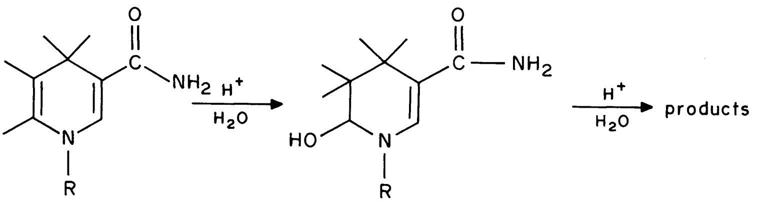
The source of the proton in large-scale electrolysis is attributed to the first step (i.e. reaction 20) or impurities of H_2O in the solvent. The absorption arising at 280 nm is due to the chromophore **1**[49]. The pseudo-first-order rate constant for this decomposition is $8.2 \times 10^{-4}\,\mathrm{s}^{-1}$ at pH 7.1. The decomposition reaction is given in equation 23.



$$-\mathrm{N}-\mathrm{C}=\mathrm{C}-\mathrm{C}-$$

(**1**)

The redox patterns of NMN$^+$ and NMNH discussed in this section are very similar to that of 1-methylnicotinamide; the $E_{1/2}$ of 1-methylnicotinamide is -1.03 V and that of NMN$^+$ is -0.99 V vs SCE. The charge-transfer schemes are identical with these molecules, as the nicotinamide ring is reduced during electrochemical reduction.



(23)

F. Diphosphopyridine Nucleotide (DPN$^+$)—Redox Scheme

The electrochemical reduction of DPN$^+$ at low pH (< 2) is hampered by catalytic evolution of hydrogen[53,54]. If the medium provides a large potential window, such as -2.0 V vs SCE, then DPN$^+$ undergoes two successive 1e reductions. Under other conditions, it undergoes only one 1e reduction. For example, at pH 4–5, a 1e reduction is generally observed at a mercury electrode, whereas between pH 8 and 10 two successive

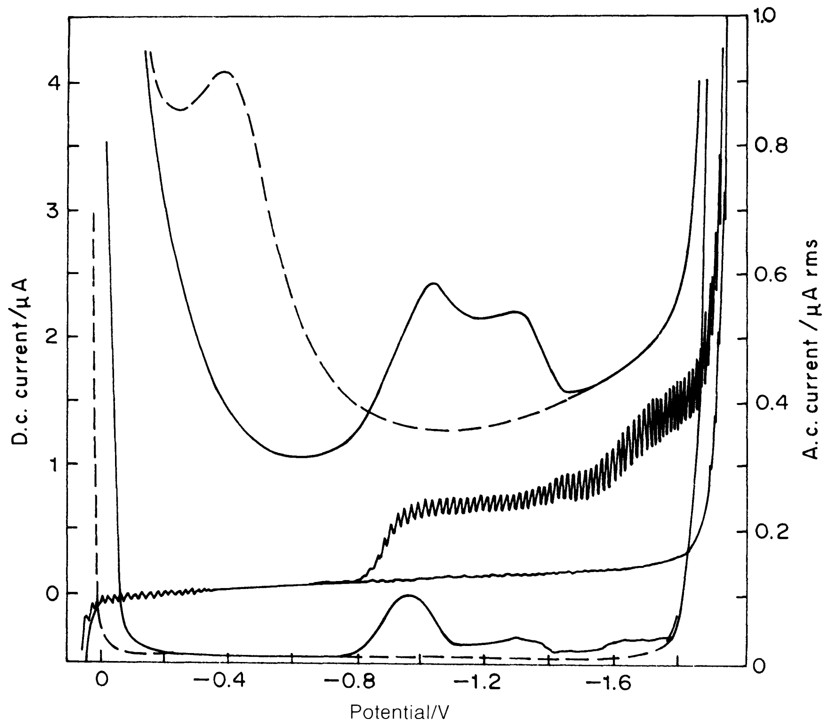


FIGURE 8. D.c. and a.c. polarograms of DPN$^+$ (0.31 mM) in pH 9.3 KCl–carbonate buffer. D.c. polarograms shown with and without the electroactive species (oscillatory curve and the one below it, respectively). A.c. polarograms: solid lines represent in-phase (lower set) and quadrature (upper set) components of total a.c. current. Dashed lines represent corresponding background current. Reprinted with permission from ref. 53. Copyright (1975) American Chemical Society.

1e reductions are observed. Above pH 10, DPN^+ undergoes hydrolysis to produce nicotinamide and a wave due to the reduction of this species is observed by both polarography and cyclic voltammetry. The decomposition rate is a function of pH; at pH 9.6 it is 1.9% decomposed and at pH 11.8 it is 88% decomposed during the same period of time[53]. As a result of these investigations, an electrochemical redox pattern is evolved at pH 9.6 where it is less decomposed.

The characteristic d.c. and a.c. polarograms of DPN^+ are shown in Figure 8. Note that the d.c. polarogram, which exhibits a maximum, is of the first kind. This can be suppressed by 0.0008% Triton or 5 mM Et_4NCl. The a.c. polarogram shows a faradaic peak (in phase component) at − 0.97 V (wave I process, quadrature component at − 1.04 V) and a barely discernible peak at − 1.65 V; this is due to the wave II process capturing 2e by DPN^+ at the electrode. The adsorption–desorption phenomena are well depicted in Figure 8. A significant depression of the differential double layer capacity is observed at − 0.65 V due to the above process.

The first 1e reduction of DPN^+ produces a neutral radical which dimerizes to produce an a.c. polarogram as shown in Figure 9; the dimer surface activity shifts the tensammetric peak ($E_s = - 1.27$ V) in the negative direction. The formation of a DPN free radical, its dimerization rate and the redox characteristics of the dimer have been investigated in detail[48,53,54]. As it is coenzyme I in several biological reactions, the redox characteristics have been examined in the pH range 0–12. The lack of a potential window up to pH 2 restricts the study of DPN^+ above pH 2. From pH 2.0 to 9.3, it undergoes a well defined 1e reduction. Above this pH, DPN^+ undergoes two successive cyclic voltammetric 1e reductions at $E^{I}_{p} = - 0.90$ V and $E^{II}_{p} = - 1.16$ V. None of the peaks shows complementary

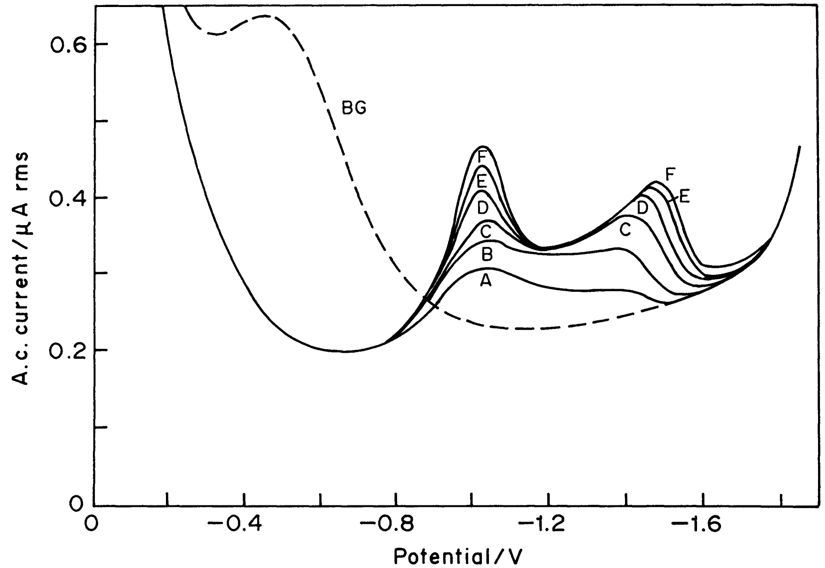


FIGURE 9. Effect of DPN^+ concentration on the adsorption-desorption behaviour of the DPN dimeric reduction product. Quadrature components of a.c. polarograms for solutions of 1.50 M in KCl and 0.25 M in carbonate buffer (pH 9.9). DPN concentration: (A) 0.04; (B) 0.12; (C) 0.34; (D) 0.88; (E) 1.26; (F) 1.76 mM.

anodic peaks at sweep rates of $< 10\,\mathrm{V\,s^{-1}}$. This sweep rate dependence on the appearance of anodic peak ($> 10\,\mathrm{V\,s^{-1}}$) has been used to obtain the dimerization rate constant for DPN^+ and the activation energy for this process. Table 6 summarizes the data for the dimerization reaction.

Controlled potential coulometry of DPN^+ at -1.20 V consumes 1e per mole, producing a dimer with $E_{1/2} = -0.25$ V (the process is due to oxidation of the dimer to DPN^+). The effect of pH on the stability of the DPN dimer is shown in Figure 10. The nature of the dimer has been identified[46,55–57] by absorption spectroscopy to be a mixture of dimers linked in the 4,4′-and 6,6′-positions. As it was not possible to isolate the products[58], subsequent studies[57] using reversed-phase HPLC and gel filtration on Sephadex G-15 and NMR spectra identified the dimer as the 4,4′-isomer. Small amounts($< 10\%$) of other isomers were also isolated. Electrolysis at -1.60 V produced a mixture of 1,4- and 1,6-dihydro isomers of DPN^+. The 1,4-dihydro isomer is 54% enzymatically active[57,58]; the 4,5-C=C bond of the 1,6-isomer has enamic nucleophilicity and exhibits a UV absorption maximum at 340 nm; conjugation with the 3,4-double bond of the pyridinium ring is removed by protonation.

The electrochemical behaviour of diphosphopyridine nucleotide in non-aqueous media was first studied by Santhanam and Elving[48]. This study established the need to have

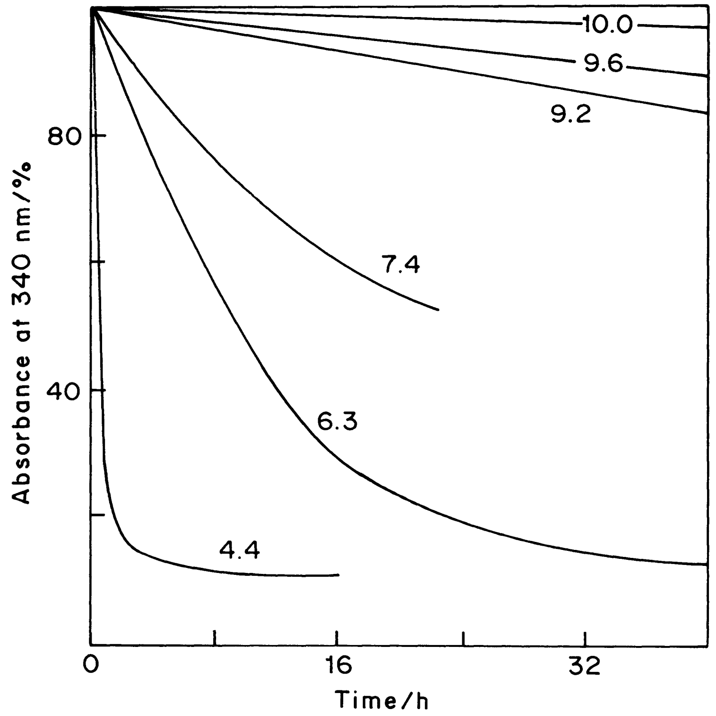
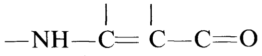


FIGURE 10. Effect of pH on stability of the DPN dimer. Buffer solutions and dimer concentrations above pH 9, carbonate buffer and 2.16×10^{-5} M; below pH 9, McIlvaine buffer and 1.89×10^{-5} M; all solutions stored under air at room temperature.

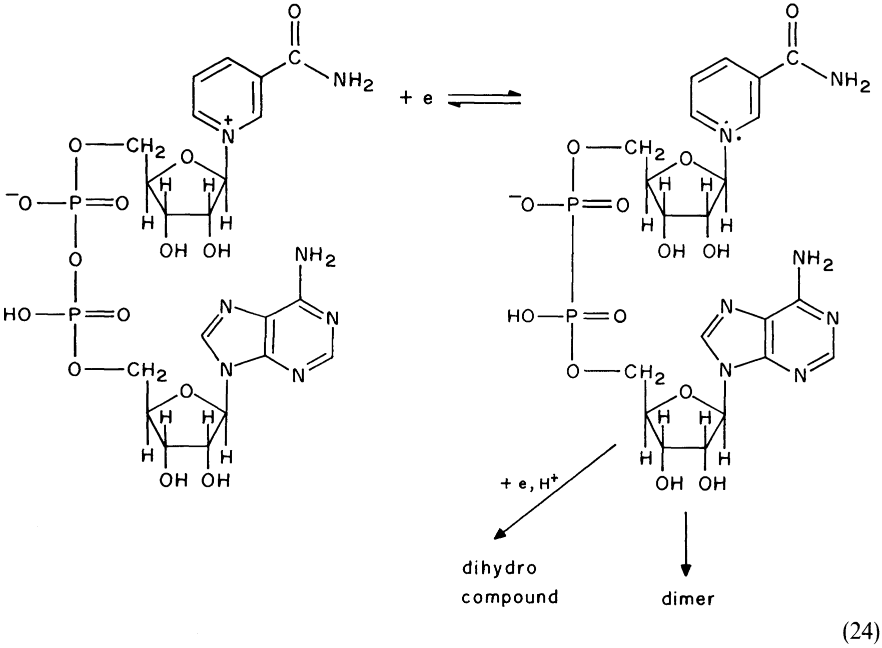
a proton environment for the reduction scheme. The reduction of DPN^+ in DMSO occurs at $E_{1/2} = -0.98$ V, with the polarographic wave having a slope of 46 mV. The diffusion coefficient of DPN^+ in DMSO is evaluated as $0.28 \times 10^{-5}\,cm^2\,s^{-1}$, which is considerably lower than in aqueous media. The cyclic voltammetric pattern is well defined with a peak at $E_{pc} = -1.03$ V vs SCE which is irreversible at slow sweep rates of $< 6.0\,V\,s^{-1}$, consuming 1e; the neutral radical of DPN dimerizes with a rate constant of $9 \times 10^5\,l\,mol^{-1}\,s^{-1}$. Based on quantum mechanical calculations, the site of dimerization is predicted to be either the 4,4′- or the 6,6′-position. A clear demonstration of the stability of the dimer in DMSO compared with aqueous media shows the proton involvement in its decomposition reaction. As the instability is due to the pyridine-derived species having a chromophore of the type **2**:



$$-NH-\overset{|}{C}=\overset{|}{C}-C=O$$

(2)

the ring structure is removed by the proton addition. The low proton activity of DMSO explains the greater stability of the dimer. Based on the results obtained in aqueous[42,57–59] and non-aqueous media[48,60,61], the redox scheme shown in equation 24 has been proposed for DPN^+.



(24)

1. Oxidation of DPNH

The electrochemical oxidation of DPNH at solid electrodes such as a glassy carbon or platinum exhibits a cyclic voltammetric oxidation peak at $E_{pa} = 0.67$ V and a complementary cathodic peak at $E_{pc} = -1.13$ V in aqueous media[49,50]. The cyclic voltammetric features are ratio of the peak currents = 0.25, $(E_{pa} - E_{pa/2}) = 80$ mV and

$(E_{pa} - E_{1/2}) = 7$ mV at pH 7.1. The value of αn_a (where α is the transfer coefficient and n_a is the number of electrons involved in the rate-determining steps) is 0.46. The above features in solvents such as DMSO are $E_{pa} = 0.89$ V, $E_{pc} = -0.95$ V, $i_{pc}/i_{pa} = 0.26$ and $n = 2$. The effect of added bases such as pyridine or tri-*n*-butylamine is to increase the peak current in acetonitrile[50], but no effect is observed in DMSO. This is probably caused by oxidation of the base taking place at the potential of DPNH. The presence of dissolved oxygen in the medium did not affect the anodic peak but it significantly shifted the cathodic process[49] as oxygen is reduced in this region. The chronoamperometric data of DPNH in the absence of a base gives an estimate of $n = 2$.

Controlled potential coulometric oxidation of DPNH yields a non-integral electron-transfer process ($n = 1.5$)[49]. This lower value has been ascribed to protonation of DPNH by the protons generated during electrochemical oxidation; this process is similar to acid-catalysed decomposition of DPNH. The process rate constant is measured as $8.5 \times 10^{-4}\,\mathrm{s}^{-1}$. The decomposition product absorbs at 280–290 nm with no peak characteristic of DPNH being present. As this reaction is slow, Jaegfeldt *et al.*[62] coupled a coulometric oxidation of DPNH to a continuous flow reactor system where the 2e product of DPNH is enzymatically reduced. By this method, the coulometric value of $n = 2$ was obtained. However, to achieve this n value, a special electrode treatment is necessary[47]. At the glassy carbon electrode very little adsorption of the final product, DPN, has been observed[48,63,64]; very significant adsorption and passivation of the electrode process have been observed on a clean platinum electrode[65].

The electrochemical oxidation of DPNH has also been carried out at chemically modified electrodes[66,67]. The catechols 4-[2-(2-naphthyl) vinyl catechol]($NSCH_2$) and 4-[2(9,10-ethano-anthracene-9-yl)vinyl catechol ($ASCH_2$) are adsorbed on a graphite electrode. The catechol moiety was tailored to move in and out of the solution, whereas the naphthalene and ethane–anthracene ring systems were attached to the electrode. The catalytic oxidation of DPNH decreased from 410 to 185 mV vs SCE at the $NSCH_2$-covered electrode in aqueous medium of pH 7.0[67]. The catalytic oxidation of the $NSCH_2$ and $ASCH_2$ electrodes between DPNH and the mediating group is much faster for the $NSCH_2$ electrode. A similar catalytic process has been observed with a 4-[2-(1-pyrenyl) vinyl catechol]($PSCH_2$) modified electrode. The reaction scheme is shown in equations 25–27.

$$\mathrm{PSCH_2} \longrightarrow \mathrm{PSC} + 2\mathrm{H}^+ + 2\mathrm{e} \tag{25}$$

$$\mathrm{PSC} + \mathrm{DPNH} + \mathrm{H}^+ \xrightarrow{k_1} \mathrm{PSCH_2} + \mathrm{DPN}^+ \tag{26}$$

Overall reaction:

$$\mathrm{DPNH} \longrightarrow \mathrm{DPN}^+ + \mathrm{H}^+ + 2\mathrm{e} \tag{27}$$

k_1 is estimated to be $1 \times 10^4\,\mathrm{l\,mol^{-1}\,s^{-1}}$[68–70]. The reaction pathway of DPNH was unravelled in several investigations[71–73]. Of these the catalytic oxidation of DPNH through electrogenerated diimines is an interesting model system[72].

An interesting experiment on phosphorylation coupled to DPNH oxidation was performed by combining two galvanic DPNH oxidation cells with a galvanic–electrolytic phosphorylation cell[74]. This scheme is depicted in Figure 11. The four galvanic cells of DPNH oxidation are

$$\mathrm{DPNH} \longrightarrow \mathrm{DPN}^+ + \mathrm{H}^+ + 2\mathrm{e} \tag{28}$$

$$2\mathrm{H}^+ + \tfrac{1}{2}\mathrm{O_2} + 2\mathrm{e} \longrightarrow \mathrm{H_2O} \tag{29}$$

and the overall reaction is

$$\mathrm{DPNH} + \mathrm{H}^+ + \tfrac{1}{2}\mathrm{O_2} \longrightarrow \mathrm{DPN}^+ + \mathrm{H_2O} \tag{30}$$

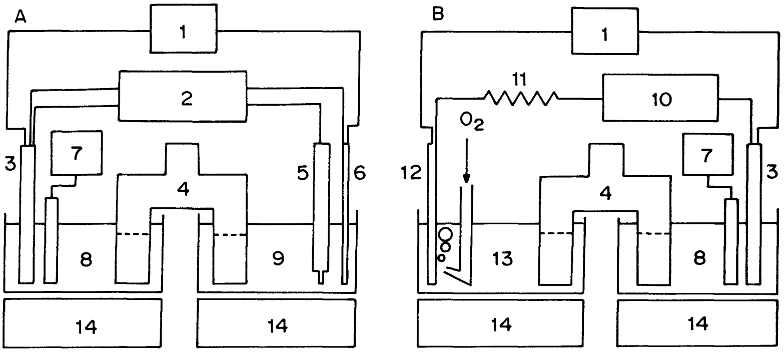


FIGURE 11. Phosphorylation set-up: Electrolytic cell (A) and galvanic cell (B). 1, Voltmeter; 2, potentiostat and coulometer; 3, anode of titanium nitroxicarbide base ceramic; 4, salt bridge; 55, saturated calomel electrode; 6, cathode (iron wire); 7, pH meter; 8, KCl aqueous solution (40 ml) containing 1–3 mM ADP and 2–6 mM acetyl phosphate for ADP phosphorylation + 1.1 mM DPNH for DPNH oxidation; 9, 0.1 M HCl (40 ml); 10, coulometer; 11, resistance (1.0 Ω); 12, cathode (platinum plate); 13, 2.8 M HCl (40 ml); 14, magnetic stirrer. Copyright (1989) Electrochemical Society.

The electrolytic cell for DPNH oxidation occurs as

$$\mathrm{DPNH} \longrightarrow \mathrm{DPN}^+ + \mathrm{H}^+ + 2\mathrm{e} \qquad (31)$$

The overall reaction is represented by

$$\mathrm{DPNH} + \mathrm{H}^+ + \tfrac{1}{2}\mathrm{O}_2 \longrightarrow \mathrm{DPN}^+ + \mathrm{H_2O} \qquad (32)$$

The galvanic cell for phosphorylation follows the reaction

$$\mathrm{ADP} + \mathrm{H_3PO_4} \longrightarrow \mathrm{ATP} + \mathrm{H_2O} + 2\mathrm{e} + 2\,\mathrm{H}^+ \qquad (33)$$

$$2\mathrm{H}^+ + \tfrac{1}{2}\mathrm{O}_2 + 2\mathrm{e} \longrightarrow \mathrm{H_2O} \qquad (34)$$

and the overall reaction is represented by

$$\mathrm{ADP} + \mathrm{H_3PO_4} + \tfrac{1}{2}\mathrm{O}_2 \longrightarrow \mathrm{ATP} + 2\mathrm{H_2O} \qquad (35)$$

The electrolytic phosphorylation cell is depicted as

$$\mathrm{ADP} + \mathrm{H_3PO_4} \longrightarrow \mathrm{ATP} + \mathrm{H_2O} + 2\mathrm{e} + 2\mathrm{H}^+ \qquad (36)$$

A comparison of the electrochemical with a non-electrochemical method, such as DPNH oxidation by a titanium-nitroxide based ceramic board, shows that the velocity of phosphorylation in the former method is faster[74]. The mechanism of oxidation of DPNH to DPN$^+$ and the reverse reduction reaction involving a one-step hydride transfer or a stepwise electron–proton–electron transfer has been investigated[75,76] by using DPN analogues.

G. Other Diphosphonucleotides

Triphosphopyridine nucleotide (TPN$^+$, coenzyme II) shows characteristic features with $E_{1/2} = -0.95$ V having a wave slope of 60 mV[53]. It is strongly adsorbed at the electrode/solution interface; this feature is observed with DDPN$^+$ (deamino diphosphopyridine nucleotide). An adsorption well or depression prior to the appearance of the first polarographic wave I is striking with DDPN^{+} [53]. The general features of all these compounds are very similar with 1 e reductions to form neutral radicals followed by their dimerization. The dimerization rate for TPN is $4.3 \times 10^{6}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ (pH 5.0) and $1.6 \times 10^{6}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ (pH 9.0) and for DDPN^{+} $1.7 \times 10^{6}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ [53]. The activation energy for the dimerization process is estimated to be 9.0 kcal mol^{-1} for TPN. The electrochemical behaviour of DDPN^{+} and TPN^{+} in a non-aqueous solvent indicates $E_{1/2} = -1.00$ V and -1.06 V vs SCE with diffusion coefficient values of 0.08×10^{-5} and $0.14 \times 10^{-5}\,\mathrm{cm^{2}\,s^{-1}}$ [48].

The synthesis of the DPN^{+} analogue having ε-adenine (etheno bridge between exocylic amine group and the N(6) atom of adenosine) instead of adenine and its electrochemical properties have been reported[77]. It gives rise to two polarographic waves in the pH range 2–12, but the mechanisms involved in acidic and alkaline media are different. The acidic medium produces the first 1e reduction of the nicotinamide ring, which is subsequently followed by reduction of the E-adenine moiety of the β-DPN^{+} molecule. This one-step successive 1e reduction is changed to two one-electron reduction steps in alkaline media as observed with DPN^{+}.

One of the important questions that is addressed in DPN^{+} redox chemistry concerns the mechanism by which it is converted into the reduced form, DPNH[78]. There are two ways by which a chemical reductant can bring out this process. One is to transfer an electron, then a proton and finally another electron[58,79], and the other is to transfer a hydride directly[78]. The discussion in the literature is oriented towards high-energy intermediates. A recent study[78] of measurements of 35 rate constants for hydride transfer in DPN^{+} analogues, and application of Marcus theory by utilizing structure-sensitive solvent reorganisation parameter, λ, overwhelmingly supports the second way. The electrochemical reduction of DPN^{+} follows a different route, however, as discussed earlier.

Pyridoxal-5′-phosphate and *n*-hexylamine form a Schiff's base, which has been investigated in detail in the pH range 2–13. Two waves were observed in d.c. polarography; the first is due to the reduction of the —CH=N— bond and the second to the reduction of pyridoxal-5′-phosphate[80]. Pyridoxal-5′-phosphate has been investigated polarographically[81]. The hydration and dehydration of pyridoxal-5′-phosphate over a wide pH range has been determined experimentally; the reaction is centred on the carbonyl group[81]. The polarographic and voltammetric data indicate that the currents are kinetically controlled.

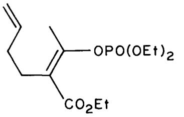
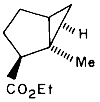
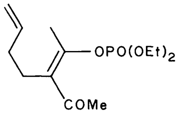
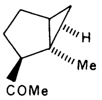
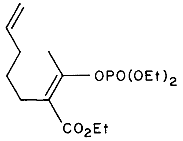
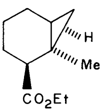
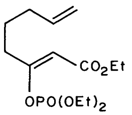
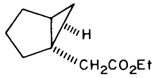
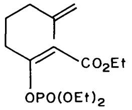
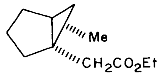
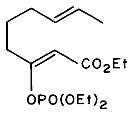
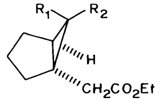
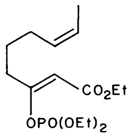
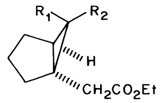
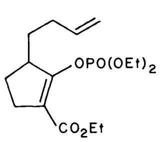
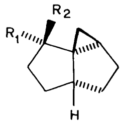
Cytidine monophosphate exhibits a reduction at $E_{1/2} = -1.45$ V in acetate buffer (pH 4.1)[82] and the reaction mechanism is kinetically controlled.

H. Flavin-5′-phosphoric acid

Flavin mononucleotide (riboflavin-5′-phosphoric acid) (FMN) and flavin adenine dinucleotide (FAD) are strongly adsorbed on electrodes, especially mercury electrodes[83]. The molecular orientation in the adsorbed state has been probed; FAD occupies a geometrical area of 280 Å^{2} corresponding to the molecular model.

The electrochemistry of FMN is very similar to that of riboflavin in both aqueous[84,85] and non-aqueous media[86]; it exhibits a prewave. Riboflavin also has similar prewave. It undergoes 1e reduction to form the riboflavin anion with $E_{\mathrm{pc}} = -0.78$ V vs SCE followed by its decomposition to give two products with one of the products undergoing reduction at -1.07 V. In aqueous media FMN reduction to an FMNH:FMNH$_{2}$ complex which is not further reduced is suggested[83]. The reversible reduction of FAD and FMN has been conclusively shown by impulse polarization; the maximum height is proportional to the concentration of prosthetic group[87].

TABLE 7. Product yields from β-dicarbonyl enol phosphate electrolysis[a]

Compound	Product	Yield (%)
		58
		55
		38
		63
		53
		51$R_1 = H$, $R_2 = Me$ 10$R_1 = Me$, $R_2 = H$
		41$R_1 = H$, $R_2 = Me$ 18$R_1 = Me$, $R_2 = H$
		26$R_1 = CO_2Et$, $R_2 = H$ 22$R_1 = H$, $R_2 = CO_2Et$

---

[a] Reprinted with permission from ref. 88a. Copyright (1990) American Chemical Society.

The electrochemluminescence of the FMN anion and the 9,10-diphenylanthracene (DPA) cation has been investigated[88]. The reaction mechanism for the production of the excited state has been proposed as in equations 37 and 38. This conclusion is supported by the effect of a magnetic field on the electroluminescence intensity. This reaction is an example of an intermolecular electron transfer between $\mathrm{FM\mathring{N}^{-}}$ and an acceptor to produce the triplet state.

$$\mathrm{FM\dot{N}^{-} + DP\dot{A}^{+} \longrightarrow {}^{1}FMN + {}^{3}DPA} \tag{37}$$

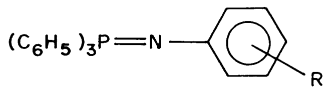
$$\mathrm{{}^{3}DPA + {}^{3}DPA \longrightarrow {}^{1}DPA^{*} + {}^{1}DPA} \tag{38}$$

The electrolysis of β-dicarbonyl enol phosphates in DMF produces α,β-unsaturated carbonyl compounds via the attack of vinyl radical produced during the electrolysis[88a]. Table 7 gives the yields obtained with various β-dicarbonyl enol phosphates. The results are indication of a double intramolecular cyclization of initially formed vinyl radicals.

IV. PHOSPHAAZENES

A. Phospha-λ^5-azenes: pπ–dπ double bonded systems

Phospha-λ^5-azene systems of type **3**, where R = *p*-NO_2, *p*-CN, *m*-NO_2, *p*-CF_3, *p*-Cl, *p*-F, H, *p*-Me, *p*-OMe and *p*-NMe_2 are unique in that they have the resonance forms



(**3**)

$$\mathrm{R_3P^{+}{-}\bar{N}{-}R' \leftrightarrow R_3P{=}N{-}R' \leftrightarrow R_3P^{+}{-}N{=}R'} \tag{39}$$

TABLE 8. Polarographic and cyclic voltammetric characteristics of phosphonitriles[a]

Compound	Structure	$E_{1/2}$ (V)	Lifetime of radical (s)[c]
I. Hexaphenyl cyclotriphosphazene	$[NPPh_2]_3$	−2.65	<1
II. Octaphenyl cyclotetraphosphazene	$[NPPh_2]_4$	−2.67	<1
III. Tris(2,3-dioxy-naphthyl)cyclo-triphosphazene	$[NP(2,3\text{-}O_2C_{10}H_6)]_3$	−1.24	>10
IV. Tris(1,8-dioxy-naphthyl)cyclo-triphosphazene	$[NP(1,8\text{-}O_2C_{10}H_6)]_3$	−1.83	>10
V. Tris(2,2′-dioxy-biphenyl)cyclotri-phosphazene	$[NP(2,2'\text{-}O_2C_{12}H_8)]_3$	−2.33	—
VI. Tris(1,3,5-triphenyl)-tris(1,3,5-trifluoroethoxy)-cyclotriphosphazne	$[NPPh(OCH_2CF_3)]_3$	−2.45	<1

[a] Potentials are referred to SCE. Reprinted with permission from ref. 100. Copyright (1969) American Chemical Society.

[b] From polarographic data.

[c] Cyclic voltammetric method.

TABLE 9. Cyclic voltammetric data for reduction of azenes[a]

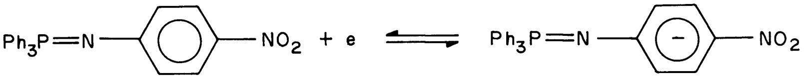
Compound	Scan rate ($V S^{-1}$)	E_{pc} (V)	E_p (V)	i_{pa}/i_{pc}	$D \times 10^{-5}$ ($cm^2 s^{-1}$)
$Ph_3P{=}NC_6H_4NO_2$-*p*	0.02	−1.728	−1.660	0.95	1.34
	0.05	−1.730	−1.658	0.96	
	0.10	−1.732	−1.655	0.97	
	0.20	−1.734	−1.652	0.99	
$Ph_3P{=}NC_6H_4NO_2$-*m*	0.02	−1.601	−1.535	0.99	1.50
	0.05	−1.603	−1.532	0.99	
	0.10	−1.606	−1.529	0.98	
	0.20	−1.610	−1.528	0.97	

[a] Medium, acetonitrile; carbon working electrode. Potentials are referred to $Ag/AgNO_3$. Reprinted with permission from ref. 103. Copyright (1986) American Chemical Society.

which involve pπ–dπ double bonds. The resonance forms and the electronic structures of the above systems have been probed[89,90] by electrochemistry and spectroscopy to gain an insight into the phosphorus–nitrogen coupling[91–99]. Phosphazines of the type $[NP(OPh)_2]_3$, $[NP(OPh)_2]_n$, $[NP(NHPh)_2]_3$, $[NP(OCH_2CF_3)_2]_3$ and $[NP(O_2C_6H_4)]_3$, where $n = 15000$, have been investigated by electrochemical and ESR methods[100] to obtain structural parameters. The cyclic voltammetric characteristics are given in Table 8.

Controlled potential electrolysis of the compounds listed in Table 8 have generated ESR spectra indicating that the reduction is a simple 1e process. The ESR spectra of radical anions of I and II produced an unresolved spectrum with $g = 2$, with a total spectral line width of 20–30 G. The ESR spectra of III, IV and V showed 13–15, 5 and 15–20 lines, respectively. The delocalization of the unpaired electron in Ph_2P is indicated in the above radicals.

N-Phenyltriphenylphospha-λ^5-azene has been examined polarographically in DMF[101] and acetonitrile[102]. The anion radical formed by 1e reduction is accompanied by protonation and further reduction. In-depth studies by Pomerantz *et al.*[103] led to the characterization of electrochemical process. Tables 9–11 summarize the cyclic voltammetric characteristics for the above compounds and *m*-NO_2-substituted azene. The mechanism for the reversible cyclic voltammetric peak is represented by equation 40. The anion radical undergoes hydrogen abstraction and a further electron transfer resulting in the formation of aniline derivatives. The characteristic diffusion coefficients of azenes are given in Table 9.



(40)

1. Oxidative patterns

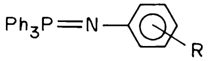
The azenes exhibit irreversible peaks in cyclic voltammetric experiments, the location of the peak potential being dependent on the nature of the substituent R[103]. Table 10 gives the characteristic peak potentials for a large number of azenes. With *p*-OMe and *p*-NMe_2 as substituents, the anodic peaks are partially reversible at a slow rate of 0.10 V s^{-1} and tend towards complete reversibility at 10 V s^{-1}. The cyclic voltammetric patterns suggest an initial electron transfer followed by a chemical reaction. The stability of the one-electron oxidation product can be correlated with the lowering of the charge density on the substituted aryl ring by the substituent.

TABLE 10. Oxidative peak potentials of azenes[a]

R[b]	E_{pa}(V)	R[b]	E_{pa}(V)
p-NO_2	0.844	p-F	0.480
p-CN	0.741	H	0.465
m-NO_2	0.752	p-CH_3	0.371
p-CF_3	0.740	p-OCH_3	0.210
p-Cl	0.512	p-$N(CH_3)_2$	−0.195

[a] Potentials are with respect to $Ag/AgNO_3$. Medium, acetonitrile; working electrode platinum. Reprinted with permission from ref. 103. Copyright (1986) American Chemical Society.

[b] Basic structure



The effect of the substituent on the primary oxidation wave for phospha-λ^5-azenes has also been successfully correlated with the ionization potential (energy of the highest occupied molecular orbital, E_{HOMO}). The observed trend is an indication of the site of electron abstraction in the azenes as the lone pair on nitrogen which is delocalized into the aromatic ring[103]; the plot of $E_{1/2}$ of anilines with the same substituents and E_{pa} of phospha-λ^5-azenes yields a straight line.

The electronic properties of phosphazenes are of importance in understanding the electron-withdrawing power[91,93,100–105] of these molecules. The redox potentials of phosphazenes bonded to ferrocene have been measured; the *trans* annular linked

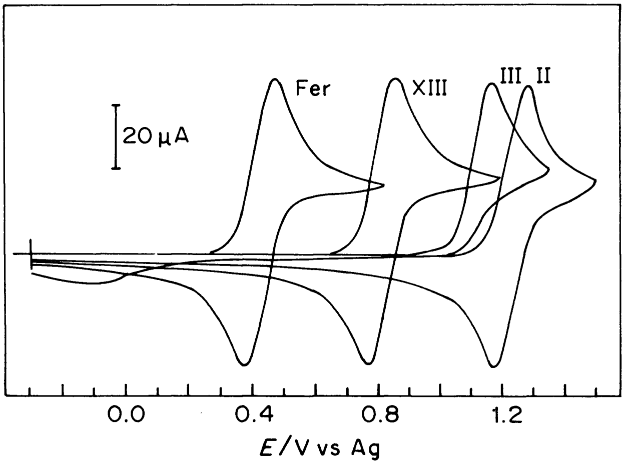
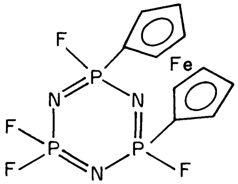
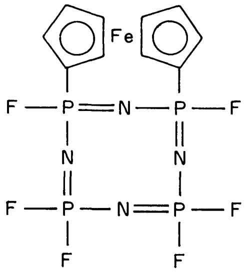


FIGURE 12. Cyclic voltammetry of 1 mM solutions of ferrocene (Fer) and XIII = $[N_3P_3F_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]$, III = $[N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe]$ and II = $[1,5\text{-}N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe]$ in acetonitrile containing 0.1 M tetraethylammonium perchlorate. Sweep rate, 0.10 V s^{-1}. Reprinted with permission from ref. 106. Copyright (1988) American Chemical Society.

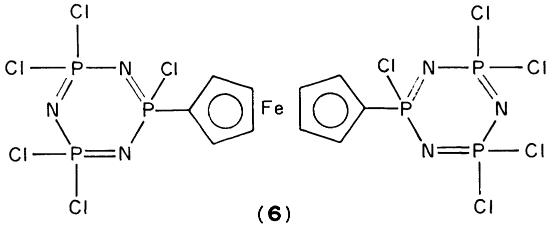
ferrocenyl phosphazenes have potentials shifted twice as much as those of the pendent analogues. The structures of a few ferrocene-substituted phosphazenes (**4**–**7**) are shown.



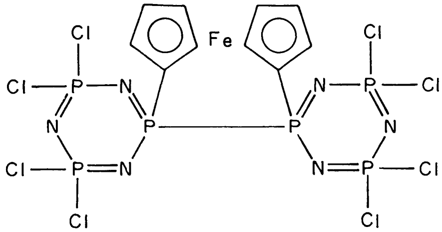
(**4**)



(**5**)



(**6**)



(**7**)

The oxidation potentials are dependent on the non-geminal site substituent. The cyclic voltammetric reversibility of phosphazenes is well defined in Figure 12.

The eletronic properties and redox conduction of ferrocene-substituted high polymeric phosphazenes[107] are markedly different from the solution behaviour of the monomers. Surface-immobilized films of $[N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe)]_n$ in CH_2Cl_2 exhibit a large difference in their oxidation and reduction peak potentials ($\Delta E_p = 0.26$ V). For $[N_3P_3(OCH_2CF_3)_5\text{-}(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)_n]_n$ the separation is negligible, showing a symmetric pattern. A similar pattern was noticed for $[N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe]_n$. The mechanism of charge transport in these polymeric films has been probed and the charge transport rates are given in Table 12. The structure of polyphosphazene (shown in Figure 13) together with the data in Table 12 suggests that the charge transport rate depends on the mobility of the ferrocene. The greater rate of charge transport observed with the rigid bridged ferrocene polymer $[N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4Fe)_2]_n$ suggests a metal-like conduction occurring in the partially oxidized form[107].

TABLE 11. Cyclic voltammetric oxidation peak potentials of phosphazenes[a]

Aryl-*P*,*P*,*P*-triphenylphospha-λ^5-azenes[b]	E_{pa}(V)	Ferrocence-substituted phosphazenes[c]	E_{pa}(V)
$Ph_3P{=}NC_6H_4NO_2$-*p*	0.844	$[N_6P_6Cl_{10}(\eta\text{-}C_5H_4)_2Fe]$	1.25
$Ph_3P{=}NC_6H_4CN$-*p*	0.741	$[1,5\text{-}N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe]$	1.21
$Ph_3P{=}NC_6H_4NO_2$-*m*	0.752	$[N_3P_3F_4(\eta\text{-}C_5H_5)_2Fe]$	1.18
$Ph_3P{=}NC_6H_4CF_3$-*p*	0.740	$[N_6P_6Cl_8(\eta\text{-}C_5H_4)_2Fe]$	1.18
$Ph_3P{=}NC_6H_4Cl$-*p*	0.512	$[N_3P_3F_3(OCH_2CH_3)(\eta\text{-}C_5H_4)_2Fe]$	1.14
$Ph_3P{=}NC_6H_4F$-*p*	0.480	$[N_6P_6(OCH_2CF_3)_{10}(\eta\text{-}C_5H_4)_2Fe]$	1.13
$Ph_3P{=}NPh$	0.465	$[N_3P_3F_3(OC_6H_5)(\eta\text{-}C_5H_4)_2Fe]$	1.12
$Ph_3P{=}NC_6H_4Me$-*p*	0.371	$[1,3\text{-}N_4P_4(OCH_2CF_3)_6(\eta\text{-}C_5H_4)_2Fe]$	1.06
$Ph_3P{=}NC_6H_4OMe$-*p*	0.210	$[1,3\text{-}N_4P_4(OCH_2CF_3)_6(\eta\text{-}C_5H_4)_2Fe]$	0.98
$Ph_3P{=}NC_6H_4NMe_2$-*p*	−0.195	$[N_3P_3(OC_6H_5)_4(\eta\text{-}C_5H_4)_2Fe]$	0.94
		$[N_3P_3F_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]$	0.86
		$[N_4P_4F_7(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]$	0.85
		$[N_3P_3(OCH_2CF_3)_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]$	0.75

[a] Pt working electrode. Medium: acetonitrile.

[b] Potentials referred to $Ag/AgNO_3$. Taken from ref. 103.

[c] Potentials referred to Ag. Reprinted with permission from ref. 107. Copyright (1988) American Chemical Society.

TABLE 12. Charge transport rates of ferrocene-substituted polyphosphazenes[a]

Polymer	$(D_{ct}^{1/2}C)_{anod.}$ $(10^{-8}\ mol\ cm^{-2})$	$(D_{ct}^{1/2}C)_{cath.}$ $(10^{-8}\ mol\ cm^{-2})$
$[N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe]_n$	1.41 ± 0.15	1.52 ± 0.24
$[N_3P_3(OCH_2CF_3)_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_n$	1.96 ± 0.18	1.81 ± 0.44
$[N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe]_n$	3.20 ± 0.20	6.19 ± 1.65

[a] Measurements were made on potential step transients. Reprinted with permission from ref. 107. Copyright (1988) American Chemical Society.

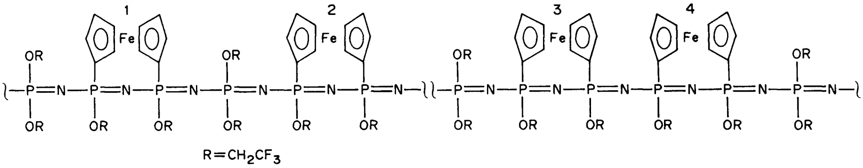


FIGURE 13. Structure of polyphosphazene. The numbers represent the number of anchored units.

V. PHOSPHORUS-BRIDGED METALLICS

A. Rhodium Phosphido-bridged Complexes

The electronic effects in phosphido-bridged complexes of transition metals have evoked a number of studies[108–113]. The electrochemistry of the Rh—Rh double bond and the isomerization of the rhodium(I) system on electrochemical reduction and reoxidation have been of interest in determining the electronic effects. A series of metal carbonyl complexes (phosphido-bridged complexes) were investigated by Winner *et al.*[114] and Dessy and coworkers[115–117]. The carbonyl complexes of rhodium provide a case for reversible geometrical isomerization[118]. Figure 14 depicts such an isomerization for a di-*tert*-butyl phosphido-bridged complex on reduction. This scheme is a typical case of electron transfer followed by chemical reaction followed by further chemical reaction (ECE), where the chemical reaction is a geometrical isomerization producing an isomer which is more easily reduced than the parent compound. The rate constant for this isomerization is estimated to be about $600\,s^{-1}$ [118]. Interestingly, the reoxidation at an electrode produces the parent species through the steps shown in Figure 15; the original geometry of the metal is restored. The cyclic voltammetric features interestingly provide a model for understanding this isomerization (see Figure 16) a typical cathodic peak followed by two anodic peaks representing an ECE process. The X-ray crystallographic structure of the dianion shows an imposed inversion centre at the middle of the Rh—Rh vector. The structure of $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ shown in Figure 17 indicates the possibility of three isomers with metal bonds of order 0, 1 and 2 extremely close in energy[119]; the square-planar–tetrahedral and square-planar–square-planar isomers are the only ones actually observed.

The electrochemical reduction of rhodium phosphido-bridged complexes places the added electron on a π^*-antibonding orbital of the metal–metal doubly bonded isomer. Further reduction of this system requires 2e to be accommodated, which forces the tetrahedral–tetrahedral configuration.

The cyclic voltammetric pattern of $[Rh(PPh_3)_3]_3(DME)(ClO_4)$ correlates well with the rhodium phosphido-bridged complexes[119–122]; it is reduced in two 1e reversible

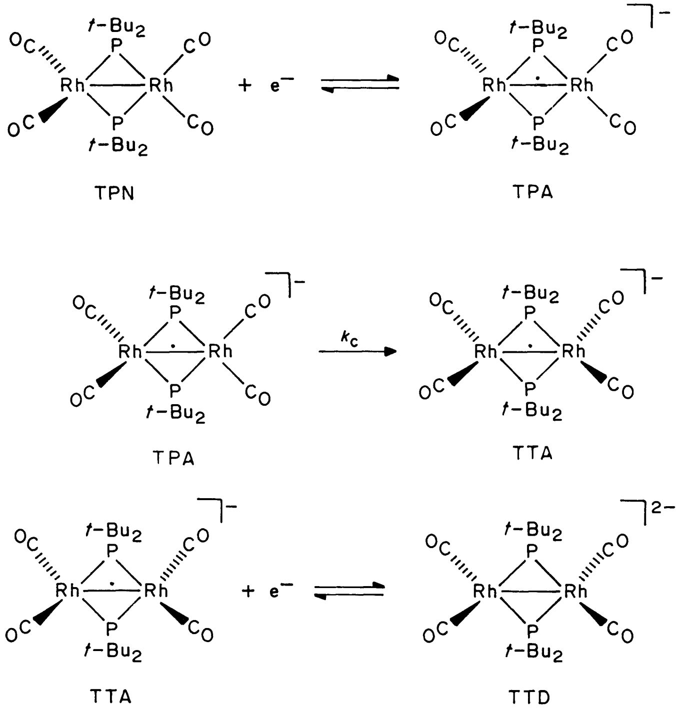


FIGURE 14. Reaction mechanism. Geometrical isomerization following the reduction of rhodium phosphido-bridged complexes. Representation of ECE mechanism is indicated. The abbreviations for each species describe the approximate geometry of the metals (T = tetrahedral, P = planar) and the charge on the complex (N = neutral, A = anion, D = dianion). Reprinted with permission from ref. 118. Copyright (1985) American Chemical Society.

steps (equations 41–44). The first reduction has $E^\circ = -1.20\,V$ and the second $E^\circ_2 = -1.73\,V$[119]. The above reaction scheme is sensitive to the excess PPh_3 concentration. The kinetic parameter for reaction[42] has been evaluated from the dependence of the scan rate on the half-wave potential; it is given in Table 13.

$$[Rh(PPh_3)]_3^+ \overset{e}{\rightleftharpoons} Rh(PPh)_3 \tag{41}$$

$$Rh(PPh_3)_3 + PPh_3 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Rh(PPh_3)_4 \tag{42}$$

$$Rh(PPh_3)_4 \overset{e}{\rightleftharpoons} [Rh(PPh_3)_4]^- \tag{43}$$

$$2Rh(PPh_3)_4 \longrightarrow [Rh(PPh_3)_4]_2 \tag{44}$$

The effect of PPh_3 concentration on the kinetic parameter is also revealed by the data in Table 13. The ESR spectrum of $[Rh(PPh_3)_4]$ obtained by controlled potential 1e reduction of $[Rh(PPh_3)_3]^+$ shows anisotropy (Figure 18) with $g_1 = 2.22$, $g_2 = 2.10$ and $g_3 = 1.99$. The interaction of the metal with one phosphorus ligand is revealed by the

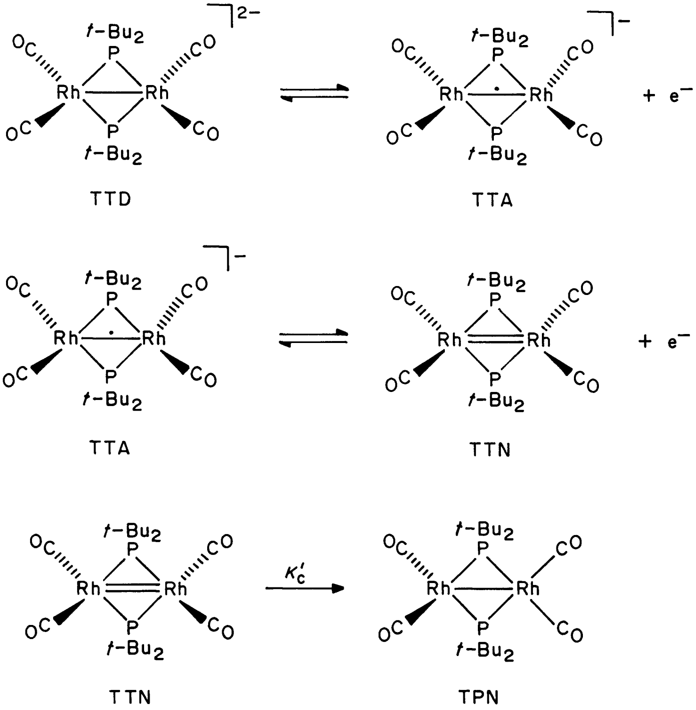


FIGURE 15. Reaction mechanism of geometrical isomerisation (reverse of that shown in Figure 14) on oxidation of the final product. The last step is a chemical step. Abbreviations as in Figure 14. Reprinted with permission from ref. 118. Copyright (1985) American Chemical Society.

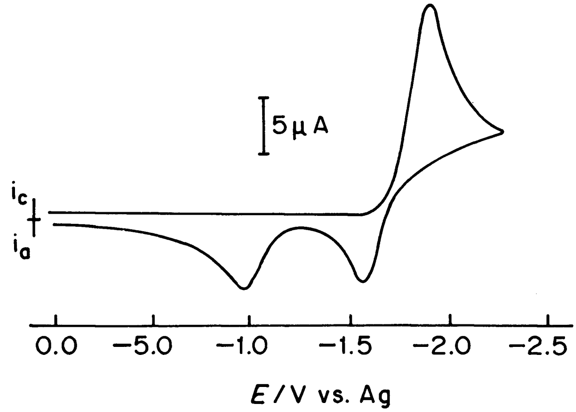


FIGURE 16. Cyclic voltammogram of $[Rh(\mu\text{-}Bu_2P)(CO)_2]_2$ in THF. Sweep rate, $0.20\,V\,s^{-1}$; working electrode, platinum disc; reference electrode, Ag wire (potential with respect to SCE, − 0.36 V). Copyright (1985) American Chemical Society.

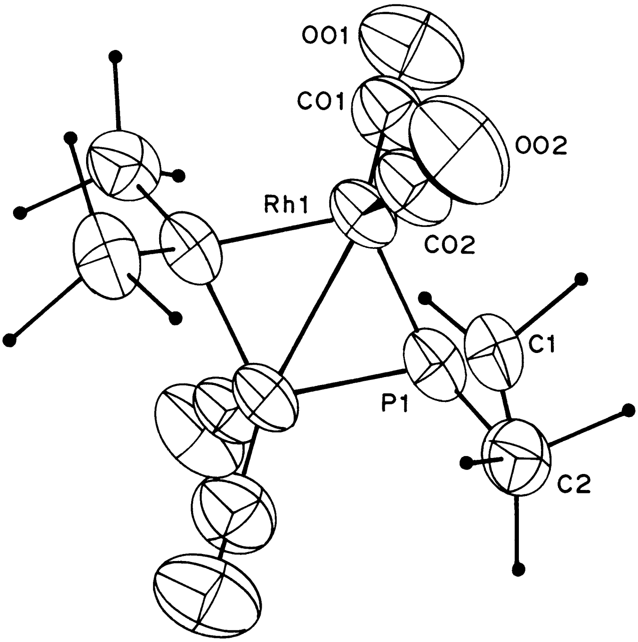


FIGURE 17. Structural view of $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO_2)]_2^{2-}$. Methyl groups on the *tert*-butyls are represented by sticks. Reprinted with permission from ref. 118. Copyright (1985) American Chemical Society.

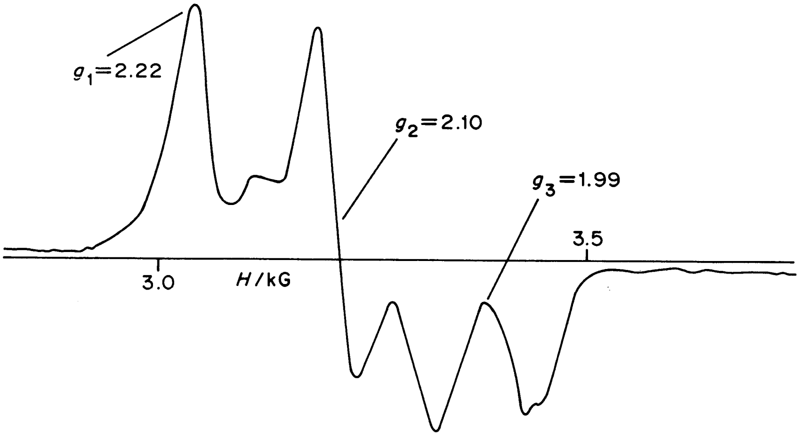


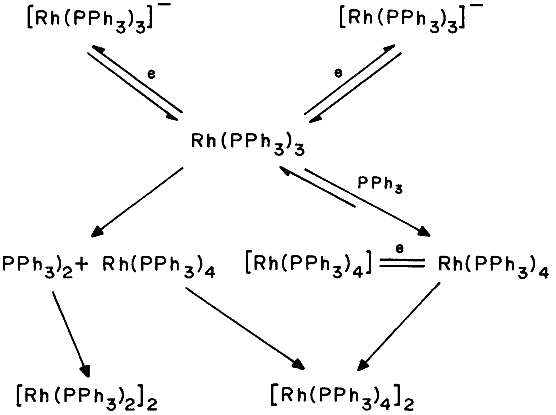
FIGURE 18. ESR spectrum of $[Rh(PPh_3)_4]$ in DME at 120 K. Reproduced by permission of Elsevier Publishers from ref. 120.

TABLE 13. Kinetics of triphenylphosphine addition to $Rh(PPh_3)$[a]

PPh_3 concentration (M)	Sweep rate ($V s^{-1}$)	$E_{p/2}$ (V)	$E_{p/2} - E^{\circ}_{p/2}$ (V)	$K(k_f + k_b)^{-1/2}$ ($s^{-1/2}$)
0.01	0.02	−1.233	0	–
	0.20	−1.239	0.006	–
	0.50	−1.245	0.013	0.23
	1.00	−1.253	0.020	0.27
	2.00	−1.258	0.023	0.24
	5.00	−1.270	0.035	0.30
0.016				0.078
0.030				0.15
0.100				0.26

[a] Concentration of $[Rh(PPh_3)_3]^+ = 1$ mM in DME; supporting electrolyte, 0.2 M tetra-*n*-butylammonium perchlorate; temperature of the experiment, 25 °C. Potentials are with respect to $Ag/AgClO_4$.

spectrum. It appears to have a distorted tetrahedral geometry. The electrochemical redox pattern of $[Rh(PPh_3)_3]^+$ is shown in Scheme 1.



SCHEME 1

The second-order rate constant for the formation of $[Rh(PPh_3)_4]$ is estimated to be $1.4 \times 10^7 l mol^{-1} s^{-1}$; ligand redistribution competes with this with a rate constant of $300 l mol^{-1} s^{-1}$, which forces us to conclude that the former process of forming $[Rh(PPh)_3)_4]$ is complete on the time scale of typical cyclic voltammetric experiments (ms to s). The second wave is well developed as the ligand addition is faster; this is depicted in Figure 19. It is possible to prepare the d^9 complex $[Rh(PPh_3)_4]$ by the electrochemical method[120].

B. Nickel Complexes with Triphenylphosphine and Ethylene

Nickel exhibits a pattern similar to rhodium in its reaction with PPh_3[122]. The redox reactions may be represented as equations 45 and 46, where $X = Cl^-$, Br^- or I^- and

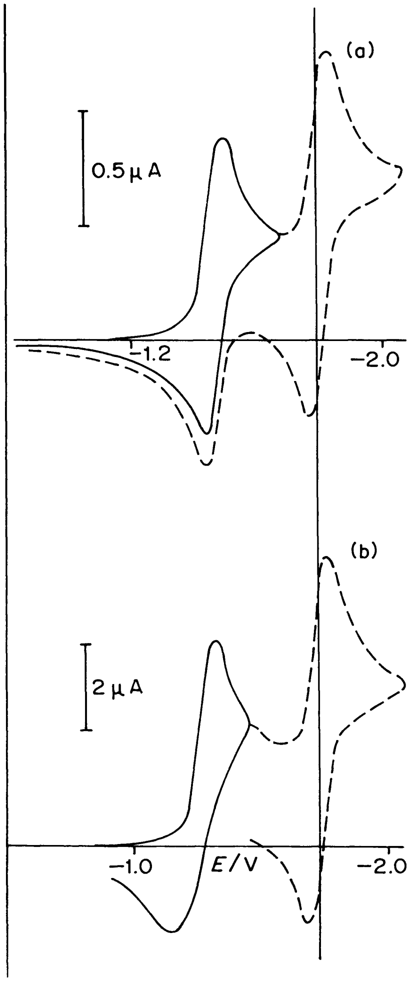


FIGURE 19. Cyclic voltammograms of 1 mM $[Rh(PPh_3)_3]^+$ in DME containing 0.2 M tetra-*n*-butylammonium perchlorate. (a) $PPh_3 = 10^{-2}$ M; sweep rate, 5.0 Vs.$^{-1}$ (b) in the presence of $PPh_3 = 10^{-1}$ M. Reproduced by permission of Elsevier Publishers.

$L = PPh_3$; $[Ni^IXL_3]$ is yellow and $[Ni^0XL_3]^-$ is red. These nickel(0) and Nickel(I) complexes can be oxidized as equations 47–49.

$$[Ni^{II}X_3L]^- + e + 2L \longrightarrow [Ni^IXL_3] + 2X^- \qquad (45)$$

$$[Ni^IXL_3] + e \rightleftharpoons [Ni^0XL_3]^- \qquad (46)$$

$$[Ni^0XL_3]^- \rightleftharpoons [Ni^0XL_3] + e \qquad (47)$$

$$[Ni^0XL_3] \longrightarrow [Ni^IXL_3] + e \quad (48)$$

$$[Ni^IXL_3 \longrightarrow e + [Ni^{II}XL_3]^+ \xrightarrow{\text{fast}} [NiX_3L]^- \quad (49)$$

These redox processes have been confirmed using *N*-methylpyrrolidinone as the solvent. When ethylene is introduced into the medium before initiating the electrochemical step, the reaction scheme is modified as in equations 50 or 51, where E represents ethylene. $[Ni^0L_2E]$ is oxidized at 0.16 V. Now,

$$[Ni^0L_3X]^- + E \longrightarrow [Ni^0L_2EX]^- + L \quad (50)$$

$$[Ni^0XL_3]^- + E \longrightarrow [Ni^0XL_2E]^- + L$$

$$[Ni^0L_3] + E \longrightarrow [Ni^0L_2E] + L \quad (51)$$

$$[Ni^0L_2EX]^- \longrightarrow Ni^{II} + 2e \quad (52)$$

$$[Ni^0L_2E] \longrightarrow Ni^{II} + 2e \quad (53)$$

Steps 52 and 53 occur at -0.40 and 0 V, respectively. The current–voltage curves depicting the above processes are shown in Figure 20.

1. *Nickel bis-1,2-diphenylphosphinoethane*

The existence of the complexes $[NiD_2]^{2+}$, $[NiD_2X]^+$ and $[NiX_2D]$, where X is Cl^- or Br^- and D = bis-1,2-diphenylphosphinoethane, were established by electrochemical work[123,124]. Using *N*-methylpyrrolidine as solvent, the electrochemical reduction produces nickel(I) or nickel(0) complexes. At a mole ratio of 1D per Ni the zerovalent

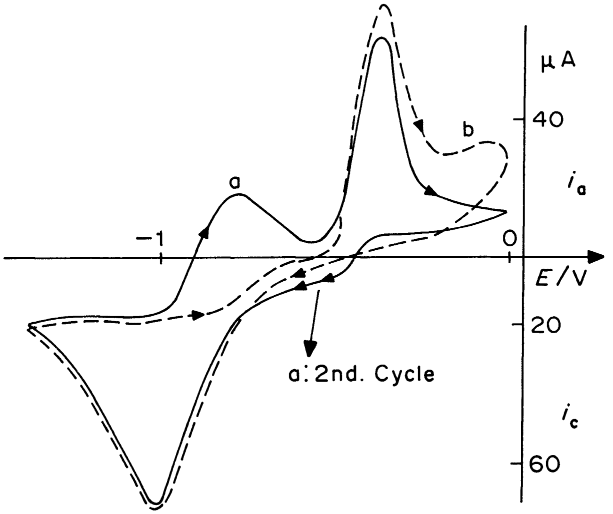


FIGURE 20. Cyclic voltammetric curves curves of NiX_2L_2 ($X = Br^-$) in *N*-methylpyrrolidone solutions at a gold micro electrode. The dashed line shows the curve in the presence of ethylene. Sweep rate, $0.1\ V\,s^{-1}$. Note the absence of an anodic peak in the presence of ethylene. Reproduced by permission of Elsevier Publishers from ref. 122.

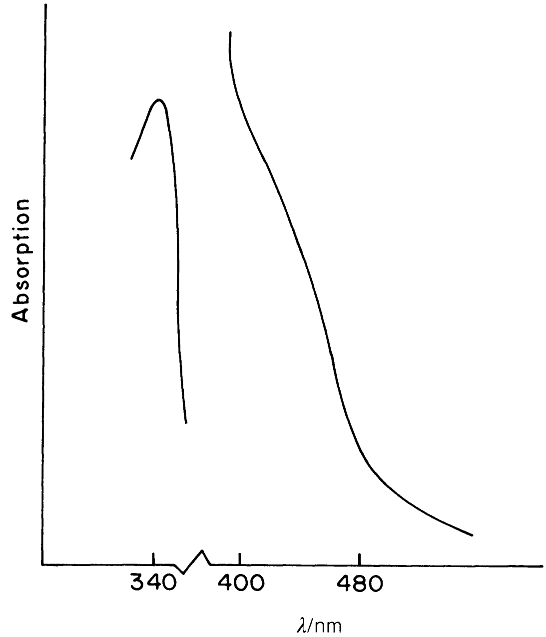


FIGURE 21. UV absorption spectrum of 2 mM $[NiClO_4D_2]$ in *N*-methylpyrrolidone.

complex reacts rapidly with organic halides (RX). The electrocatalytic reduction of halide is proposed which has a hypothetical intermediate [RNiXD][119,120]. The establishment of an equilibrium for D:Ni ratios of $\geqslant 2$ is to produce $[NiD_2]^{2+}$ through the equations 54 and 55.

$$[Ni(ClO_4)_2D_2] \longrightarrow 2ClO_4^- + [NiD_2]^{2+} \rightleftharpoons Ni^{2+} + 2D^- \qquad (54)$$

$$[Ni^{II}D_2]^{2+} \overset{e}{\rightleftharpoons} [Ni^{I}D_2]^+ \overset{e}{\rightleftharpoons} [Ni^{0}D_2] \qquad (55)$$

The species $[Ni^{II}D_2]^{2+}$ is yellow and shows the absorption spectrum as shown in Figure 21. Nickel(II) species disproportionate more in acetonitrile than in *N*-methylpyrrolidinone. The disproportionation reaction leads to nickel(0) species via reaction 56. The pK of disproportionation $= \Delta E_{1/2}/0.06 \approx 2$. The reactivity of $[Ni^{II}D_2]^{2+}$ towards halides has been examined[125]; when the ratio $Br^-:[Ni^{II}D_2]^{2+} = 1.0$, a 2e reversible reduction is observed (equation 57). As this ratio increases and reaches an excess in Br^-, an irreversible 2e reduction process is observed due to reaction 58. Notice that the end products of reactions 57 and 58 are the same except for the higher numbered moles of Br^- generated in reaction 61. The corresponding reaction for Cl^- (in place of Br^-) is shown in equation 59.

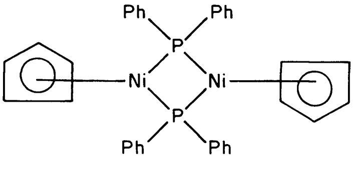
$$[2Ni^{I}D_2]^+ \rightleftharpoons [Ni^{II}D_2]^{2+} + [Ni^{0}D_2] \qquad (56)$$

$$[NiD_2Br]^+ + 2e \rightleftharpoons [Ni^{0}D_2] + Br^- \qquad (57)$$

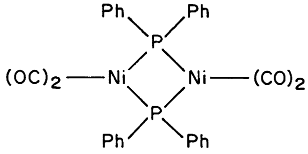
$$[NiBr_2D] + D + 2e \longrightarrow [Ni^{0}D_2] + 2Br^- \qquad (58)$$

$$[NiCl_2D] + D + 2e \longrightarrow [Ni^{0}D_2] + 2Cl^- \qquad (59)$$

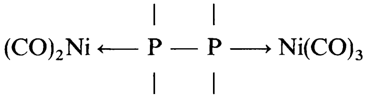
Dessy and coworkers[115,117] arrived at an interesting generalization based on the electrochemical patterns of nickel carbonyl complexes, namely that a reversible electron transfer requires a metal—metal bond to exist in the complex to obtain a stable radical anion. For example, $[(\pi\text{-}C_5H_5)NiPPh_2]_2$ (**8**) produces a stable radical anion on electrochemical reduction at -2.30 V vs a $Ag/AgClO_4$ electrode, giving an ESR spectrum of 10 G wide with a *g* value of 2.060. The nickel carbonyl species **9** also produces a reversible cyclic voltammetric wave at -1.75 V; an exhaustive electrochemical reduction at this potential generates an ESR spectrum of a purple anion radical with a total width of 6 G having a characteristic $g = 1.979$[116]. On the other hand, a species without a metal—metal bond having structure **10**, where the nickel atoms are separated by phosphorus, produces an irreversible wave at -2.40 V; in this case the anion could not be generated[116] for this compound. Popdoko *et al.*'s[126] results on nickel(II) complexes with diphenylphosphine are in parallel with those for the above-mentioned carbonyl complexes.



(8)



(9)

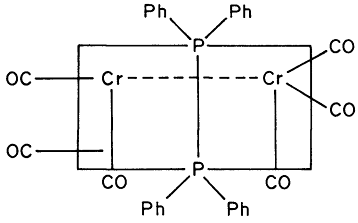


$$(CO)_2Ni \leftarrow P - P \rightarrow Ni(CO)_3$$

(10)

C. Chromium Carbonyls Bound to Phosphorus

Dessy *et al.*[116] suggested the formation of a metal—metal bond in chromium complexes of the type $[Cr(CO)_4PMe_2]_2$. The structure is visualized as **11**, where the metal—metal bond is shown by the dashed line. The electrochemical reduction of **11** occurs at $E_{1/2} = -1.85$ V; the wave is reversible owing to the presence of the metal–metal bond. The 2e reduction product gives an ESR spectrum having a 1:2:1 triplet arising from the interaction of the odd electron with both phosphorus nuclei; a phosphorus splitting constant of 13 G and a proton splitting constant of 12 G are observed in the spectrum.



(11)

This spectrum is attributed to reactions 60 and 61, where X represents **11**. The radical anion shows an infrared stretching frequency which is shifted by $100\,\mathrm{cm}^{-1}$ relative to the neutral species[116]. This arises from the interaction of $d\pi$ orbitals of the metal with the carbonyl antibonding $2\pi^*$ orbitals. The chromium carbonyl complex containing phosphorus ligands has an octahedral configuration about each chromium with the two octahedra sharing an edge which is occupied by PMe_2 bridges. Metal—metal bond formation is indicated by the diamagnetism studies[116].

$$X + 2e \rightleftharpoons X^{2-} \tag{60}$$

$$X^{2-} + X \longrightarrow 2X^{-} \tag{61}$$

The redox chemistry of tricarbonyl derivatives of chromium complexed with polycyclic tridentates shows[127–132] two reversible 1e oxidation processes. Bond *et al.*[132] observed isomerization, cross-redox and self-exchange reactions in $[Cr(CO)_3P_3]^{1\,0+}$, where P represents monodentate phosphorus ligands $P(OMe)_3$, $P(OPh)_3$, $P(OMe)_2Ph$ and PMe_2Ph. The electrochemical data are summarized in Table 14 and indicate quasi-reversible electron transfer processes. The stereochemistry in the facial (*fac*) and meridional (*mer*) forms forces the following redox equilibria in $[Cr(CO)_3P_3]^{1\,0+}$:

$$\begin{tikzcd} fac^0 \arrow[r, shift left, harpoon] \arrow[d, shift left] & fac^+ + e \arrow[l, shift left, harpoon] \arrow[d, shift left] \\ mer^0 \arrow[r, shift left, harpoon] \arrow[u, shift left] & mer^+ + e \arrow[l, shift left, harpoon] \arrow[u, shift left] \end{tikzcd} \tag{62}$$

The electrochemical characteristics indicate a cross-redox reaction (63).

$$fac^+ + mer^0 \rightleftharpoons fac^0 + mer^+ \tag{63}$$

The controlled potential oxidation of *fac*^{0} generates *mer*-$[Cr(CO)_3P_3]$. It is represented by the above reaction[63]. A cyclic voltammetric study shows (see Table 15) that at −57 °C, the isomerization of *fac*$^+$ to *mer*^{0} is inhibited. The isomerization of *fac*$^+$ to *mer*^{0} is extremely slow in dichloromethane, but the conversion of *mer*$^+$ to *fac*$^+$ is very fast. The ESR spectra of *mer*-$[Cr(CO)_3(PMe_2Ph)_3]^+$ at 273 and 213 K and of *mer*-$[Cr(CO)_3(P(OMe)_2Ph)_3]^+$ at 298, 273 and 213 K are depicted in Figure 22. The spectral features include a doublet of triplets due to ^{31}P hyperfine coupling, which is consistent with meridional form of the chromium(I) cation. These spectra show no hyperfine splitting due to ^{53}Cr ($I = 3/2$). The spectrum of *mer*-$[Cr(CO)_3(P(OMe)_2Ph)_3]^+$ is broad at room temperature owing to fast exchange between the cation and the netural species. In both 18- and

TABLE 14. Electrochemical data for the oxidation of $[Cr(CO)_3P_3]$ complexes[a]

Compound	$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (V)	E_p^{ox} (V)	E_p^{red} (V)
mer-$[Cr(CO)_3(P(OMe)_3)_3]$	0.356	0.056	0.400	0.322
mer-$[Cr(CO)_3(P(OPh)_3)_3]$	0.732	0.0555	0.784	0.674
mer-$[Cr(CO)_3(P(OMe)_2Ph)_3]$	0.287	0.070	0.347	0.237
fac-$[Cr(CO)_3(P(OMe)_3)_3]$	0.456	0.057	0.561	0.475
fac-$[Cr(CO)_3(PMe_2Ph)_3]$	0.219	0.062	0.290	0.205
mer-$[Cr(CO)_3(PMe_2Ph)_3]$	−0.067	0.060	−0.005	−0.100

[a] Solvent, CH_2Cl_2; working electrode, Hg electrode; E_p values recorded at $500\,\mathrm{mV\,s^{-1}}$; reference electrode, Ag/AgCl. Taken from ref. 132. Copyright American Chemical Society.

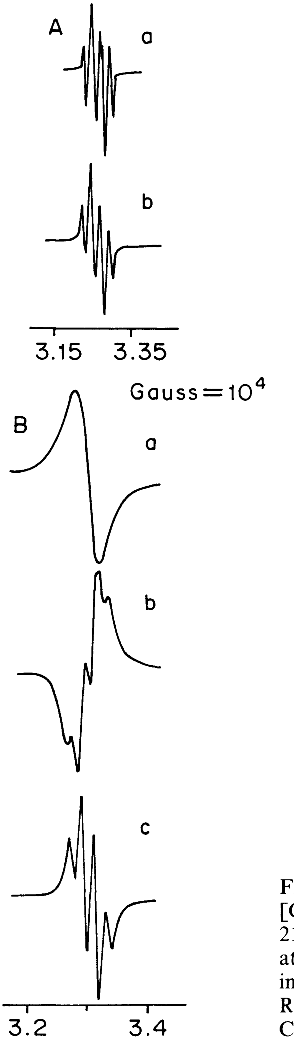


FIGURE 22. ESR spectra of (A) *mer*-$[Cr(CO)_3(PMe_2Ph_3]^+$ at (a) 273 K and (b) 213 K and (B) *mer*-$[Cr(CO)_3(POMe)_2Ph_3]^+$ at (a) 298 K, (b) 273 K and (c) 213 K. Abscissa in gauss; 1 = unit = 10^3 G. Solvent CH_2CL_2. Reprinted with permission from ref. 132. Copyright (1984) American Chemical Society.

17-electron complexes, the *mer*-isomer is favoured and the line broadening occurs due to reaction 64.

$$mer^+ + mer^0 \rightleftharpoons mer^0 + mer^+ \qquad (64)$$

Chromium tricarbonyl bis[bis(diphenylphosphino)] methane and bis[1,2-bis(diphenylphosphino)]ethane complexes are susceptible to 1e redox reactions. The electrochemical characteristics of meridional and facial forms are given in Table 16. The stepwise conversion processes are shown in reaction 65. The second electron step occurring at positive potentials, close to the solvent (CH_2Cl_2) limit, results in the generation of chromium (reaction 66), where dppm = $Ph_2PCH_2PPh_2$ and dppe = $Ph_2PCH_2CH_2PPh_2$.

TABLE 15. Cyclic voltammetric oxidation of *fac*-$[Cr(CO)_3(PMe_2Ph)_3]^a$

Temperature (°C)	Sweep rate (mV s^{-1})	$E_p^{ox^b}$ (V)	$E_p^{red^b}$ (V)	$E_p^{ox^c}$ (V)	$E_p^{red^c}$ (V)
18	500	0.34	0.18	0.00	−0.13
	50	0.26	d	−0.03	−0.10
−15	500	0.36	0.15	0.01	−0.15
	50	0.30	0.17	−0.03	−0.09
−43	500	0.40	0.13	0.03	−0.17
	50	0.30	0.17	^{d}	^{d}
−57	500	0.46	0.09	^{d}	^{d}
	50	0.31	0.15	^{d}	^{d}

[a] Working electrode, Pt electrode; medium, CH_2Cl_2 containing 0.1 M Bu_4NClO_4. Potentials are vs Ag/AgCl. Reprinted with permission from ref. 132. Copyright (1984) American Chemical Society.

[b] For process $fac \rightleftharpoons fac^+ + e$
$$\begin{array}{c} \downarrow \\ mer^+ \end{array}$$

[c] For process $mer \rightleftharpoons mer^+ + e$.

[d] No peak observed.

TABLE 16. Electrochemical data for the $[Cr(CO)_3(\eta^1\text{-PP})(\eta^2\text{-PP})]$ complexes[a]

Compound	Solvent	E_p^{ox} (V)	E_p^{red} (V)	E^0 (V)	T (V)
mer-$[Cr(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})]$	CH_2Cl_2	0.15	0.02	0.09	20
	Acetone	0.08	−0.00	0.04	20
mer-$[Cr(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})]^+$	CH_2Cl_2	1.27			20
	Acetone	1.00			
fac-$[Cr(CO)_3(\eta^1\text{-dppe})(\eta^2\text{-dppe})]$	CH_2Cl_2	0.47	0.38	0.43	−78
	CH_2Cl_2	0.43	–	–	20
mer-$[Cr(CO)_3(\eta^1\text{-dppe})(\eta^2\text{-dppe})]$	CH_2Cl_2	0.22	0.13	0.18	20
mer-$[Cr(CO)_3(\eta^1\text{-dppe})(\eta^2\text{-dppe})]^+$	CH_2Cl_2	1.24	–	–	20

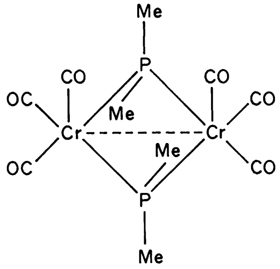
[a] Potentials are referred to Ag/AgCl. Reprinted with permission from ref. 131. Copyright (1986) American Chemical Society.

The facial form of $[Cr(CO)_3(\eta^1\text{-dppe})(\eta^2\text{-dppe})]$ shows a similar 1e oxidation wave but the product decomposes to chromium(II). The cation is more stable at −78 °C.

$$mer\text{-}[Cr(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})] \rightleftharpoons mer\text{-}[Cr(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})]^+ + e \tag{65}$$

$$\begin{array}{c} mer\text{-}[Cr(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})]^+ \\ \downarrow \\ mer\text{-}[Cr(CO)_3(\eta^1\text{-dppm})(\eta^2\text{-dppm})]^{2+} + e \\ \downarrow \\ Cr^{II} + 2dppm + 3CO \end{array} \tag{66}$$

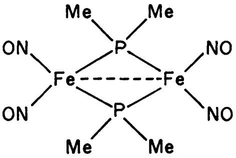
Bis-(μ-phosphido)dichromium species exhibit reversible voltammetric waves with $n = 2$[134]. The resulting dianion disproportionates to give a monoanion and the ESR spectrum of the anion radical shows hyperfine couplings with two identical phosphorus atoms and the triplet split into a 13-fold multiplet due to Me groups of the compound (**12**).



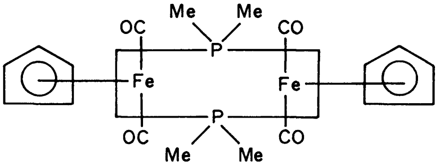
(12)

D. Iron Carbonyls and Nitrosyl Complexed to Diphenylphosphine

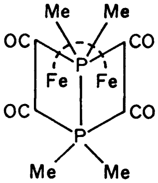
Iron derivatives are useful in understanding metal—metal bond interactions[116] in compounds such as **13**–**15**. The octahedral configuration around the metal in $[(\pi\text{-}C_5H_5)Fe(CO)PPh_2]_2$ shows essentially two octahedral sharing an edge; this compound exhibits a polarographic wave at -0.20 V vs $Ag/AgClO_4$, oxidizing to a deep-blue radical cation. The wave is reversible and on exhaustive electrolysis the product shows a featureless ESR spectrum which is 12.5 G wide. The second polarographic wave is located at -0.50 V; this wave is attributed to dication formation[116]. When an Fe—Fe bond exists in the complex, such as in $[(CO)_3FePMe_2]_2$, the structure is octahedral around each iron, with the octahedral sharing a face; the metal—metal bond occupies one of the ligand positions. It undergoes a 2e reduction with $E_{1/2} = -2.10$ V. The dianion shows no ESR signal but on addition of the parent produces a radical anion exhibiting a line width of 75 G, which is difficult to resolve further. The radical anion has $g = 1.977$[116].



(13)



(14)



(15)

The tetrahedral configuration that exists in the nitroso compound $[(NO)_2FePPh_2]_2$ has $E^{I}_{1/2} = -1.70$ V $Ag/AgClO_4$ and $E^{II}_{1/2} = -2.19$ V vs $Ag/AgClO_4$. The formation of a radical anion and dianion is confirmed by ESR studies. The anion gives a phosphorus triplet (1:2:1) with $\Delta H_p = 20$ G with $g = 1.937$.

Several dialkylamino phosphorus iron carbonyls have been synthesized from bis(diisopropylamino)phosphine with iron carbonyls by King and Fu[131]. These carbonyl complexes have an unusual property of rapid and selective cleavage of one diisopropylamino group on reaction with hydrogen halides; this selective cleavage might be caused by radical cation formation.

E. Molybdenum Carbonyl Bond to Phosphorus

The molybdenum cluster system $[PhMoPPh_2(CO)]_3$ produces an ill-defined irreversible polarographic wave. It does not produce a radical species on exhaustive reduction in DME[116], at the first polarographic wave. Complexes of the type $[Mo(CO)_4R_2P(CH_2)_3PR_2]$, where R = F, Cl, C_6F_5, MeO, Ph, Me or C_6H_{11} show characteristic quasi-reversible oxidations as in reaction 67.

$$[M(CO)_4L] \rightleftharpoons [M(CO)_4L]^+ + e \qquad (67)$$

The effectiveness of the phosphorus ligands to remove a charge from the metal follows qualitatively the order of electronegativity of the substituent on the donor phosphorus atom, i.e. F > Cl > C_6F_5; C_6FH_5 > Me > C_6H_{11}[133]. The cyclic voltammetric data for the above complexes are given in Table 17. For comparison, data for the corresponding chromium complexes are also included. The $E_{1/2}$ of the two series correlate very well, as shown by Figure 23.

The complexes of $[Mo(CO)_3P_3]$, where P is a monodentate phosphorus ligand, undergo oxidation by the scheme in equation 68. The *fac*-form undergoes oxidation in CH_2Cl_2 with $E_p^{ox} = 0.68$ V and the *mer*-form at $E_{pa} = 0.42$ V.

$$\begin{array}{c}
fac\text{-}[Mo(CO)_3(\eta^1\text{-dppe})(\eta^2\text{-dppe})] \longrightarrow fac[Mo(CO)_3(\eta^1\text{-dppe})(\eta^2\text{-dppe})]^+ + e \\
\downarrow \\
mer\text{-}[Mo(CO)_3(\eta^1\text{-dppe})(\eta^2\text{-dppe})]^+ \\
\downarrow \\
mer\text{-}[Mo(CO)_3(\eta^1\text{-dppe})(\eta^2\text{-dppe})]^{2+} + e \\
\downarrow \\
[Mo(CO)_3)(\eta^2\text{-dppe})_2]^{2+}
\end{array} \qquad (68)$$

TABLE 17. Electrochemical data for $[M(CO)_6]$ and $[M(CO)_4R_2P]CH_2PR_2$ complexes in CH_2Cl_2 and acetonitrile[a]

Solvent	R	M = Mo			M = Cr		
		(V)	(V)	(V)	(V)	(V)	(V)
CH_2Cl_2	C_6F_5	1.46	1.10	1.28	1.235	0.860	1.05
	MeO	1.38	1.04	1.21	1.15	0.840	0.995
	Ph	1.24	0.86	1.05	1.025	0.690	0.860
	Me	0.710	0.470	0.530	0.560	0.260	0.410
MeCN	$M(CO)_6$	1.65			1.49	1.320	1.410
	F	1.37			1.32	1.18	1.250
	C_6F_5	1.23			1.01	0.87	0.940
	MeO	1.18			0.96	0.82	0.890
	Me	0.46			0.35	0.19	0.270

[a] Voltages are vs SCE. Working electrode, glassy carbon; supporting electrolyte, Bu_4NClO_4; $E_{1/2} = (E_a + E_c)/2$. Reprinted with permission from ref. 133. Copyright (1984) American Chemical Society.

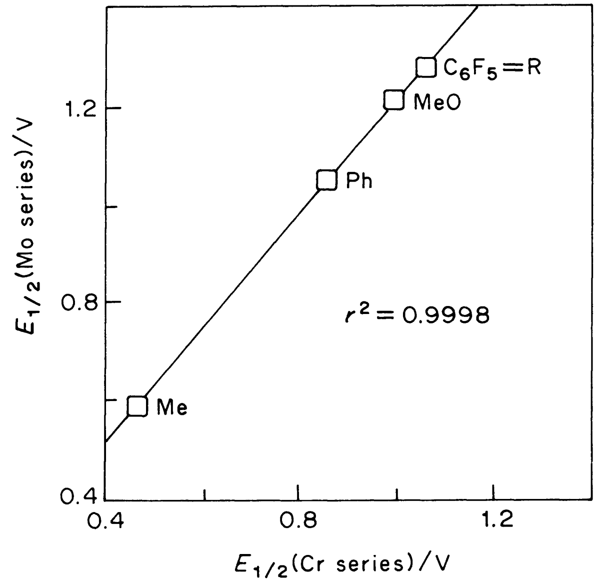


FIGURE 23. Correlation of half-wave potentials for $[M(CO)_4R_2PCH_2PR_2]$ complexes in CH_2Cl_2. Reprinted with permission from ref. 133. Copyright (1984) American Chemical Society.

VI. PHOSPHONIUM SALTS

By oxidation of Ph_3P using ferricinium ion in a nitrogen atmosphere, a phosphonium salt. Ph_4P^+, has been prepared[135]. This oxidation produces ferrocene in 100% yield. Schiavon *et al.*[136] proposed the oxidation scheme shown in equations 69–71 and the overall reaction 72. The reduction of Ph_3P^+ is observed at -2.20 V.

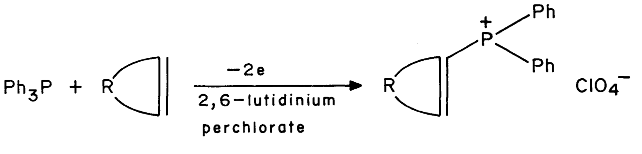
$$Ph_3P \longrightarrow Ph_3P^+ + e \tag{69}$$

$$Ph_3P^+ + PhPPh_2 \longrightarrow Ph_3\overset{+}{P}C_6H_4PPh_2 + H^+ + e \tag{70}$$

$$H^+ + Ph_3P \rightleftharpoons Ph_3PH^+ \tag{71}$$

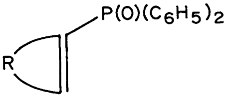
$$3Ph_3P \longrightarrow Ph_3\overset{+}{P}C_6H_4PPh_2 + Ph_3PH^+ + 2e \tag{72}$$

Cycloalk-1-enyl phosphonium salts are prepared in reasonable yields by a constant-current electrolysis of Ph_3P in dichloromethane at a graphite anode in the presence of cycloalkenes by reaction 73[137]. The phosphonium salts are converted to the



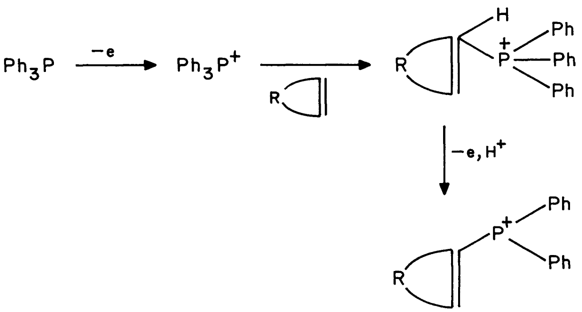
(73)

corresponding phosphine oxide by treatment with NaOH dissolved in aqueous ethanol[138]. The oxides have structure **16**. The yields and the melting point of



(16)

phosphonium salts are given in Table 18. The oxidation of triphenylphosphine at a controlled potential at 1.40 V vs silver wire results in the formation of cycloalk-1-enyl phosphonium salts (equation 74).



(74)

The charge-transfer salt formed by reaction of tetracyanoquinodimethane (TCNQ) and diphosphonium iodide undergoes a 2e oxidation at a carbon paste electrode[139]; reactions 75 and 76 occur in acetonitrile. Similar schemes can be generated for $D'P^{2+}$, where $D'P^{2+} = PhMeP^{+}CH{=}CHP^{+}MePh_2$[139].

$$DPI_2 + 4TCNQ \longrightarrow DP(TCNQ)_4 + I_2 \tag{75}$$

$$DP(TCNQ)_4 \longrightarrow DP^{2+} + 4TCNQ + 2e \tag{76}$$

The phosphonium salts are electrochemically reduced to phosphines[140] through reactions 77 and 78, but the neutral radial $R^{\bullet}$ is electrochemically active and undergoes reactions 79–81.

$$R_4P^{+} + e \rightleftharpoons R_4P^{\bullet} + e \longrightarrow R_4P^{-} \tag{77}$$

$$R_4P^{\bullet} \longrightarrow R_3P + R^{\bullet} \tag{78}$$

TABLE 18. Electrochemical preparation of cycloalk-1-enyl phosphonium salts[a]

Cycloalkene	Yield (%)	M.p. (°C)
Cyclopentene	53	277–279
Cyclohexene	53	290–291
Cycloheptene	56	214–216
Cyclooctene	53	197–199
Norbornene	66	192–104

[a] 3 mmol of Ph_3P and 15 mmol of cycloalkene in CH_2Cl_2 containing 0.2 M 2,6-lutidinium perchlorate at 1.07 mA cm^{-2}. Electrolysis is carried out for 8 h.

$$\mathrm{R^{\bullet} + e \longrightarrow R^{-\bullet}} \tag{79}$$

$$\mathrm{2R^{-\bullet} \longrightarrow 1/2\,(R{-}R)} \tag{80}$$

$$\mathrm{R + H^{+} \longrightarrow RH^{+}} \tag{81}$$

Table 19 gives the half-wave potentials, diffusion currents and the number of electrons consumed in the reaction for different substituents. The half-wave potentials for $[\mathrm{Ph_3P(CH_2)_{\mathit{n}}PPh_3]Br_2}$ for $n = 1$–12 show the trend represented in Figure 24. Cleavage of the phosphorus—carbon bond occurs in all the phosphonium salts[140]. This can be used successfully in the analytical determination of phosphonium salts (phenyltrimethylphosphonium iodide and tetra-*O*-tolyphosphonium iodide) in the range 0.001–0.005 M[141]; the reductions consist of two successive 1 e steps.

The electrolytic reductive cleavage of cyanoalkyl phosphonium compounds of the type $\mathrm{Ph_3P^{+}(CH_2)_{\mathit{n}}CNX^{-}}$, where $n = 1$–4, has been demonstrated by Wagenknecht and Baizer[142] through polarographic and controlled potential electrolysis. The anion X

TABLE 19. Electrochemical characteristics of phosphonium compounds[a]

Phosphonium bromide	$-E_1$ (V)	i_d (μA)	n_1	n_2
Methyltriphenyl-	1.862	2.60	2.7	1.1
Cyclohexyltriphenyl-	1.859	2.94	1.6	
	2.092	0.28	1.2	
Ethyltriphenyl-	1.837	1.79	3.1	
	1.970	0.80	1.7	
Isopropyltriphenyl-	1.833	1.56	9.1	1.2
	2.092	2.14	0.7	
n-Propyltriphenyl-	1.822	1.36	2.3	
	1.962	0.72	1.4	
	2.075	0.14	2.2	
n-Butyltriphenyl-	1.802	1.16	2.1	
	1.984	1.22	1.2	
2-Butyltriphenyl-	1.709	1.38	6.3	
	2.686	1.20	1.0	
Isobutyltriphenyl-	1.720	1.26	2.4	
	2.039	1.28	0.6	
tert-Butyltriphenyl-	1.657	0.86	2.0	
	2.041	0.54	2.2	
Allyltriphenyl-	1.626	2.10	1.4	
	1.775	0.20	0.9	
	2.065	0.45	2.2	
	2.468	1.35	2.1	
Benzyltriphenyl-[b]	1.552	2.80	1.3	
Cyanomethyltriphenyl-[b]	1.301	1.62	0.9	
	2.051	0.84	0.9	
Benzhydryltriphenyl-	1.271	0.58	1.3	
	2.067	0.13	2.2	
Dimethyldiphenyl-	2.087	4.38	1.3	
Trimethylphenyl-	2.271	5.10	0.9	
Diethyldiphenyl-	2.031	2.58	2.1	0.7
4-Bromo-*n*-butyltriphenyl-	1.160	0.46	0.4	
	1.766	2.25	3.4	
	2.151	1.25	0.6	
Methylenebistriphenyl-	1.195	2.50	0.8	
	1.817	0.95	1.7	

(*continued*)

TABLE 19. (*continued*)

Phosphonium bromide	$-E_1$ (V)	i_d (μA)	n_1	n_2
	1.932	1.19	2.7	
Dimethylbistriphenyl-	1.475	2.50	1.9	
	2.064	2.70	2.2	
Trimethylbistriphenyl-	1.307	0.40	2.7	
	1.712	5.40	2.1	
	2.054	1.00	2.0	
Tetramethylenebistriphenyl-	1.798	8.80	1.8	
	2.058	0.90	2.1	
Pentamethylenebistriphenyl-	1.807	5.04	3.6	
Hexmethylenebistriphenyl-	1.822	4.75	1.8	
	2.000	1.10	0.8	
Octamethylenebistriphenyl-	1.732	3.70	2.3	
	1.971	1.50	1.2	
Decamethylenebistriphenyl-	1.715	1.25	t0.9	
	1.916	0.65	2.2	
	2.073	0.45	–	
Dodecamethylenebistriphenyl-	1.664	1.50	2.7	
	1.944	2.50	0.9	
n-Propyltri-*p*-anisyl-	1.934	0.68	0.7	
	2.109	1.12	0.9	
	2.364	0.90	0.7	
Methyltrisdimethylamino-	1.642	0.31	0.3	
	2.098	0.64	0.7	
Benzyltrisdimethylamino-	1.637	0.17	0.5	
	2.230	2.65	6.3	
Benzyltris-*N*-trimorpholino-	1.627	0.31	–	
	2.206	6.40	0.4	
Methyltris-*p*-dimethylaminophyenyl-	1.697	0.17	–	
Benzyltris-*p*-dimethylaminophenyl-	1.279	0.36	0.8	
	1.886	0.21	–	
p-Hydroxyphenyltriphenyl-[b]	1.000	2.40	0.7	
	2.046	0.50	3.0	
p-Anisyltriphenyl-	1.835	1.26	1.4	
	1.988	0.26	1.8	
	2.128	0.56	1.9	
p-Aminophenyltriphenyl-	1.801	0.88	2.0	
	1.916	0.34	1.3	
	2.144	0.30	2.3	
	2.473	1.56	1.2	
p-Dimethylaminophenyltriphenyl-	1.777	2.60	2.1	0.7
	2.091	0.41	1.1	
p-Tolyltriphenyl-	1.692	2.50	2.0	0.8
	2.073	0.26	1.7	
m-Tolyltriphenyl-	1.684	2.28	2.0	0.7
	2.066	0.46	1.9	
Tetraphenyl-	1.680	2.80	2.1	0.6
	2.068	0.15	1.5	
o-Tolyltriphenyl-	1.678	2.12	2.0	0.3
	2.061	0.21	1.8	
p-Benzhydrylphenyltriphenyl-	1.668	0.60	1.0	0.6
p-Cumyltriphenyl-	1.654	2.78	1.7	0.7
	2.056	0.40	1.3	

(*continued*)

TABLE 19. (*continued*)

Phosphonium bromide	$-E_1$ (V)	i_d (μA)	n_1	n_2
p-Carbohydroxyphenyltriphenyl-	1.630	1.10	0.6	0.2
	2.346	2.70	0.6	
1-Naphthyltriphenyl-	1.439	0.88	3.5	1.1
	1.781	0.50	0.9	
	2.054	0.45	1.9	
	2.326	1.70	0.8	
	2.488	1.30	2.0	
2-Naphthyltriphenyl-	1.554	1.80	2.0	
	1.653	0.75	1.4	
	2.049	0.44	1.4	
	2.207	1.00	1.1	
	2.325	2.20	1.0	
	2.494	1.65	1.4	
p-Biphenylytriphenyl-	1.527	1.70	2.4	0.9
	1.655	0.35	1.1	
	2.076	0.29	1.6	
	2.279	1.30	1.0	
	2.490	4.70	1.2	
p-Nitrophenyltriphenyl-	0.454	2.90	3.1	1.5
	1.502	1.35	1.1	
	1.831	0.65	2.0	
	2.118	0.50	1.8	
p-Phenylenebistriphenyl-	1.155	0.40	1.6	
	1.269	0.08	1.5	
	1.477	1.24	1.2	
	1.667	2.48	1.6	
	2.069	0.24	1.5	
	2.435	4.70	3.1	
p-Trifluoromethylphenyltriphenyl-	1.410	7.85	1.1	
	2.077	0.35	2.2	
	2.323	7.90	0.7	
	2.482	1.20	3.3	
p-Phenylsulphophenyltriphenyl-	1.227	2.06	1.8	
	1.677	0.65	3.1	
	1.954	1.15	1.3	
	2.083	0.17	1.3	
	2.350	1.65	1.4	
	2.490	1.05	2.0	
Di-*p*-tolyldiphenyl-	1.695	2.48	1.5	0.9
	2.092	1.18	0.9	
Tri-*p*-tolylphenyl-	1.727	2.60	2.1	1.2
	2.071	0.32	3.0	
Di-*p*-anisyldiphenyl-	1.790	0.908	1.3	
	1.954	3.12	–	
Tri-*p*-anisylphenyl-	1.848	1.30	1.2	
	2.006	0.22	2.1	
	2.128	0.74	2.9	
Tri-*p*-toly-*p*-cumyl-	1.713	2.50	2.2	0.6
	2.004	0.46	2.5	
	2.455	0.28	1.6	

---

[a] Concentration of phosphonium salt: 10^{-3} M. Potentials are vs SCE. Reproduced by permission of Elsevier Publishers from ref. 140.

[b] Phosphonium chloride.

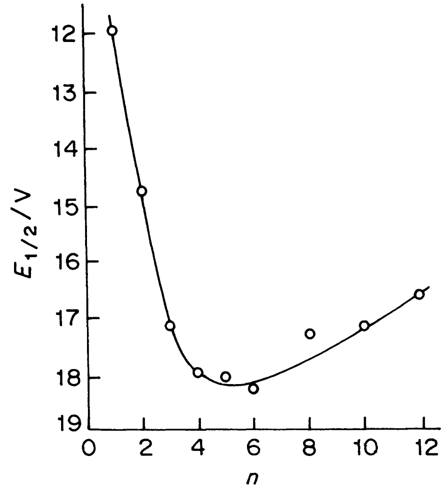


FIGURE 24. Half-wave potentials of $Ph_3P(CH_2)_nPPh_3Br_2$ vs the number of CH_2 groups. Reproduced by permission of Elsevier Publishers from ref. 140.

generally represents a halide or *p*-toluenesulphonate. The compounds produce three or four polarographic waves depending on the value of *n*. The first wave is attributed to reactions 82–84. The second wave appears to be due to the reduction of **19**, represented by reaction 85. Species **18** decomposes by reaction 86. The third wave is observed due to the reduction of Ph_3P formed in reaction 86[1]. The electrolytic reductive coupling has been demonstrated by the isolation of the products. Table 20 gives the yields of the products obtained in electroreduction of $[Ph_3P^+(CH_2)_nCN]$ in the presence of styrene; styrene captures the carbonion formed in the reductive cleavage. Ph_3PO is formed due

TABLE 20. Yields of products in the reduction of $[Ph_3P^+(CH_2)_nCN]X^-$ in the presence of styrene[a]

	Yield (%)			
Product	$n = 1$, X = Br	$n = 2$, X = T[c]	$n = 3$, X = Br	$n = 4$, X = Br
Ph_3P	26.4	58–74	82.5	57
Ph_3PO	23.6	–	–	–
$Me(CH_2)_nCN$	[b]	[b]	[b]	[b]
C_6H_6	–	14	–	10
$[CN(CH_2)_n]_2Hg$	–	[b]	[b]	[b]
$CH_2{=}CHCN$	–	[b]	–	–
$CN(CH_2)_nCN$	–	[b]6	–	–
$CN(CH_2)_nCHPh$ | $CN(CH_2)_nCHPh$				

[a] The data are for the passage of 1 faraday per mole. Reprinted with permission from ref. 142. Copyright (1966) American Chemical Society.

[b] Product isolated, but yield not determined.

[c] T = Tolyl.

to reaction of $Ph_3P{=}CHCN$ with water during the isolation of the products. Pardini *et al.*[143] have investigated benzyl cinnamyl polyenylphosphonium salts in a similar way.

$$Ph_3P^+(CH_2)_nCN \xrightarrow[Hg]{+e} \underset{\mathbf{(17)}}{Ph_3P(CH_2)_nCN/Hg} \qquad (82)$$

$$\mathbf{17} \longrightarrow \underset{\mathbf{(18)}\ \text{(in solution)}}{Ph_3P(CH_2)_nCN + Hg} \qquad (83)$$

$$\mathbf{17} \longrightarrow \underset{\mathbf{(19)}}{Ph_3P(Hg(CH_2)_nCN]} \qquad (84)$$

$$\mathbf{19} + e \longrightarrow Hg + (CH_2)_nCN^- \qquad (85)$$

$$\mathbf{18} \longrightarrow \underset{\text{(in solution)}}{Ph_3P + (CH_2)_nCN} \qquad (86)$$

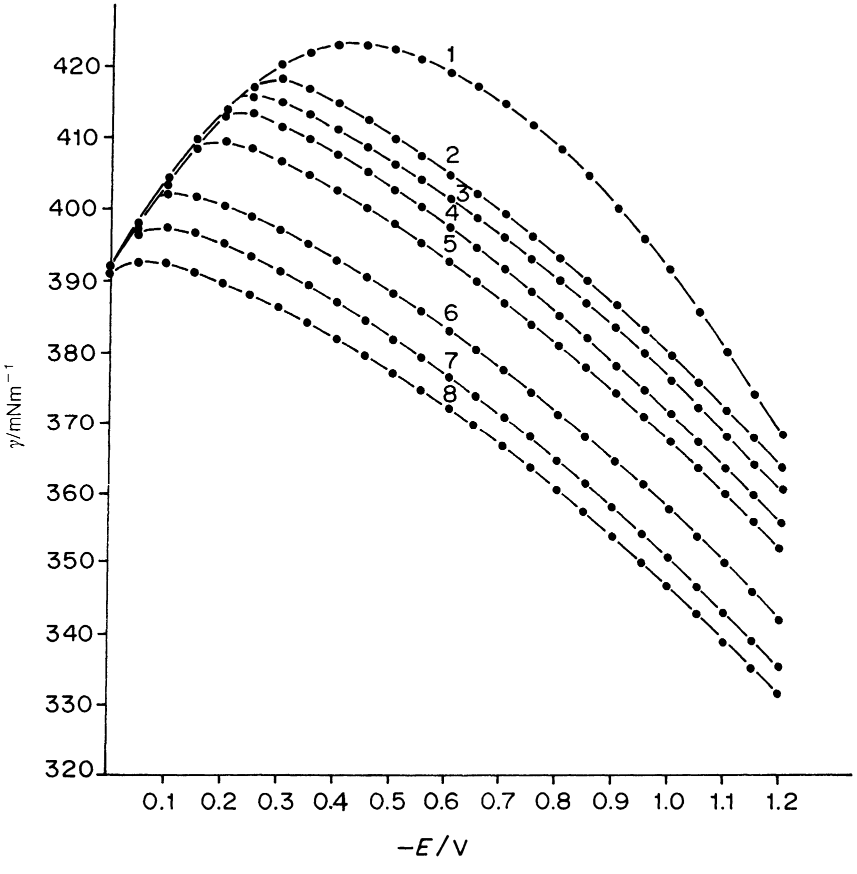


FIGURE 25. Electrocapillary curves of phosphine oxides at various concentrations in 0.1 M H_2SO_4: (1) 0; (2) 2×10^{-4}; (3) 4.98×10^{-4}; (4) 9.9×10^{-4}; (5) 1.96×10^{-3}; (6) 1×10^{-2}; (7) 2×10^{-2}; (8) 5×10^{-2} M. Reproduced by permission of Elsevier Publishers.

VII. INTERFACIAL ADSORPTION BEHAVIOUR OF PHOSPHORUS(V) COMPOUNDS

The adsorption of phosphine oxides of the type dialkyl-, phenyl-, alkyldimethyl- and alkyldiethyl-phosphine oxides at the mercury/electrolyte solution interface is a common feature[144] with the extent of adsorption controlled by the composition of the medium and the structure of phosphine oxides. The interaction constant of the oxide is also dependent on its nature. The electrocapillary curves of phosphine oxides are shown in Figure 25. The surface tension, γ, values in the presence of $C_5H_{11}(C_2H_5)_2PO$ systematically decrease as the bulk concentration of the oxide increases. An increase in chain length by one CH_2 group causes a decrease in γ by about $7\,mN\,m^{-1}$. This effect is observed for the homologous dialkylphenylphosphine oxides. The adsorption of the phosphine oxides is analysed through the Frumkin isotherm defined by equation 87, where b is the adsorption coefficient and a is the lateral interaction constant; θ is the degree of coverage, defined by $(C_0 - C)/(C_0 - C_s)$, where C_0 is the differential capacity of the supporting electrolyte, C is the differential capacity for the phosphine oxide at any concentration and C_s is the saturation differential capacity. Table 21 gives estimates of the adsorption parameters of phosphine oxides. The parameters a and b increase by an order of magnitude on increasing the chain length.

$$bc(1-\theta) = \theta \exp(-2a\theta) \qquad (87)$$

The areas occupied by adsorbed phosphine oxides in aqueous solutions were experimentally evaluated at 0.63, 0.57 and $0.52\,nm^2$ for Ph_3PO, $EtPh_2PO$ and $MePh_2PO$, respectively. The calculated area values based on structural considerations for these three molecules are 0.71, 0.63 and $0.57\,nm^2$, respectively. The lower experimental values are attributed to multi-layer adsorption[145,146].

Adsorption of phosphine oxides influences the rate of electrochemical reductions[147,148]. The three homologous dialkylphenylphosphine oxides PhR_2PO, where R = Et, Pr and Bu, influences the reduction of Cu^{2+} with the rate being proportional to the adsorbed

TABLE 21. Interfacial adsorption characteristics of phosphine oxides[a]

Molecule[b]	E_{max} (V)	$\sigma^{M\,d}_{max}$ ($\mu c.cm^{-2}$)	$\Gamma_5 \times 10^{10}$ ($mol\,cm^{-2}$)	a	b ($10^3\,dm^3\,mol^{-1}$)	$-\Delta G^{0\,e}_A$ ($kJ.mol^{-1}$)
Et_2PhPO	−0.80	–	2.7	1.3 ± 0.2	4.00	30
Pr_2PhPO	−0.75	–	2.6	1.5 ± 0.3	38.66	36
Bu_2PhPO	–	–	2.5	1.7 ± 0.5	43.0	43
$BuPh_2PO$	–	–	–	1.3 ± 0.1	4.31	30
$PeMe_2PO$	−0.75	–	2.9	1.0 ± 0.1	0.92	26
$HxMe_2PO$	−0.75	–	2.8	1.4 ± 0.2	4.16	30
$HxEt_2PO$	−0.73	–	2.4	1.2 ± 0.3	120.4	38
Ph_3PO	−0.72	−5.85	2.65	–	–	–
$EtPh_2PO$	−0.75	−5.95	2.93	–	–	–
$MePh_2PO$	−0.76	−6.00	3.22	–	–	–
Ph_3PO[c]	−0.90	−6.40	2.36	–	–	–
$EtPh_2PO$[c]	−0.95	−6.90	2.66	–	–	–
$MePh_2PO$[c]	−1.02	−7.50	2.91	–	–	–

[a] Aqueous solution. Adsorption on Hg surface.

[b] Pe = pentyl; Hx = hexyl.

[c] Methanolic solution.

[d] σ^M_M = Electrode change.

[e] ΔG^0_A = Adsorption free energy change.

Reproduced by permission of Elsevier Publishers from refs. 144 and 145.

film pressure. There appears to be a surface reaction between adsorbed reactant and the electroactive species. Electrosorption of tri-*n*-octylphosphine oxide in methanol and methanol–water solutions has been examined at a polarized mercury electrode[148–151].

Several dithiophosphates and bis(diphenyldithiophosphine) disulphides exhibit catalytic currents due to their adsorption on mercury[151–153]. Trialkyl phosphine oxides, on the other hand, inhibit non-metallic reactions at the electrode[154].

VIII. REFERENCES

1. K. S. V. Santhanam, in *The Chemistry of Organophosphorus Compounds*, (Ed. F. R. Hartley), Vol. 1, Wiley, Chichester, 1990, p. 103.
2. K. S. V. Santhanam, in *Standard Potentials in Aqueous Solution* (Eds A. J. Bard, R. Parsons and J. Jordon), Marcel Dekker, New York, 1985, p. 104.
3. M. Losada, *J. Electroanal. Chem. Bioelectrochem. Bioenerg.*, **5**, 296 (1978).
4. M. Losada, *J. Electroanal. Chem. Bioelectrochem. Bioenerg.*, **6**, 205 (1979).
5. R. E. Dessy, *J. Am. Chem. Soc.*, **94**, 746 (1972).
6. (a) B. B. Damaskin, O. A. Petrii and V. V. Batrakov, *Adsorption Organischer Verbindungen an Elektroden*, Akademie Verlag, Berlin, 1975.
   (b) B. B. Damaskin, O. A. Petrii and V. V. Batrakov, *Adsorption of Organic Compounds or Electrodes*, Plenum Press, New York, 1971.
7. A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980, p. 496.
8. R. Payne, *J. Electroanal. Chem.*, **41**, 277 (1973).
9. S. Wawzonek and J. H. Wagenknecht, *Polarography—1964*, Macmillan, London, 1966, p. 105.
10. R. E. Dessy, T. Chives and W. Kitching, *J. Am. Chem. Soc.*, **88**, 467 (1966).
11. K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **90**, 118 (1968).
12. A. V. Illyasov, Yu. M. Kargin, Ya. A. Levin, L. D. Morozova, B. V. Mel'nikov, A. A. Vafina, N. N. Stonikova and V. S. Galeev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2841 (1968).
13. J. M. Saveant and S. K. Binh, *J. Electroanal. Chem.*, **88**, 27 (1978).
14. A. V. Illyasov, Yu. M. Kargin, Ya. A. Lenin, I. D. Morozova, B. V. Melnikov, A. A. Vafina, N. N. Sotnikova and V. S. Galeev, *Izv. Akad. Nauk SSSR, Ser. Khim*, 770 (1971), *Chem. Abstr.*, **75**, 87826u.
15. W. M. Gulick, Jr, and D. H. Geske, *J. Am. Chem. Soc.*, **88**, 2928 (1966).
16. K. S. V. Santhanam, L. O. Wheeler and A. J. Bard, *J. Am. Chem. Soc.*, **89**, 3386 (1969).
17. K. S. V. Santhanam and A. J. Bard, *J. Electroanal. Chem.*, **25**, Appendix 6 (1970).
18. F. Fichter, *Grganische Elektrochemie*, Verlag von Theodor Steinkopff, Dresden, Leipzig, 1942, p. 144.
19. T. Kitagawa, T. Layloff and R. N. Adams, *Anal. Chem.*, **36**, 925 (1964).
20. M. E. Peover and J. S. Powell, *J. Electroanal. Chem.*, **20**, 427 (1969).
21. M. Heyrovsky and S. Vavricka, *J. Electroanal. Chem.*, **28**, 409 (1970).
22. B. Miller and S. Bruckenstein, *Anal. Chem.*, **46**, 2026 (1972).
23. R. F. Nelson, A. K. Carpenter and E. T. Seo, *J. Electrochem. Soc.*, **120**, 206 (1973).
24. H. Sadek and B. A. Abd-el-Nabey, *Electrochim. Acta*, **17**, 511 (1971).
25. K. S. V. Santhanam, L. O. Wheeler and A. J. Bard, *J. Am. Chem. Soc.*, **89**, 3386 (1967).
26. K. S. V. Santhanam, and A. J. Bard, *J. Electroanal. Chem.*, **25**, App. 6, (1970).
27. W. O. Davies and E. Stanley, *Acta Crystallogr.*, **15**, 1092 (1962).
28. B. Allen and A. Bond, *J. Phys. Chem.*, **68**, 2439 (1964).
29. H. Jaffe, L. Freedman and G. Doak, *J. Am. Chem. Soc.*, **75**, 2209 (1953).
30. E. Muller, H. Eggenspergen and K. Scheffler, *Ann. Chem.*, **658**, 103 (1962).
31. M. Losada, M. Hervas, M. A. De La Rosa and F. F. De La Rosa, *J. Electroanal. Chem. Bioelectrochem. Bioenerg.*, **11**, 193 (1983).
32. V. M. Clark, D. W. Hutchinson, G. W. Kuby and S. A. Todd, *J. Chem. Soc.*, 715 (1961).
33. A. Todd, *Proc. Natl. Acad. USA*, **45**, 1389 (1959).
34. V. M. Clark, D. W. Hutchinson and A. Todd, *J. Chem. Soc.*, 729 (1961).
35. V. M. Clark, G. W. Kirby and A. Todd, *Nature* (*London*), **181**, 1650 (1958).
36. A. Lapidot and D. Samuel, *Biochim. Biophys. Acta*, **65**, 164 (1962).
37. A. Lapidot and D. Samuel, *J. Am. Chem. Soc.*, **86**, 1886 (1964).
38. C. A. Chambers and J. Q. Chambers, *J. Am. Chem. Soc.*, **88**, 2922 (1966).

39. B. T. Allen and A. Bond, *J. Phys. Chem.*, **68**, 2439 (1964).
40. M. Losada, *J. Electroanal. Chem. Bioelectrochem. Bioenerg.*, **5**, 296 (1978).
41. P. Mitchell, *Trends Biochem. Sci.*, **3**, N 58 (1978).
42. P. Mitchell, *Science*, **206**, 1148 (1979).
43. L. S. Morowitz and H. J. Morowitz, *Biochem. Biophys. Res. Commun.*, **82**, 727 (1978).
44. E. P. Nangniot, *Anal. Chim. Acta*, **31**, 166 (1964).
45. C. O. Schmakel, K. S. V. Santhanam and P. J. Elving, *J. Electrochem. Soc.*, **121**, 1033 (1974).
46. R. W. Burnett and A. L. Underwood, *Biochemistry*, **7**, 3328 (1968).
47. H. Jaegfeldt, *J. Electroanal. Chem. Bioelectrochem. Bioenerg.*, **128**, 355 (1981).
48. K. S. V. Santhanam and P. J. Elving, *J. Am. Chem. Soc.*, **95**, 5482 (1973).
49. R. D. Braun, K. S. V. Santhanam and P. J. Elving, *J. Am. Chem. Soc.*, **97**, 2591 (1975).
50. W. J. Bladel and R. G. Haas, *Anal. Chem.*, **42**, 918 (1970).
51. P. Leduc and D. Thevenot, *J. Electroanal. Chem. Bioelectrochem. Bioenerg.*, **1**, 96 (1974).
52. H. Berg and H. Hanschmann, unpublished results.
53. C. O. Schmakel, K. S. V. Santhanam and P. J. Elving, *J. Am. Chem. Soc.*, **97**, 5083 (1975).
54. R. W. Burnett and A. L. Underwood, *Biochemistry*, **7**, 3330 (1968).
55. J. F. Biellmann and C. Lapinte, *Tetrahedron Lett.*, **7**, 683 (1978).
56. J. Cavelli, M. E. Cardinali and M. G. Bonicelli, *Ann. Chim. (Rome)*, **67**, 89 (1977).
57. H. Jaegfeldt, *J. Electroanal. Chem. Bioelectrochem. Bioenerg.*, **128**, 355 (1981).
58. P. J. Elving, C. O. Schmakel and K. S. V. Santhanam, *Crit. Rev. Anal. Chem.*, May, 1 (1976).
59. K. S. V. Santhanam, C. O. Schmakel, and P. J. Elving, *J. Electroanalel. Chem. Bioelectrochem. Bioenerg.*, **1**, 147 (1974).
60. C. Carruthers and V. Suntzeff, *Arch. Biochem. Biophys.*, **45**, 140 (1953).
61. W. M. Schwartz, E. M. Kosower and I. Shain, *J. Am. Chem. Soc.*, **83**, 3164 (1961).
62. H. H. Jaegfeldt, A. Torstensson and G. Johansson, *Anal. Chim. Acta*, **97**, 221 (1978).
63. W. A. Bladel and R. A. Jenkins, *Anal. Chem.*, **46**, 1952 (1974).
64. W. A. Bladel and R. A. Jenkins, *Anal. Chem.*, **47**, 1337 (1975).
65. H. Jaegfeldt, *J. Electroanal. Chem.*, **110**, 295 (1980).
66. N. S. Sundaresan, V. Swayambunathan and K. S. V. Santhanam, *Trans. Eoc. Adv. Electrochem. Sci. Technol.*, **13**, 195 (1978).
67. H. Jaegfeldt, A. B. C. Torstensson, L. G. O. Gorton and G. Johansson, *Anal. Chem.*, **53**, 1979 (1981).
68. H. Jaegfeldt, T. Kuwana and G. Johansson, *Anal. Chem.* in press.
69. H. Jaegfeldt, A. Torstensson, L. Gorton and G. Johansson, *Anal. Chem.*, **153**, 1979 (1981).
70. D. C. S. Tse and T. Kuwana, *Anal. Chem.*, **50**, 1315 (1978).
71. F. Pragst, B. Kaltofen, J. Volke and J. Kuthan, *J. Electroanal. Chem.*, **119**, 301 (1981).
72. A. Kitani and L. Miller, *J. Am. Chem. Soc.*, **103**, 3595 (1981).
    (a) T. Matsue, H. Yamada, H. C. Chang and I. Uchida, *J. Electroanal. Chem. Bioelectrochem. Bioenerg.*, **299**, 347 (1990).
    (b) P. J. Elving, W. T. Bresnahan, J. Moiroux and Z. Samec, *J. Electroanal. Chem. Bioelectrochem. Bioenerg.*, **9**, 365 (1982).
    (c) T. Matsue, M. Duda, I. Uchida, T. Ato, U. Akiba and T. Osa, *J. Electroanal. Chem.*, **234**, 163 (1987).
    (d) B. W. Carlson, L. L. Miller, P. Neta and J. Grodkowski, *J. Am. Chem. Soc.*, **106**, 3850 (1984).
73. A. Kitani, Y. O. So and L. Miller, *J. Electroanal. Chem.*, **103**, 7636 (1981).
74. N. Takenchi, *J. Electrochem. Soc.*, **136**, 96 (1989).
75. B. N. Carlson and L. L. Miller, *J. Am. Chem. Soc.*, **107**, 479 (1985).
76. (a) L. L. Miller and J. R. Valentine, *J. Am. Chem. Soc.*, **110**, 3983 (1988).
    (b) P. Hapiot, J. Moiroux and J. M. Saveant, *J. Am. Chem. Soc.*, **112**, 1337 (1990).
77. E. Bojarska and B. Czochralska, *J. Electroanal. Chem. Bioelectrochem. Bioenerg.*, **212**, 287 (1986).
78. M. M. Kreevoy, D. Ostonic, I. S. H. Lee, D. A. Binder and G. W. King, *J. Am. Chem. Soc.*, **110**, 525 (1988).
79. A. Ohno, T. Shio, H. Yamamoto and S. Oka, *J. Am. Chem. Soc.*, **103**, 2045 (1982).
80. M. Dominguez, J. M. Sevilla, F. Garcia-Blanco and M. Blasquez, *J. Electroanal. Chem. Bioelectrochem. Bioenerg.*, **212**, 317 (1986).
81. R. Izquierdo, M. Blazquez, M. Dominquez and F. Garcia-Blanco, *J. Electroanal. Chem. Bioelectrochem. Bioenerg.*, **12**, 25 (1984).

82. J. W. Webb, B. Janik and P. J. Elving, *J. Am. Chem. Soc.*, **95**, 991 (1973).
83. B. Janik and P. J. Elving, *Chem. Rev.*, **68**, 295 (1968).
84. A. Ehrenberg, *Electronic Aspects of Biochemistry*, Academic Press, New York, 1964, p. 379.
85. R. Bridicka, *Z. Elektrochem.*, **47**, 721 (1948).
86. S. V. Tatwawadi, K. S. V. Santhanam and A. J. Bard, *J. Electroanal. Chem.*, **17**, 411 (1968).
87. F. Scheller, G. Stinad, B. Neumann, M. Kuhn and W. Ostrowski, *J. Electroanal. Chem.*, **104**, 117 (1979).
88. F. Vaz and K. S. V. Santhanam, *Indian J. Phys.*, **51B**, 446 (1977).
    (a) P. G. Gassman and C. Lee, *J. Am. Chem. Soc.*, **111**, 737 (1990).
89. R. F. Huson, *Structure and Mechanism in Organo-phosphorus Chemistry*", Academic Press, New York, 1965, p. 3.
90. H. Kwart and K. G. King, *d-Orbitals in the Chemistry of Silicon, Phosphorus and Sulphur*, Springer, Berlin, 1977.
91. M. J. S. Dewar, E. A. C. Lucken and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).
92. D. P. Craig, *J. Chem. Soc.*, 997 (1959).
93. K. A. R. Mitchell, *Chem. Rev.*, **699**, 157 (1969).
94. D. P. Crag and N. L. Paddock, *J. Chem. Soc.*, 4118 (1962).
95. D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).
96. N. L. Paddock, *Q. Rev. Chem. Soc.*, **18**, 168 (1964).
97. K. A. R. Mitchell, *J. Chem. Soc.*, 2683 (1968).
98. D. A. Brown and C. G. McCormack, *J. Chem. Soc.*, 5385 (1964).
99. D. P. Crag, M. L. Hefferman, R. Mason and N. L. Paddock, *J. Chem. Soc.*, 1376 (1961).
100. H. R. Allcock and W. J. Birdsall, *J. Am. Chem. Soc.*, **91**, 7541 (1969).
101. V. V. Perilkovskii, Yu. Egorov and G. S. Shapoval, *J. Gen. Chem. USSR* (*Engl. Transl.*), **41**, 742 (1972).
102. C. M. Park and W. M. Gulick, Jr, *J. Korean Chem. Soc.*, **18**, 341 (1974).
103. M. Pomerantz, D. S. Marynick, K. Rajeshwar, W. N. Chou, L. Throckmorton, E. W. Tsai, P. C. Y. Chen and T. Chain, *J. Org. Chem.*, **51**, 1223 (1986).
104. M. J. S. Dewar, E. A. C. Lucken and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).
105. H. R. Allock, *Phosphorus–Nitrogen Compounds*, Academic Press, New York, 1972, Chapters 2 and 3.
106. R. A. Saraceno, G. H. Riding, H. R. Allock and A. G. Ewing, *J. Am. Chem. Soc.*, **110**, 980 (1988).
107. R. A. Saraceno, G. H. Riding, H. R. Allock and A. G. Ewing, *J. Am. Chem. Soc.*, **110**, 7254 (1988).
108. R. A. Jones, A. L. Stuart and T. C. Wright, *J. Am. Chem. Soc.*, **105**, 7459 (1981).
109. R. A. Jones and T. C. Wright, *Organometallics*, **2**, 1842 (1983).
110. R. A. Jones, T. C. Wright, A. L. Atwood and W. E. Hunter, *Inorg. Chem.*, **22**, 993 (1983).
111. R. A. Jones, T. C. Wright, A. L. Atwood and W. E. Hunter, *Organometallics*, **2**, 470 (1983).
112. L. S. R. Yeh and A. J. Bard, *J. Electrochem. Soc.*, **124**, 189 (1973).
113. R. A. Jones, A. L. Stuart, J. L. Atwood and W. E. Hunter, *Organometallics*, **2**, 874 (1983).
114. F. L. Winner, M. R. Snow and A. M. Bond, *Inorg. Chem.*, **13**, 1617 (1974).
115. R. E. Dessy and R. L. Pohl, *J. Am. Chem. Soc.*, **90**, 1995 (1968).
116. R. E. Dessy, R. Kornmann, C. Smith and R. Hayter, *J. Am. Chem. Soc.*, **90**, 2001 (1968).
117. R. E. Dessy, A. L. Rheingold and G. D. Howard, *J. Am. Chem. Soc.*, **94**, 746 (1972).
118. J. G. Gaudiello, T. C. Wright, R. A. Jones and A. J. Bard, *J. Am. Chem. Soc.*, **107**, 888 (1985).
119. S. K. Kang, T. A. Allright, T. C. Wright and R. A. Jones, *Organometallics*, in press.
120. D. Zotti, S. Zecchin and G. Pilloni, *J. Electroanal. Chem.*, **175**, 241 (1984).
121. G. Pilloni, S. Valcher and M. Martelli, *J. Electroanal. Chem.*, **40**, 63 (1972).
122. Y. Rollin, M. Troupel, G. Meyer and J. Perichon, *J. Electroanal. Chem.*, **183**, 247 (1985).
123. O. Sock, M. Troupel, J. Perichon, C. Chevrot and A. Jutand, *J. Electroanal. Chem.*, **183**, 247 (1985).
124. M. Troupel, Y. Rollin, S. Sibilee, J. F. Fauvarque and J. Perichon, *J. Chem. Res.*, **173**, 24 (1980).
125. G. Bontempelli, F. Magno, B. Corain and G. Schiaron, *J. Electroanal. Chem.*, **103**, 243 (1979).
126. N. R. Popodko, A. A. Pozdeeva, V. V. Kaverin, Z. I. Zhdanov, L. B. Reznik and V. P. Yuv'ev, *Zh. Obshch. Khim.*, **54**, 2770 (1984).
127. S. P. Gubin and V. S. Khandkarova, *J. Organomet. Chem.*, **22**, 449 (1970).
128. M. K. Lloyd, J. A. McCleverty, J. A. Connor and E. M. Jones, *J. Chem. Soc., Dalton Trans.*, 1768 (1973).

129. R. D. Rieke, S. N. Milligen, I. Tucker, K. A. Dowler and B. R. Willeford, *J. Organomet. Chem.*, **C25**, 218 (1981).
130. M. A. Fox, K. A. Campbell and E. P. Kyba, *Inorg. Chem.*, **20**, 4163 (1981).
131. R. B. King and W. K. Fu, *Inorg. Chem.*, **25**, 2384 (1986).
132. A. M. Bond, S. W. Carr and R. Colton, *Inorg. Chem.*, **23**, 2343 (1984).
133. R. L. Cook and J. G. Morse, *Inorg. Chem.*, **23**, 2332 (1984).
134. R. E. Dessy, A. L. Rheingold and G. D. Howard, *J. Am. Chem. Soc.*, **94**, 746 (1972).
135. W. P. Fehlammer and C. Moinet, *J. Electroanal. Chem.*, **158**, 187 (1983).
136. G. Schiavon, S. Zecchin, C. Cogoni and G. Bontempelli, *J. Electroanal. Chem.*, **48**, 425 (1973).
137. H. Ohmori, T. Takhanami and M. Masui, *Tetrahedron Lett.*, **26**, (18), 2199 (1985).
138. G. Saleh, T. Minami, Y. Ghshirs and T. Agawa, *Chem. Ber.*, **112**, 355 (1979).
139. M. Lamache, S. Wuryanto, M. Leguan and R. M. Leguan, *Electrochim. Acta*, **30**, 455 (1985).
140. L. Horner and J. Haufe, *J. Electroanal. Chem.*, **20**, 245 (1969).
141. E. L. Colichman, *Anal. Chem.*, **26**, 1204 (1954).
142. J. H. Wagenknecht and M. M. Baizer, *J. Org. Chem.*, **31**, 3885 (1966).
143. V. L. Pardini, L. Roulker, H. P. James and A. Webber, *J. Chem. Soc., Perkin Trans. 2*, 1520 (1981).
144. E. Muller, H. Emons, J. Lipkowski and H. D. Dorfler, *J. Electroanal. Chem.*, **160**, 261 (1984).
145. P. Nikitas, A. Pappa-Louise and D. Jannakoudakis, *J. Electroanal. Chem.*, **171**, 369 (1984).
146. E. Muller, H. Emons, H. D. Dorfler and J. Lipkowski, *J. Electroanal. Chem.*, **142**, 39 (1982).
147. H. D. Horfler, R. Phillip, J. Dittrich and E. Muller, *Electrohim. Acta*, **32**, 475 (1987).
148. A. Pappa-Louisi, P. Nikitas and D. Jannakoudakis, *Electrochim. Acta*, **29**, 4 (1984).
149. Yu. Kulyako, S. A. Perevalov, I. A. Lebdev and B. F. Myasoedov, *Radiokhimiya*, **26**, 140 (1984).
150. A. Christodoublou, A. Anastopoulos and D. Jannakoadakis, *Can. J. Chem.*, **64**, 2279 (1986).
151. M. G. Gabdullin, A. R. Garifzyanov and V. F. Toropova, *Electrokhimya*, **21**, 924 (1985).
152. M. J. Hutchings, G. J. Moody and J. D. R. Thomas, *Analyst*, **112**, 601 (1987).
153. A. Schischkov, S. Dentocher and C. Malakova, *Talanta*, **31**, 69 (1984).
154. J. Dittrich, R. Phillip and E. Muller, *Electrochimica Acta*, **32**, 47 (1987).

CHAPTER **4**

Photochemistry of phosphine chalcogenides

M. DANKOWSKI

Degussa AG, Inorganic Chemical Products Division, D-6000 Frankfurt, Germany

---

The chemistry of organophosphorus compounds, Volume 2, Phosphine oxides, sulphides, selenides and tellurides
Edited by Frank R. Hartley. ISBN: 0-471-93056-3

I. INTRODUCTION

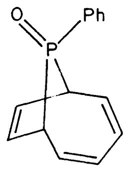
The number of publications in the field of preparative photochemistry has increased continuously. In 1958 Schönberg wrote one of the first systematic reviews on this topic, which was revised in 1968[1]. The most important publications since then have been reviewed[2]. The photochemistry of phosphine chalcogenides[3] had its beginnings with the investigations of Niebergall[4] concerning the addition of phosphine sulphides and allylsilanes. Selected results are published annually[5]. A recent review dealing with irradiation of organophosphorus(III) compounds by Dankowski appeared in Volume 1 of this series[6]. This chapter covers the photochemical reactions of phosphine chalcogenides, mainly the preparative aspects. Reactions concerning stabilizers, polymers and complexes are excluded.

II. PHOSPHINE DERIVATIVES

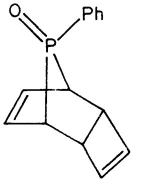
A. Molecular Reactions

1. *Oxides*

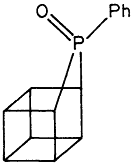
Photolysis of bridged phosphine oxide **1** in benzene through Pyrex glass yields, presumably by an intermediate **2**, the phosphine oxide **3** and some cyclooctatetraene. A similar result has been achieved by irradiation in acetone. Irradiation of a mixture of



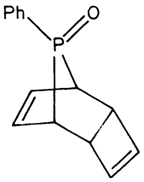
(1)



(2)



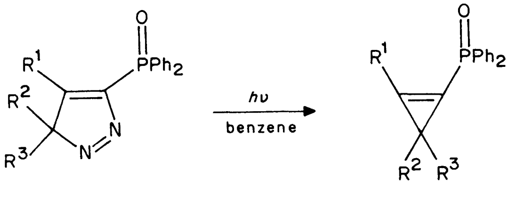
(3)



(4)

1, 2 and **4** in benzene–acetone through Corex glass also gives the oxide **3**[7]. The difference in mechanism between this reaction and that of the corresponding phosphines lies in the singlet character of the former[8] and the triplet character of the latter[9], and naturally leads to different products.

Irradiation of 5-diphenylphosphoryl-3*H*-pyrazoles (**5**) generates the phosphorylated cyclopropenes **6** via ring fissure and N_2 loss, yielding as an intermediate the corresponding (diphenylphosphorylvinyl)carbene. The use of the 4,5-isomer results in a similar product[10] (equation 1).



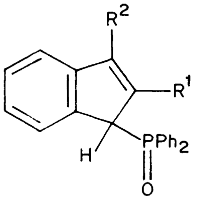
(1)

(5) **(6)**

R^1 = H, Me, Ph

$R^2 = R^3$ = Me or Ph

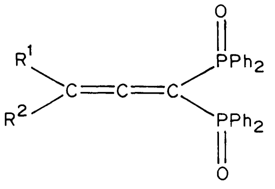
Photolysis of a 3*H*-pyrazole with a phenyl group in the C_3 position leads to the indene derivative **7**[10]. 4,5-Bis(diphenylphosphoryl)-3*H*-pyrazoles [$R^1 = P(O)Ph_2$] not only give the cyclopropene derivative but also a corresponding allene with geminal PO substituents (**8**). When R^1 = Me and R^2 = Ph, the acetylene **9** is available by a 1,3-sigmatropic shift[10]. The fact that the allene **8** is equally produced by irradiation of the cyclopropene **6** proves that the mechanism involves ring fissure and a 1,2-shift of the diphenylphosphoryl group[10].



(7)

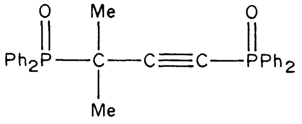
R^1 = H, Ph

R^2 = Me, Ph



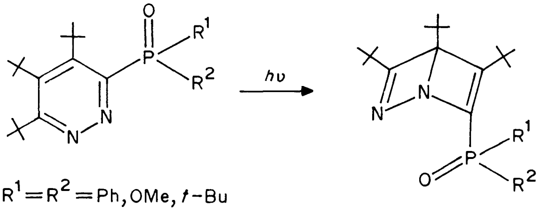
R^1=R^2=Me or Ph

(8)



(9)

On irradiation of various pyridazines **10** in benzene or pentane, the extremely thermostable 1,2-dewar pyridazines **11** are formed by an electrocyclic ring closure between N_1 and C_4[11] (equation 2). In the presence of Hg and UV light dimerization of phosphine oxide is observed[12]. Measurements of the kinetics and quantum yield of the photoisomerization reaction have been performed with 4-diphenylphosphorylstilbenes using different substituents at the second aromatic ring[13]. UV irradiation of tris(trifluoromethyl)phosphine oxide for 200 h yields a mixture of carbonyl fluoride, hexafluoroethane and phosphorus trifluoride in addition to tris(trifluoromethyl)phosphine and some uncondensable material and the educt[14].

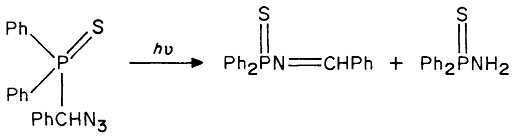


R^1=R^2=Ph, OMe, *t*-Bu
R^1=OMe, R^2=Ph

(10) **(11)** (2)

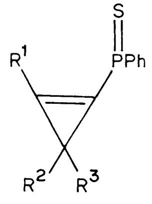
2. Sulphides

Investigations of the photochemical degradation of phenyl(diphenylthiophosphoryl)methyl azide (**12**) showed that the formation of N_2 followed by benzylideneaminodiphenylthiophosphorane (**13**) and aminodiphenylthiophosphorane (**14**) takes place, analogous to the thermally induced reaction (equation 3). This reaction is the first example of a thiophosphorus group migration[15]. Photolysis of 5-diphenylthiophosphoryl-3*H*-pyrazoles leads, like the oxophosphoranes, to the corresponding thiophosphoryl cyclopropenes (**15**) via ring fissure, N_2 elimination and ring closure of the resulting carbene[10].



$$Ph_2P(S)CH(Ph)N_3 \xrightarrow{h\nu} Ph_2P(S)N{=}CHPh + Ph_2P(S)NH_2 \quad (3)$$

(12) **(13)** **(14)**



(15)

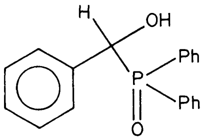
$R^1 = H, Me, Ph$

$R^2 = R^3 = Me$ or Ph

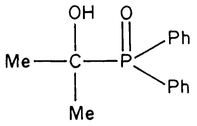
B. Reactions with Carbonyl Compounds

1. Oxides

Diphenylphosphine oxide, formed by photolysis of benzoyldiphenylphosphines, generates the corresponding alcohols **16** and **17** by addition of a carbonyl[16,17]. The reaction with phenanthrene quinone takes place analogously[18]. Formation of the reactive OPR_2 radicals is realized by H-abstraction from the corresponding phosphine oxides[19]. Irradiation of the entirely substituted phosphine oxide, however, leads to the phosphino radical PPh_2[20]. These intermediates may be trapped by reactions with carbonyl compounds, e.g. quinones[20,21].



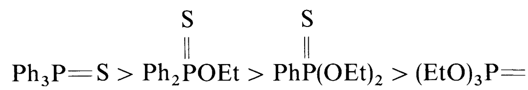
(16)



(17)

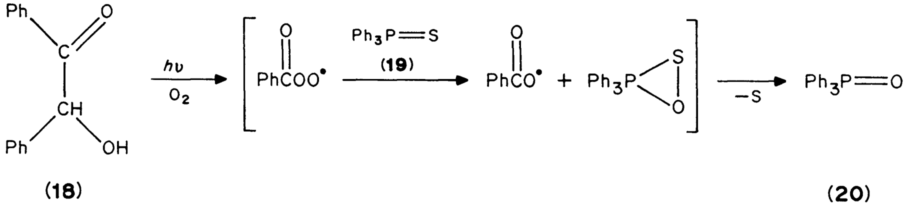
2. Sulphides

1,2-Dicarbonyl compounds, e.g. quinones and benzoin, sensitize the photooxidation of pentacovalent phosphine sulphides. Hence, photooxidative desulphurization of triphenylphosphine sulphide in the presence of benzil, biacetyl, acenaphthaquinone, pyruvic acid, methyl pyruvate, butyl pyruvate, benzoin, 2,3-dichloro-5,6-dicyano benzoquinone or 2,3,5,6-tetrachlorobenzoquinone results in conversion of the P=S group to a P=O group[22]. Whereas irradiation of phosphine sulphides in oxygenated solution in the presence of singlet oxygen sensitizers such as Rose Bengal and Methylene Blue does not lead to a reaction, the 1,2-dicarbonyl compounds do give the expected result[22]. 1,4-Quinone react with oxygen to form 1,4-biradicals which can be trapped by olefins[22,23]. The reactivity of some phosphorus compounds with regard to this reaction increases in the following series[22]:



$$Ph_3P{=}S > Ph_2\overset{\overset{\displaystyle S}{\|}}{P}OEt > Ph\overset{\overset{\displaystyle S}{\|}}{P}(OEt)_2 > (EtO)_3P{=}S$$

UV irradiation of benzoin (**18**) in the presence of oxygen leads via a Norrish type I fission process to give the corresponding peroxy radical. The latter reacts with triphenyl-



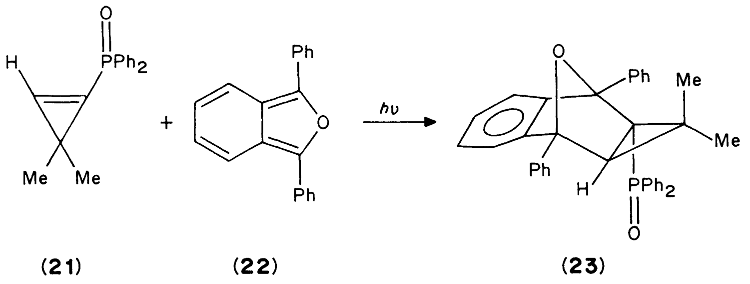
(4)

phosphine sulphide (**19**) with desulphurization to generate triphenylphosphine oxide (**20**) and sulphur[22,24,25] (equation 4). Further investigations have led to similar results concerning the irradiation of acylphosphine oxides and acylphosphonates in the presence of triphenylphosphine sulphide as a photoinitiator[26].

C. Reactions with Unsaturated Compounds

1. Oxides

Phosphine oxides are easily and quantitatively added to vinyl- or allyl-silanes in a photochemical reaction. Polyvinylsiloxanes may be employed in the same way. For example, dibutylphosphine oxide reacts with divinyldichlorosiloxane in its hydrolysed and polycondensed form to give poly{bis-[2-(dibutylphosphonyl)ethyl]siloxane}[4]. Irradiation of the phosphorylated cyclopropene **21** in the presence of diphenylisobenzofuran (**22**) as a 1,3-diene leads to a Diels–Alder reaction forming the exo-configured adduct **23**[10] (equation 5).

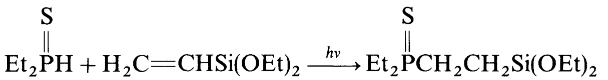


(5)

Whereas the reaction of tris(trifluoromethyl)phosphine oxide with ethylene does not result in a well characterized product, the use of tetrafluoroethylene yields a mixture of carbonyl fluoride, phosphorus trifluoride and hexafluoroethane in addition to recovered educt and polytetrafluoroethylene[14].

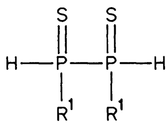
2. Sulphides

On irradiation, diethylphosphine sulphide (**24**) easily adds to the olefinic bond of triethoxyvinylsilane (**25**), generating 1-diethylthiophosphoryl-2-triethoxysilyl ethane (**26**)[4] (equation 6). Photoreaction of diethylphosphine sulphide with acrylonitrile results quantitatively in the formation of cyanoethyldiphenylphosphine sulphide[27]. Diphosphine sulphides of the general formulae **27** and **28** react in the same way. While experiments trying to add *sec*-phosphine sulphides to isocyanates or activated olefins under alkaline conditions failed, this reaction proceeds well under UV irradiation[28].

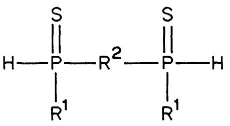


$$Et_2\overset{\overset{S}{\|}}{P}H + H_2C{=}CHSi(OEt)_2 \xrightarrow{h\nu} Et_2\overset{\overset{S}{\|}}{P}CH_2CH_2Si(OEt)_2 \qquad (6)$$

(24) **(25)** **(26)**



(27)



(28)

R^1 = alkyl or alkenyl, cycloalkyl or cyclolalkenyl or aryl group

R^2 = alkylene or arylene group

D. Reactions with Other Compounds

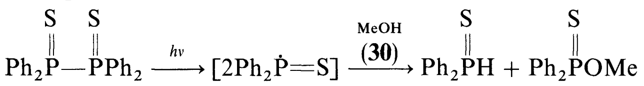
1. Oxides

Using chlorine as a radical initiator, cyclohexane reacts with phosphorus compounds having a coordination number of four and a H-substituent to yield the corresponding phosphoryl compounds[29]. In a similar manner this reaction proceeds using phosphonic acid and phosphinic acid derivatives. Chlorohexane is formed as a by-product in all cases. An explanation is to be found on the one hand in the low selectivity of the chlorine atom and on the other in the similarity of the bond energies of the cyclohexyl C—H bond[30] and the P—H bond[31].

sec-Phosphine oxide	Phosphine oxide	Yield (%)
$Et_2P(O)H$	$Et_2(C_6H_{11})PO$	84
$(C_6H_{11})_2P(O)H$	$(C_6H_{11})_3PO$	80
$Ph_2P(O)H$	$Ph_2(C_6H_{11})PO$	30

2. Sulphides

UV-irradiation of tetraphenyldiphosphine disulphide (**29**) in the presence of methanol (**30**) under a nitrogen atmosphere using a mercury lamp leads to diphenylphosphine sulphide (**31**) and *O*-methyl diphenylphosphinothioate (**32**). The reaction mechanism is explained by a homolytic fission of the P(S)—P(S) bond[32] (equation 7). A similar reaction of tetraphenyldiphosphine in alcohols is reported to occur both photolytically and thermolytically respectively(33).



$$Ph_2\overset{\overset{S}{\|}}{P}-\overset{\overset{S}{\|}}{P}Ph_2 \xrightarrow{h\nu} [2Ph_2\dot{P}{=}S] \xrightarrow{\substack{\text{MeOH}\\ \textbf{(30)}}} Ph_2\overset{\overset{S}{\|}}{P}H + Ph_2\overset{\overset{S}{\|}}{P}OMe \qquad (7)$$

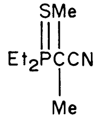
(29) **(31)** **(32)**

While the irradiation of tetraethyldisphosphine disulphide in carbon disulphide or methanol in the presence of Rose Bengal as a sensitizer and oxygen does not lead to the insertion product **33**, reaction in benzene does produce this product, sulphur and

$$Et_2\overset{\overset{\displaystyle S}{\|}}{P}O\overset{\overset{\displaystyle S}{\|}}{P}Et_2$$

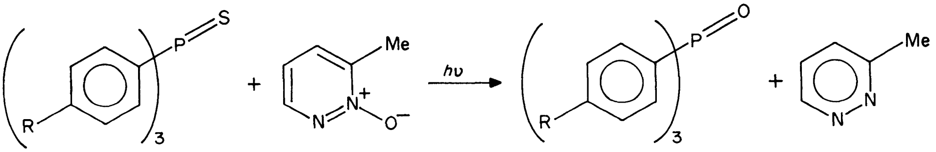
(33)

diethylphosphinic acid. The last is generated by oxidative desulphurization of the P=S group[32]. Photoreaction of tetraethyldiphosphine disulphide with α,α′-azobisisobutyronitrile in benzene solution only yields IR and mass spectroscopically determined amounts of diethyl-1-cyano-1-methylethylphosphine sulphides (**34**)[32].



(34)

Investigations of the photochemically induced transfer of oxygen atoms of heterocyclic *N*-oxides to phosphine sulphides have primarily been undertaken with *P*-substituted phosphine sulphides (**35**) and 3-methylpyridazine-2-oxides (**36**) yielding the corresponding *P*-oxides (**37**) and the pyridazine **38**[34] (equation 8).



(35) **(36)** **(37)** **(38)**

R=Me, MeO, H, Cl, MeO$_2$C

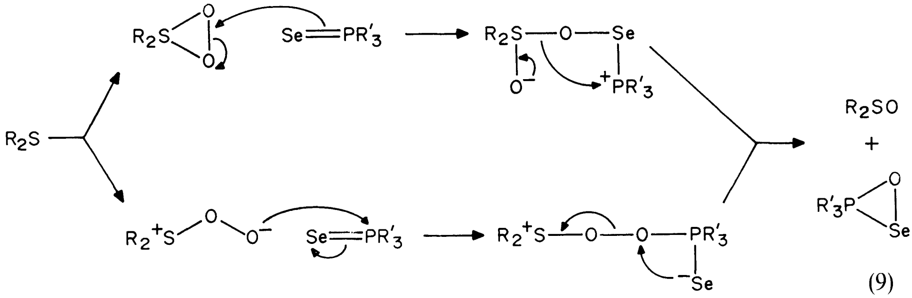
(8)

On photolysis of pyridazine oxides in the presence of *para*-substituted triarylphosphine sulphides, no significant dependence on substitution is shown in the formation of the resulting phosphine oxides[35]. The lack of a substitution effect implies either that the oxygenating species is not a strong electrophile or, being an electrophile, that the reactivity towards thiophosphoryl species is very high and, therefore, the selectivity is low. A similar effect is known in carbene chemistry[36]. Such oxidation reactions are presumably of high ecological importance for the use of organophosphorus insecticides in agriculture[37,38].

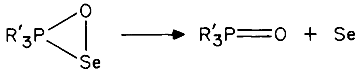
Photooxidation of dialkyl sulphides leads to the corresponding sulphur peroxidic species, which react with phosphine sulphides to give dialkyl sulphoxides[39].

3. Selenides

The oxidation desulphurization at pentacovalent phosphorus by photogenerated peroxidic species also proceeds as a deselenation, similar to the reaction of sulphides already described. The reaction mechanisms in equations 9 and 10 have been proposed[39]. The reaction is not restricted to dialkyl sulphides but also finds applications in the photooxidation of diphenyldiazomethane with benzophenone as product instead of sulphoxides[39].

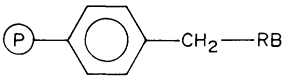


(9)



(10)

Photooxidation of triphenylphosphine selenide in the presence of Rose Bengal or polystyrene- and silica gel-supported Rose Bengal exhibits different reactivities in the formation of triphenylphosphine oxide in different solutes[40]:

RB	$Me_2C{=}O < MeCN < MeOH < MeOH\text{-}CHCl_3$
	$MeOH < MeCN <$ benzene $< CCl_4 <$ benzene—$MeOH < CH_2Cl_2 < CHCl_3 < CH_2Cl_2\text{-}MeOH$
Ⓢ—$(CH_2)_3$—RB	$MeOH < MeCN <$ benzene $< CH_2Cl_2\text{-}MeOH < CHCl_3 < CH_2Cl_2 < CCl_4$

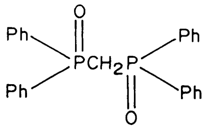
RB = Rose Bengal; Ⓟ = polystyrene copolymer; Ⓢ = silica gel

The formation of phosphine oxides is inhibited by the addition of a typical singlet oxygen quencher, 1,4-diazobicyclo[2.2.2]octane (dabco), especially in non-polar solvents[40].

E. Radiolysis

1. *Oxides*

Tetraphenylmethylenediphosphine dioxide (**39**) in $CHCl_3$ shows high stability to γ-radiation[41].

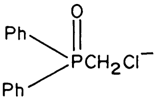


(39)

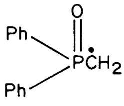
F. Miscellaneous

1. *Oxides*

Numerous EPR-investigations have been performed concerning the formation of radicals, e.g. photochemical reactions of quinonoid compounds[19], carbenes and ketones[21], 3-methyl-3-nitrosobutan-2-one, nitroso-*tert*-butane, nitrosobenzene and α-phenyl-*N*-*tert*-butylnitrone[42] with phosphine oxides. These have involved kinetic and spectroscopic characterization of the diarylphosphonyl radical[43]. X-irradiation of phosphine oxides leads to phosphino radicals[44] or to phosphonyl radicals[20], whereas on using (chloromethyl)diphenylphosphine oxide at 3 K the chloro-anion **40** is formed, although the C-radical **41** is formed at 70 K[44]. Formation of the corresponding radicals on γ-irradiation has been investigated using the following substrates: triamylphosphine oxide[45], tri-*n*-butylphosphine oxide[46], trimethylphosphine oxide[47] and triphenylphosphine oxide[48].



(40)



(41)

2. Sulphides

Numerous EPR investigations provide proof of radical formation, e.g. diphenylphosphino radicals are generated on X-irradiation of single crystals of triphenylphosphine sulphide[20,44]. Diphenylphosphine sulphide gives the thiophosphonyl radical[49] and *tert*-phosphine sulphides yield thiophosphonyl radicals instead of the corresponding phosphoranyl radicals[50]. Quantum chemical computations have been performed for the dialkylphosphine sulphide[51] and the trialkylphosphine sulphide[52] systems. Investigations have been published describing the generation of radicals by γ-irradiation of triphenylphosphine sulphide[48,53] and tetramethyldiphosphine disulphide[54].

3. Selenides

Radical formation has been identified by single crystal EPR measurement, e.g. methylphenylpropylphosphine selenide gives a σ^* radical anion[50]. The measurements provide detailed information about its geometric and electronic structure. After X-irradiation of trimethylphosphine selenide, two different phosphorus-centred radicals are observed in the EPR experiment[52], similarly to the photolysis of tricyclohexylphosphine selenide[52].

III. ACYLPHOSPHINE DERIVATIVES

A. Molecular Reactions

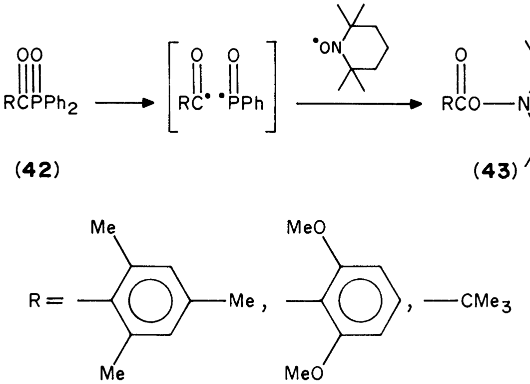
1. Oxides

Photolysis of acylphosphine oxides yields radicals via type I fission of their triplet states[55].

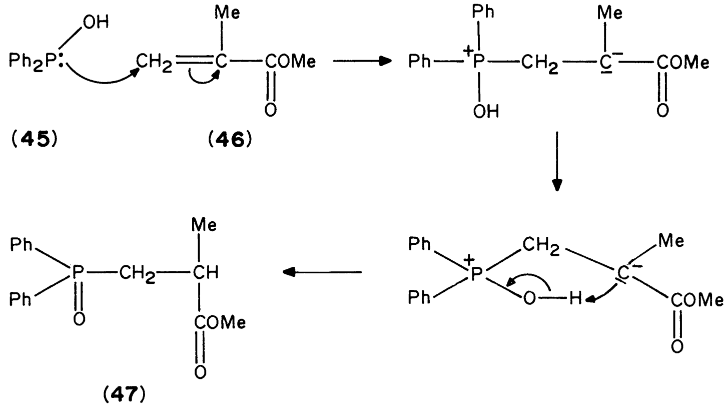
B. Reactions with Other Compounds

1. Oxides

Photoinduced α-fission of acylphosphine oxide **42** leads to the adducts **43** and **44** by radical intermediates which can be scavenged using 2,2,6,6-tetramethylpiperidine-1-oxyl (tmpo)[56] (equation 11). Chemical trapping experiments using tmpo have proved to be a valuable means for the elucidation of reaction mechanisms[57–59]. Irradiation of trimethylbenzoyldiphenylphosphine oxide leads, in the presence of *N*-methyldiethanolamine, to the corresponding ester and diphenylphosphinous acid[60]. This can be explained by attack of the amino alcohol on the electron-deficient carbonyl group. The pentavalent form of the tautomeric pair diphenylphosphine oxide–diphenylphosphinous acid prevails because of the possibility of dπ–pπ bond formation. Nevertheless, the nucleophilic character of the phosphinous acid **45** is revealed by the Michael addition of methyl methacrylate (**46**) yielding **47**[60] (equation 12).

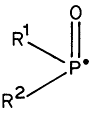


(11)



(12)

The phosphonyl radicals **48** show high reactivity towards olefins such as methacrylonitrile, styrene, methyl methacrylate, acrylonitrile, methyl acrylate, butyl vinyl ether and vinyl acetate[61]. This can be ascribed to their tetrahedral structure. In the presence of



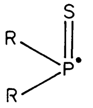
(48)

R^1,R^2 = Ph,Ph
Ph,OCHMe$_2$
Me,OMe
OMe,OMe
OEt,OEt

oxygen the radicals formed by a Norrish type I cleavage process cause oxidative desulphurization at pentacovalent phosphorus.

2. *Sulphides*

Acylphosphine sulphides react in a similar manner to their oxygen analogues. Compared with the phosphine oxides their reactivity towards olefins is about one order of magnitude lower[62]. Here, the reactive agent is the thiophosphonyl radical **49**.

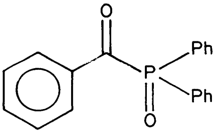


(49)

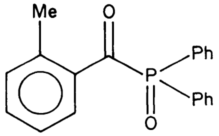
C. Use as Polymerization Initiators

1. *Oxides*

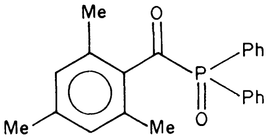
The results of the investigations described in the last section point to the most important application of acylphosphine oxides as photoinitiators[63]. Compared with acetophenones they show a red shift of the UV absorption maximum of about 50 nm[64]. The first species to be investigated which were stable against solvolysis were phosphine oxides (**50**–**53**) prepared by Arbuzov synthesis[64–66].



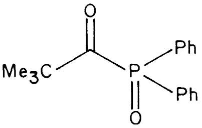
(50)



(51)



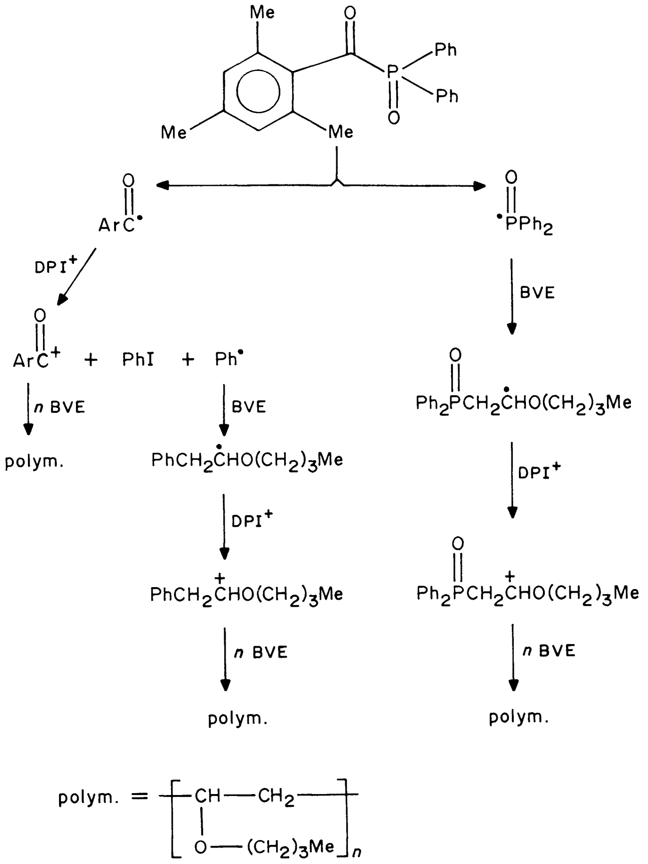
(52)



(53)

Reactions of acylphosphine oxides and also other photoinitiators are described phenomenologically[67]. Trimethylbenzoyldiphenylphosphine oxide promotes the cationic polymerization of butyl vinyl ether in the presence of diphenyliodonium ions. The reaction mechanism shown in equation 13 is proposed[68].

Although stable onium salts have been shown to be good photoinitiators for cationic polymerization[69], it has to be admitted that in the absence of acylphosphine oxide the reaction described above does not yield the polymer. Investigations of the mechanism have been performed similarly using tetrahydrofuran[68,70] and (3,4-epoxycyclohexylmethyl)-3′, 4′ -epoxycyclohexane carboxylate[71]. The reactivity of several acylphosphine oxides is comparable to that of the corresponding acetophenone derivatives[65].

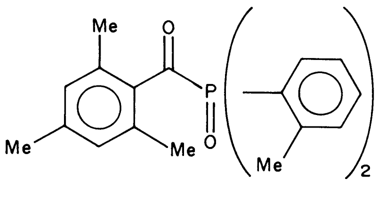


(13)

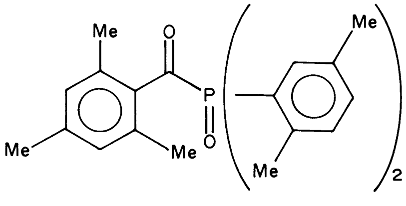
BVE = butyl vinyl ether
DPI$^+$ = diphenyliodonium ion

Photochemical polymerization yielding copolymers containing isocyanate groups can be achieved with acylphosphine oxides. For example, reaction of vinyl isocyanate, 2-ethylhexyl acrylate, methyl acrylate, methyl acetate and *tert*-butyl chloride in the presence of 2,4,6-trimethylbenzoyldiphenylphosphine oxide all lead to the corresponding polymers[63]. Photopolymerization of acrylates is enhanced by the addition of a leuco dyestuff such as triphenylmethane rosaniline[72]. Photoinitiators are used in the production of acrylic resins in both non-pigmented[73] and TiO_2-pigmented systems[74]. Different P=O and C=O units containing initiators have been compared by the method of thin-film polymerization of acrylates[66] and unsaturated polyesters[75] using laser nephelometry.

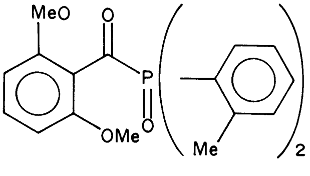
Acylphosphine oxides can be used as photoinitiators for unsaturated polyesters with[73,76,77] and without[76,78] using solvents. For example, a hardened film is developed by irradiation of a TiO_2 containing styrene solution of the unsaturated polyesters derived from tetrahydrophthalic anhydride, maleiic anhydride and diethylene glycol[79]. Various useful phosphine oxides (**54–70**) have been synthesized and characterized[76,79,80]. The sunlight-induced photohardening of some polymer systems can be achieved by using additional initiators such as benzil dialkyl ketals and/or methylthioxanthone together with phosphine oxides[81].



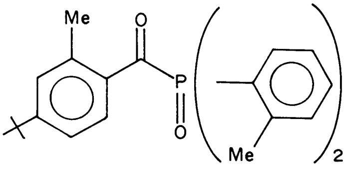
(54)



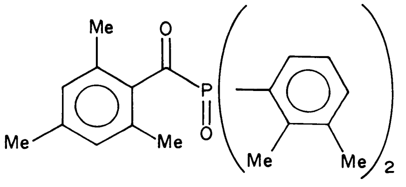
(55)



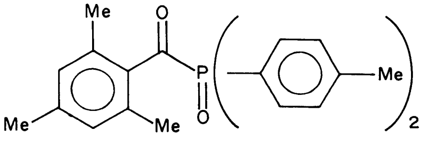
(56)



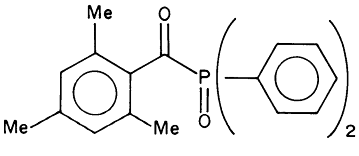
(57)



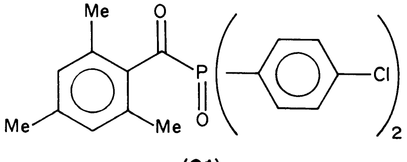
(58)



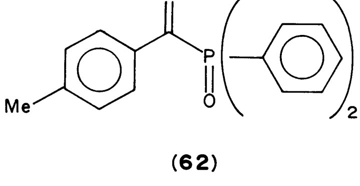
(59)



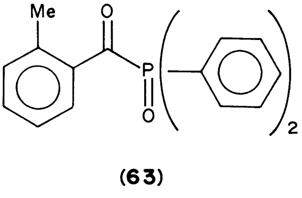
(60)



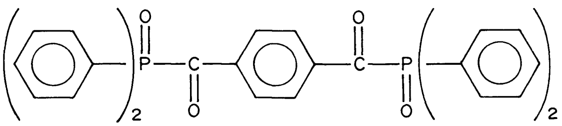
(61)



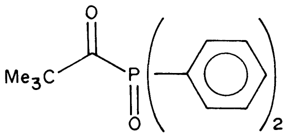
(62)



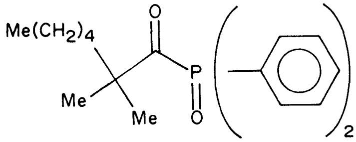
(63)



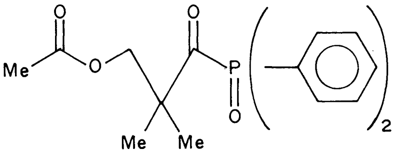
(64)



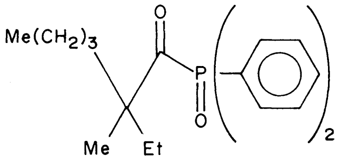
(65)



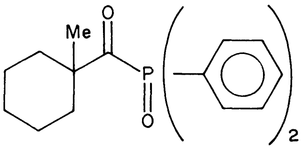
(66)



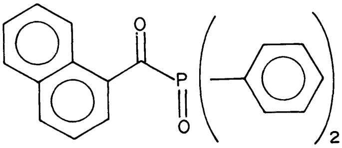
(67)



(68)



(69)



(70)

2. Sulphides

In the presence of acylphosphine oxides or sulphides, photopolymerization can be induced of oligomeric epoxyacrylates such as bisphenol A diglycidyl ether, trimethylpropane triacrylate, Michler's ketone (tetramethyl-*p*,*p*-diaminobenzophenone) and Victoria Blue[72]. The exposure times are as follows:

Initiator	Irradiation cycle
2,4,6-Trimethylbenzoyldiphenylphosphine oxide	5
2,4,6-Trimethylbenzoyldiphenylphosphine sulphide	5
2,4,6-Trimethylbenzoylditolylphosphine oxide	5
2,4,6-Trimethylbenzoylditolylphosphine sulphide	7

The time of exposure required to obtain a sufficient degree of polymerization is extended in the absence of a sensitizer, e.g. Michler's ketone[72]. Acylphosphine sulphides can also be used as initiators in the polymerization of unsaturated polyesters[77].

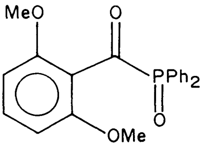
D. Miscellaneous

1. Oxides

Kinetic and mechanistic aspects concerning the initiation of free radical polymerization by acylphosphine oxides have been reported[82,83]. These compounds show relatively strong absorptions at 350–400 nm[84]. Flash photolysis of *o*-methylbenzoyldiphenylphosphine oxide indicates that α-fission competes with enolization (triplet state). A high quantum yield is found for the formation of the diphenylphosphonyl radical[82,83]. The bimolecular rate constants for the reaction of phosphonyl radicals with several monomers in cyclohexane have been reported[83].

Absorption measurements of 2,4,6-trimethylbenzoyldiphenylphosphine oxide in dilute solutions of benzene, methanol and dichloromethane using 20-ns flashes of 347 nm radiation indicate the formation of phosphonyl radicals. The singlet and triplet lifetimes were estimated as $\tau < 1$-ns, the singlet energy being around 288 kJ mol^{-1}. Rate constants for the reaction with olefinic compounds are 6.0×10^7 (styrene and methyl methacrylate), 2.7×10^7 (methylcrylate), 1.8×10^7 (acrylonitrile), 5.0×10^6 (*tert*-butyl vinyl ether) and 2.0×10^6 (vinyl acetate). The quantum yield of radical formation lies in the range $\phi = 0.5$–0.7[85].

The influence of methyl substitution in benzoyldiphenylphosphine oxides has been investigated under flash photolytic conditions[86] in addition to reactions of pivaloyldiphenylphosphine oxide[87]. The use of Fourier transform infrared (FTIR) spectroscopy gave helpful hints in the determination of the photoinitiative efficiencies of acylphosphine oxides, e.g. 2,4,6-trimethylbenzoyldiphenylphosphine oxide[88]. The flash photolysis ESR method together with chemically induced dynamic electron polarization (CIDEP) allowed the mechanism of photochemical reactions leading to the formation of radicals to be explained[89,90]. After photolysis of 2,6-dimethoxybenzoylphosphine oxide (**71**) with a 308-nm laser, the ESR signals have been evaluated by time integration spectroscopy (TIS)[91].

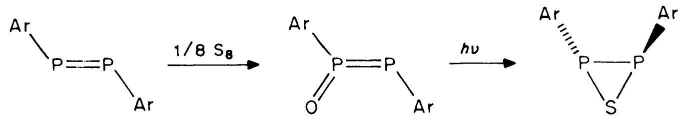


(71)

IV. PHOSPHENE DERIVATIVES

A. Sulphides

Reactions of phosphorus (III) compounds with pπ–pπ double bonds have occasionally been investigated[92,93]. The sterically stable educt (*E*)-bis(2,4,6-tri-*tert*-butylphenyl)-diphosphene (**72**) readily reacts with elemental sulphur to give the monosulphide **73**.



(14)

(72) **(73)** **(74)**

Ar = 2,4,6-tri-*t*-BuC$_6$H$_2$

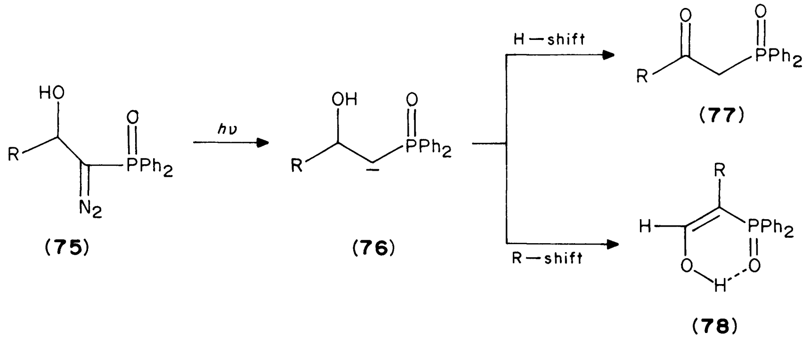
After UV irradiation in toluene solution, (*E*)-2,3-bis(2,4,6-tri-*tert*-butylphenyl)-1,2,3-thiadiphosphirane (**74**) is formed quickly[94] (equation 14). Even in the solid state the sulphide **73** after irradiation gives the isomeric diphosphirane **74**.

V. DIAZOPHOSPHINE DERIVATIVES

A. Molecular Reactions

1. Oxides

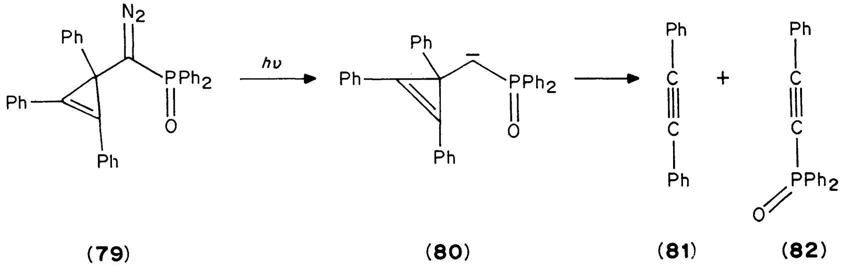
Diazo compounds produced in an aldol-like reaction of (diazomethyl)diphenylphosphine oxide with aldehydes show two competing reaction pathways after UV irradiation: H- and R-migration. For example, photolysis of (1-diazo-2-hydroxypropyl)diphenylphosphine oxide (**75**) yields the carbene **76** which undergoes H-shift predominantly to form (2-oxopropyl)diphenylphosphine oxide (**77**). In other cases the carbenes are less reactive and undergo R-migration to form (2-hydroxyvinyl)diphenylphosphine oxide (**78**)[95] (equation 15). This reaction occurs similarly to the copper(I) acetylacetonate-catalysed thermolysis[95].



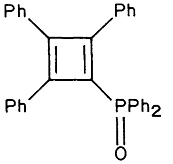
(15)

R = Me, 4-MeC$_6$H$_4$, Ph, 4-NCC$_6$H$_4$, 2-naphthenyl, 2-thienyl

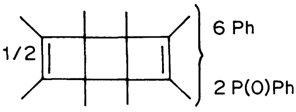
After irradiation of (diazomethyl)cyclopropene (**79**), the carbene **80** is obtained, which decays to give the acetylenes **81** and **82** in a sort of chelatropic reaction, whereas by widening of the ring the phosphorylated cyclobutadiene **83** is formed, which in turn dimerizes to give **84**[96] (equation 16).



(16)



(83)

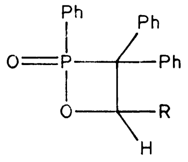


(84)

B. Reactions with Carbonyl Compounds

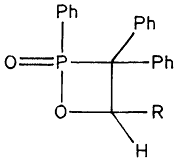
1. Oxides

After irradiation with UV light (diazobenzyl)diphenylphosphine oxide yields the phosphorylcarbene with N_2 loss, showing a 1,2-phenyl shift from phosphorus to the carbene carbon atom[97,98]. A short-lived intermediate is (diphenylmethylene)phenylphosphine oxide with the rare coordination number of 3. Isolation of the reactive 'phosphene' species has not been achieved in this system[99]. With carbonyl compounds trapping of these phosphines is possible. For example, irradiation of (diazobenzyl)-diphenylphosphine oxide in the presence of benzaldehyde or 1-naphthaldehyde in benzene yields the corresponding 1,2-oxaphosphetanes **85** and **86** in addition to the cyclopropanated solvent by [2 + 2]-cycloaddition of the carbene with the aldehydes[100].



R = Ph

(85)

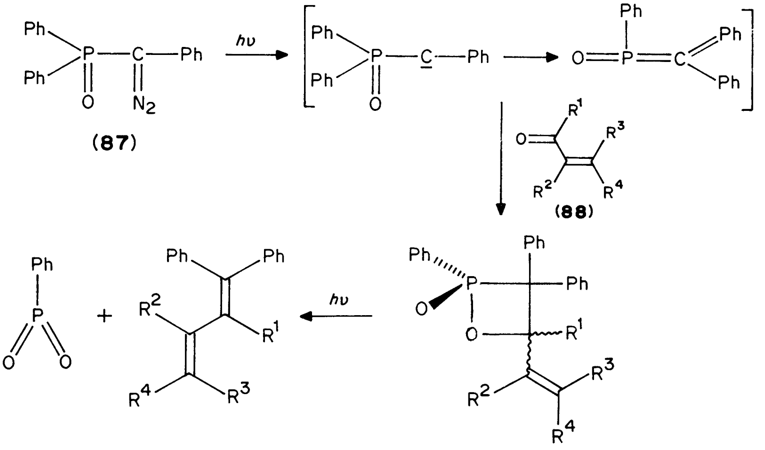


R = α-naphthyl

(86)

Irradiation of the (diazo)phosphine oxide **87** in the presence of α,β-unsaturated carbonyl compounds **88** yields 2-oxo-2,3,3-triphenyl-4-vinyl-1,2-oxaphosphetanes (89) via the intermediates described above. A subsequent cycloreversible reaction, such as an olefination, leads to butadienes or hexatrienes (**90**), respectively and dioxophenylphosphorane (**91**)[101-103] (equation 17). The carbene PhP(O)CPhBz, produced photochemically from the corresponding diazo compound, undergoes [4 + 2]-cycloaddition with aldehydes and ketons, e.g. BzPh, *p*-RPhBz (R = OMe, Me, Cl), AcMe, AcPh, cyclohexanone, $AcCMe_3$, AcH, BzH, Cl_3CCHO, crotonaldehyde and cinnamaldehyde. In the case of BzPh the heterocyclic **91–94** are obtained[104].

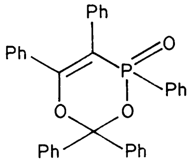
Triphenylphosphene **95**, produced in a photoreaction, reacts with tropone[96] in an [8 + 2]-cycloaddition reaction to give 3,3α-dihydro-2,3,3-triphenyl-2*H*-cyclohept[d]-1,2-oxaphosphole-2-oxide (**97**) (equation 18). The [2 + 2]-adduct is not obtained[105]. Comparisons with the *C*-analogue diphenyl ketene have been published[106]. The reaction of the carbene with tetracyclone yields the [6 + 2]-adduct **98** and the [12 + 2]-adduct **99**[105]; the structure of **98** is known from X-ray analysis.



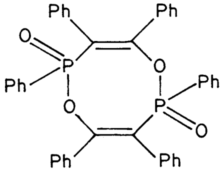
(87) (88) (89) (90) (91)

(17)

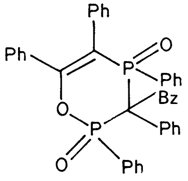
R^1 = Ph, *p*-MePh, H, Me, *p*-CH=CHPhOMe, CH=CMe3
R^2 = H, Me
R^3 = H, Ph, Me
R^4 = *p*-MeOPh, *p*-MePh, H, Ph, Me



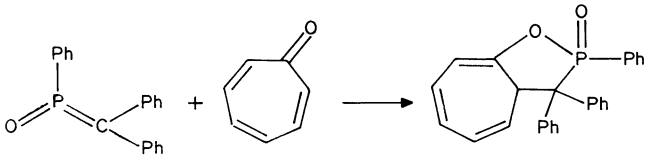
(92)



(93)

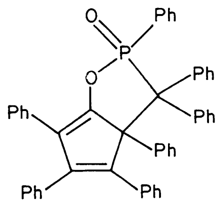


(94)

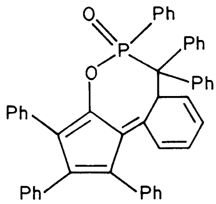


(95) (96) (97)

(18)



(98)

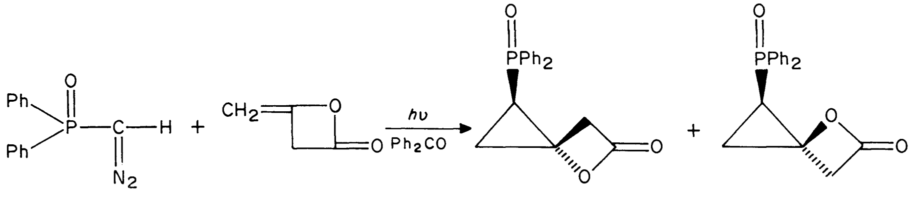


(99)

C. Reactions with Other Compounds

1. Oxides

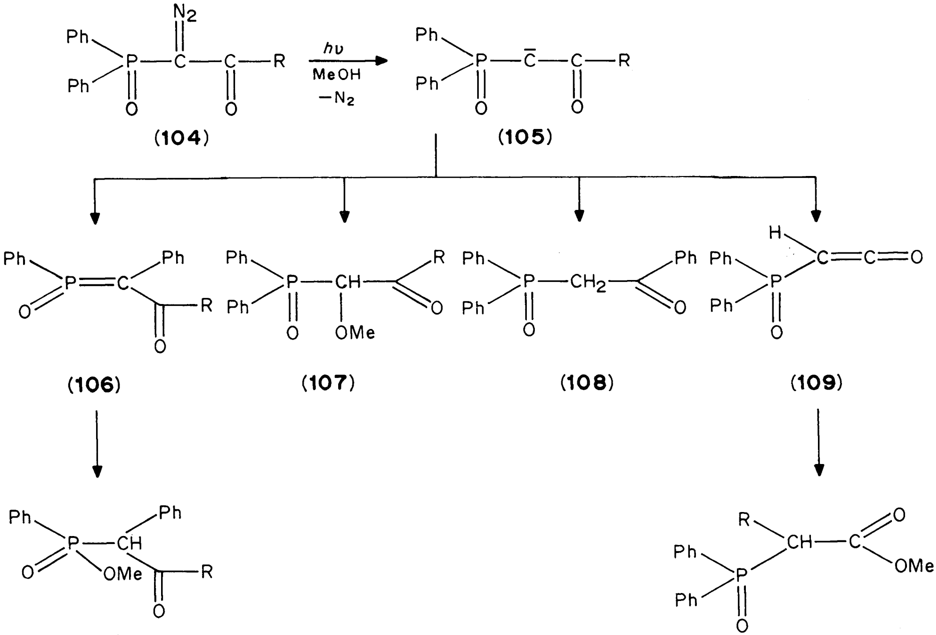
Photolysis of (diazobenzyl)diphenylphosphine oxide in benzene yields 7-(*exo*-diphenylphosphoryl)-7-*endo*-phenylnorcaradiene as the adduct of the carbene with the solvent[100,101]. After reaction of (diazomethyl)diphenylphosphine oxide (**100**) with ketene **101** in the presence of benzophenone in CH_2Cl_2 under nitrogen, two products showing a spiro structure are obtained, i.e. (*E*)-1-(diphenylphosphinyl)-5-oxo-4-oxaspiro[2.3]-hexane (**102**) and the corresponding *Z*-isomer **103**[107] (equation 19). In a similar manner diketene reacts with α-diazoketones[108-110].



(100) **(101)** **(102)** **(103)**

(19)

The carbene reactions of substituted (diazomethyl)diphenylphosphine oxide **104** in methanol proceed in a complex sequence. At the carbene stage (**105**), P/C—Ph shift competes with formation of the phosphinic ester **110** via the intermediate **106** and with



(104) **(105)**

(106) **(107)** **(108)** **(109)**

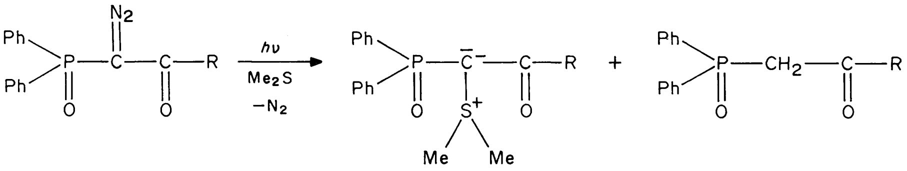
(110) **(111)**

R = Me, Ph, *p*-BrPh, *p*-MeOPh, *p*-Me₂NPh, *p*-O₂NPh

(20)

formation of the carboxylic ester **111** via C/C—R shift and the ketenes **109**. OH-insertion yields the methoxy compound **107** and the acyl methane **109** is formed via reductive N_2 elimination[111] (equation 20). The methoxy compound **107** may undergo cyclomerization to the corresponding oxetanes by intramolecular reduction of the carbonyl group[111]. This reaction should proceed via the diradical similarly to the formation of cyclobutanol[112,113]. Presumably for steric reasons, only the *trans* isomers (P—/acyl group) of the resultant oxetanes could be detected[111].

(Diazobenzyl)diphenylphosphine oxide reacts with H_2O with OH insertion and via a Wolff rearrangement with H_2O addition to give the α-hydroxyphosphine oxide and the diphenylmethyl phenylphosphinic acid[114]. Using (diazomethyl)diphenylphosphine oxide it could be shown that the P/C—Ph shift product also reacts with other protic nucleophiles than H_2O and methanol, e.g. with isopropanol, morpholine and aniline[111]. Photolysis of the (diazo)phosphine oxides **112** in dimethyl sulphide leads to a reaction similar to a radical trap reaction to form dimethylsulphonio methanides **113** and, sometimes, the methylene compounds **114**[115] (equation 21). The first ylide syntheses were performed using bis(phenylsulphono)diazomethane[116], tetraphenydiazocyclopentadiene[117] and diazomalonic esters[118].

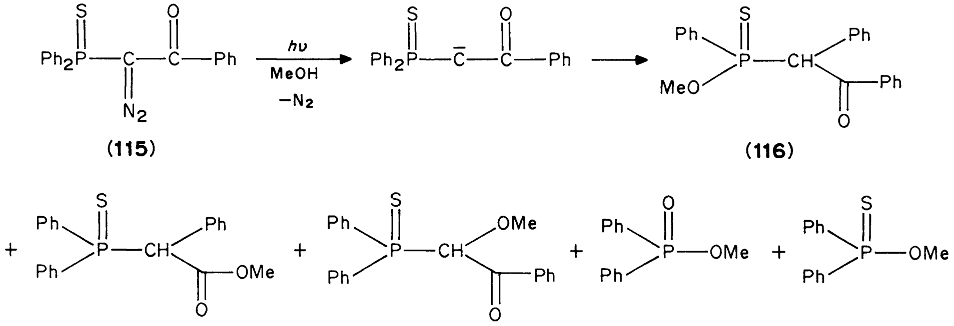


(112) **(113)** **(114)**

R = Me, Ph, *p*-BrPh, *p*-Me_2NPh, OEt, NH_2 (21)

2. Sulphides

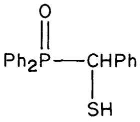
UV irradiation of benzoyldiphenylthiophosphoranyldiazomethane (**115**) in methanol yields the thiophosphinate **116** and the sulphides **117** and **118**. In methanol–benzene mixtures also the phosphinate **119** and the thiophosphinate **120** are formed[119] (equation 22).



(117) **(118)** **(119)** **(120)**

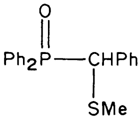
(22)

Sulphur migration is observed in the photolysis of (diazobenzyl)diphenylphosphine sulphide in alcoholic solution[120]. The mechanism can be explained by the formation of a three-membered ring intermediate. These thiirenes are found to be very reactive[121,122]. The last step can be viewed as an intramolecular Arbuzov-type reaction. Analogously, *N*-methylanilinophosphonium iodide reacts with alkoxide and thiol[123]. Consequently, in dioxane–water α-mercaptobenzyldiphenylphosphine oxide (**121**) is obtained whereas in methanol–xylene α-methylthiobenzyldiphenylphosphine oxide (**122**) is formed[120]. Irradiation in pure xylene leads only to the carbene dimer[120]. Analogously to the phosphine oxides, a 1,2-phenyl migration occurs, and phosphine sulphides yield the corresponding products to the oxides[120].



$Ph_2P(=O)\text{—}CH(SH)Ph$

(121)



$Ph_2P(=O)\text{—}CH(SMe)Ph$

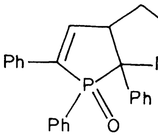
(122)

VI. PHOSPHOLE DERIVATIVES

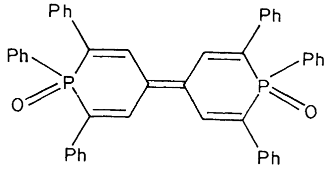
A. Molecular Reactions

1. *Oxides*

When a solution of 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide in dry peroxide-free tetrahydrofuran is photolysed under a nitrogen atmosphere, orange crystals of 3,3′,4,4′,5,5′-hexaphenyl-4,4′ -diphosphabi(cyclohexyl-2,5-dienylidene)-4,4′-dioxide are obtained in good yield[124]. Irradiation of the structurally similar pyrazoline **123** leads to the same reaction product **124**[124]. Analytical data for the product **124** are similar to those of Märkl's compound[125].

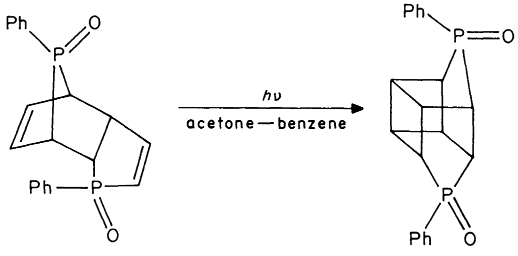


(123)



(124)

Sensitized irradiation of 1-phenyl-3-phospholene oxide dimer (**125**) led to the cage product **126** in nearly quantitative yield[126] (equation 23). Analytical investigation of this

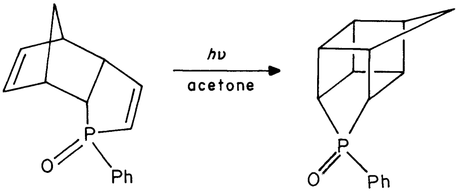


(23)

(125) **(126)**

structure indicates a cage structure obtained by intramolecular [2 + 2]-cycloaddition of the *endo*-Diels–Alder product **125**[127].

Photolysis of 3-phospholene-1-oxides yields stereoisomeric dienes depending on the substituents used only if the phenylphosphinidene oxide that is formed simultaneously is trapped[128,129]. Reaction of buta-1,3-diene with phenyldibromophosphine followed by bromination, dehydrobromination with triethylamine and [2 + 4]-addition with cyclopentadiene leads to the Diels–Alder adduct **127**. Reacting as a dienophile, the cage product **128** is formed with photochemical initiation in acetone[130] (equation 24).



(127) **(128)**

(24)

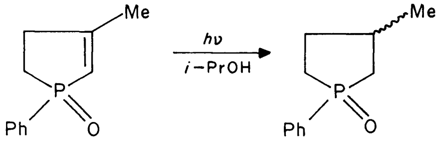
2. *Sulphides*

Irradiation of 3,4-dimethyl-1-phenyl-3-phospholene-1-sulphide in solutions of acetonitrile, diethyl ether, tetrahydrofuran or dioxane yields a polymer and the basic material. If, however, precautions are taken to ensure that the reactive phenylphosphinothiolidene intermediate is fully consumed, the corresponding dienes are obtained[128].

B. Reactions with Alcohols

1. *Oxides*

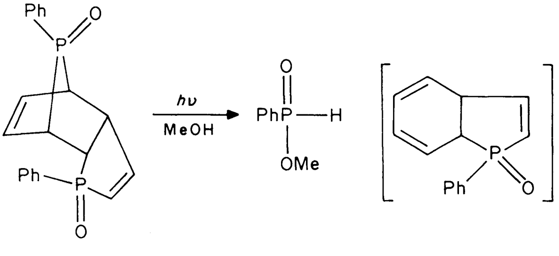
2-Phospholene oxide (**129**) is photochemically reduced in the presence of isopropyl alcohol to yield a mixture of isomeric phospholanes (**130**)[131,132] (equation 25). After irradiation of **129** in methanol–xylene, the possible ROH adducts are not obtained[131,132]. Photolysis of 1-phenyl-3-methyl-3-phospholene oxide in methanol yields methyl phenylphosphinate as the only isolable products, whereas some isoprene is detected in the reaction mixture[133]. The existence of the presumed intermediate phosphinidene oxide is proved by the following method: photolysis of phospholene oxide in benzene, addition of methanol as a trapping agent in the dark and detection of 10% methyl phenylphosphinate[133]. The reaction is assumed to proceed via a poly(phosphinidene oxide) intermediate[134].



(129) **(130)**

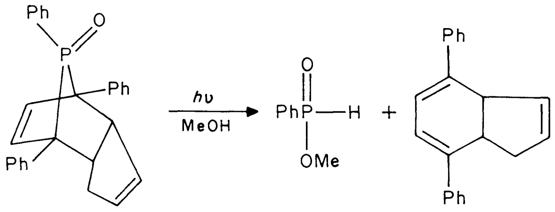
(25)

Photolysis of 1-phenyl-3-phosphole oxide dimer (**131**) in methanol yields methyl phenylphosphinate (**132**); the expected dihydrophosphindole product **133** could not be isolated[126] (equation 26). However, after irradiation in methanol solution, the adduct **134** from triphenylphosphole oxide[135] and cyclopentadiene leads to the phosphinate **135** and the dihydroindene derivative **136**[130] (equation 27).



(131) **(132)** **(133)**

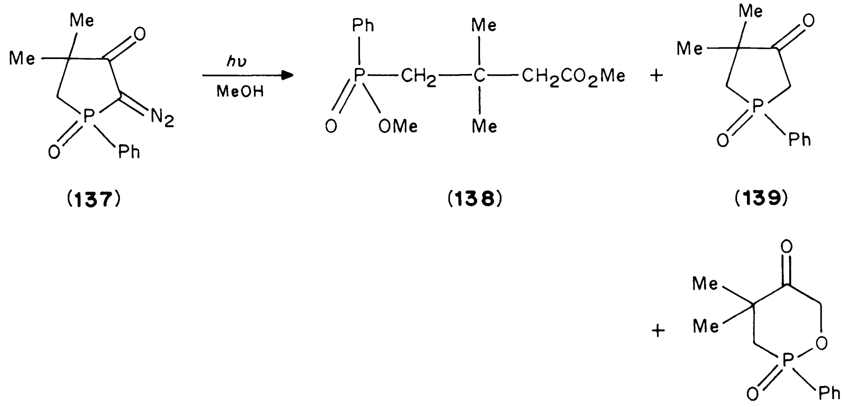
(26)



(134) **(135)** **(136)**

(27)

Photolysis of 2-diazo-4,4-dimethyl-1-phenyl-λ^5-phospholane-1,3-diene (**137**) in methanol does not show a phosphorylcarbene–methyleneoxophosphorane rearrangement[99] but formation of the carboxylic ester **138**, presumably by solvolysis and Wolff rearrangement. Further, the cyclic α-oxophosphine oxide **139** is formed by reductive nitrogen elimination[136] and the 1,2,λ^5-oxaphosphorinane **140** by O/H insertion, ether cleavage and isomerization[137] (equation 28). This isomerization to **140** corresponds to the 'diphenyl reduction' of 2,3-dihydroxy-1,3-diphenylprop-2-en-1-one[138].



(137) **(138)** **(139)**

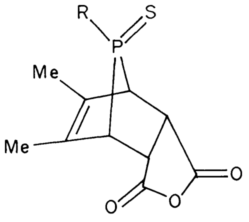
(28)

(140)

2. Sulphides

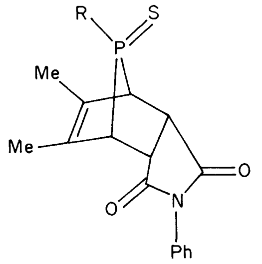
UV irradiation of 3,4-dimethyl-1-phenyl-3-phospholene-1-sulphide in methanol yields 2,3-dimethylbuta-1,3-diene, *O*-methyl phenylphosphinothioate and *O*,*O*-dimethyl phenylphosphonothioate. The product ratio depends on the length of irradiation[128]. Several methyl-substituted 3-phospholene sulphides have been investigated to determine their ability to generate dienes[128].

Different species **141–143** have been probed in relation to photofission of 7-phosphanorbornene in methanol[139]. Likewise, investigation were undertaken to determine whether the very high strain existing in the 3-phospholene ring would improve the yield of the photoreaction. Thermolysis, however, shows loss to the RP=S bridge[140–142].



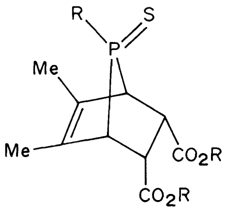
R=Ph, *n*-Bu

(141)



R=Ph, *n*-Bu

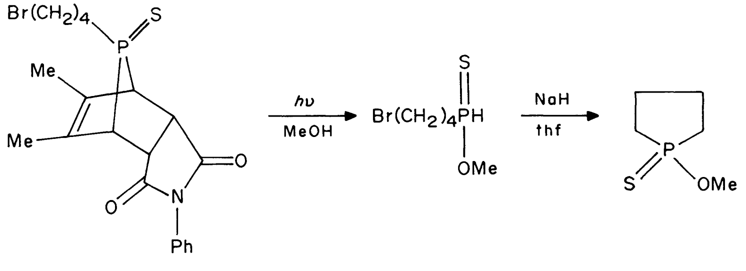
(142)



R=Me, H

(143)

For example, photolysis of 7-(4-bromobutyl)-7-phosphanorbornene (**144**) leads to *O*-methyl (4-bromobutyl)phosphinothioate (**145**) in good yield, reacting after treatment with NaH–thf to give an interesting carbon phosphorus heterocyclic 1-methoxyphospholane sulphide (**146**)[139] (equation 29). This reaction sequence is also applicable to the production of ring systems such as phosphorinanes and phosphepanes[139]. After irradiation in methanol, the adduct from triphenylphosphole sulphide and cyclopentadiene generates the corresponding thiophosphinate and diphenyldihydroindene[130].

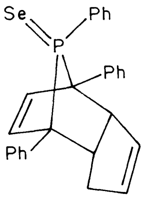


(29)

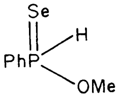
(144) **(145)** **(146)**

3. Selenides

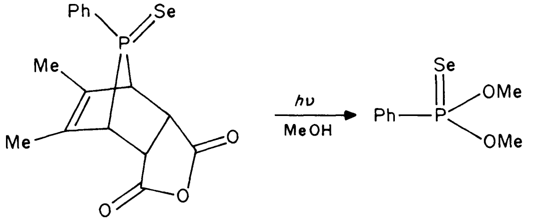
After UV irradiation in methanol, the phosphine selenide **147** reacts to give the selenophosphinate **148** via the intermediate phenyl selenoxophosphine PhP=Se[130]. Photolysis of 5,6-dimethyl-8-*anti*-phenyl-3a,4,7,7a-tetrahydro-4,7-phosphinideneisobenzofuran-1,3-dione-8-selenide (**149**) in the presence of methanol leads, after a sufficient irradiation time, to the product *O*,*O*-dimethylphenylselenophosphinate (**150**) via the corresponding phosphinate[143,144] (equation 30). A similar mechanism is shown by 5,6-dimethyl-2, 8-*anti*-diphenyl-3a, 4, 7, 7a-tetrahydro-4, 7-phosphinideneisoindole-1, 3-dione-8-selenide[144]. The central point of the reactions described above is the intermediate PhP=X (X = Se, S, O) as a typical example of the very interesting compounds with $\lambda^3\sigma^2$-phosphorus[145–149].



(147)



(148)



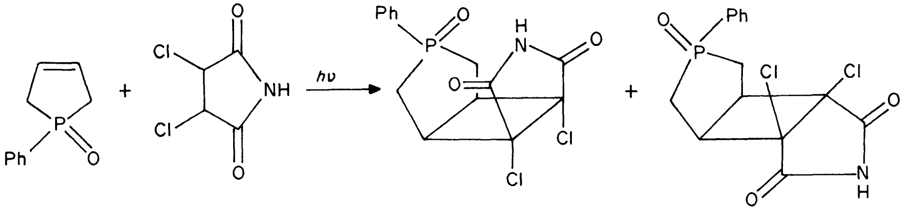
(149) **(150)**

(30)

C. Reactions with Other Compounds

1. Oxides

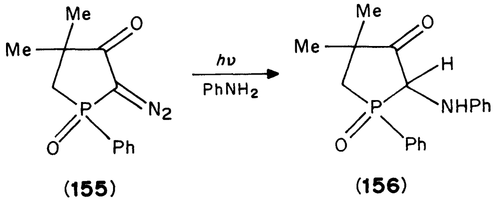
Photochemical initiation of a cycloaddition between 1-phenyl-3-phospholene-1-oxide (**151**) and dichloromaleimide (**152**) yields the two isomeric forms **153** and **154**. Their structure follows from their chemistry and the stereochemistry of their fission products[150] (equation 31). Using these compounds, the synthesis of 1-phenyldihydrophosphepin-1-oxide and some other dihydrophosphepins can be realized[150].



(151) **(152)** **(153)** **(154)**

(31)

In a similar manner, 1-methyl-3-phospholene-1-oxide, 1-ethoxy-3-phospholene-1-oxide and 1-chloro-3-phospholene-1-oxide react with dichlorovinylene carbonate. In the presence of acetophenone this addition is stereoselective. The adducts may be used as educts for the synthesis of 3-phospha[3.1.0]bicyclohexanes[151]. The cyclic α-diazo-β-oxophospholane oxide **155** undergoes photolysis in aniline via N/H insertion to give the secondary amine **156**. The difference to the reaction in basic methanol (methanolate ion) is due to the weaker nucleophilic character of the aniline[137] (equation 32).



(32)

D. Miscellaneous

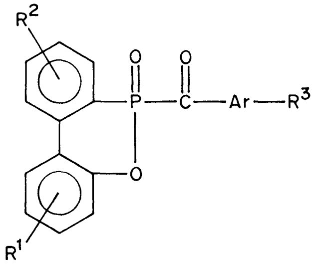
The reaction rate and the stereospecificity of the photochemical extrusion of phosphinidene oxide from the excited singlet states of 3-phospholene oxides are dependent on the configuration of the asymmetric leaving group. Consequently a steric influence on the transition state exists[129].

An effect of the elements in the phospholene chalcogenide group during the photofragmentation of 3,4-dimethyl-1-phenyl-3-phospholene derivatives has been reported, as has a methyl substitution effect in the 3-phospholene-1-sulphide species[128]. The rate of photochemical diene generation from 3-phospholene-1-sulphide is comparable to that from the corresponding oxides[128].

VII. PHOSPHORIN DERIVATIVES

A. Oxides

Although, strictly, the oxaphosphorin oxides are not phosphorus chalcogenides, they may be compared with the acylphosphine oxides because of the similarity of the reactive molecular site and the homologous reaction meachanisms. For example, the 6-acyl-(6*H*)-dibenz[*c*,*e*][1,2]oxaphosphine-6-oxides **157** are used as photoinitiators in polymerization[152]. Investigations performed on the effect of γ- and α-rays in the exatraction of americium(III) and curium(III) with tetraphenylmethylenediphosphorin dioxide in chloroform from aqueous nitric acid solution showed an unusually high resistance to radiation. Up to 15 kJ ml^{-1} could be observed[153].



R^1,R^2,R^3=halo, alkyl, alkoxy

(157)

VIII. REFERENCES

1. (a) A. Schönberg, *Präparative Organische Photochemie*, Springer, Berlin, Göttingen, Heidelberg, 1958;
   (b) A. Schönberg, G. O. Schenk and O. A. Neumüller, *Preparative Organic Photochemistry*, 2nd ed., Springer, Berlin, Heidelberg, New York, 1968.
2. D. Bryce-Smith, *Photochemistry*, Vol I, Chemical Society, London, 1969.
3. M. Dankowski, *Chem. Ztg.*, **108**, 303 (1984).
4. H. Niebergall, *Makromol. Chem.*, **52**, 218 (1962).
5. R. S. Davidson, *Organophosphorus Chemistry*, Vol 1, Chemical Society, London, 1970.
6. M. Dankowski, *The Chemistry of Organophosphorus Compounds* (ed. F. R. Hartley), Vol 1, Wiley, Chichester, 1990.
7. T. J. Katz, J. C. Carnahan, Jr, G. M. Clarke and N. Action, *J. Am. Chem. Soc.*, **92**, 734 (1970).
8. J. Saltiel, R. M. Coates and W. G. Dauben, *J. Am. Chem. Soc.*, **88**, 2745 (1966).
9. H. E. Zimmerman and P. S. Mariano, *J. Am. chem. Soc.*, **91**, 1718 (1969).
10. H. Heydt and M. Regitz, *J. Chem. Res.* (*S*), 326 (1978).
11. P. Eisenbarth and M. Regitz, *Chem. Ber.*, **117**, 445 (1984).
12. R. H. Crabtree and S. H. Brown (Yale University), *US Pat.*, 4 874 488A (1989).
13. M. V. Kuz'menko, M. G. Kuz'min, L. Alder, D. Gloyna and H. G. Henning, *Vestn. Mosk. Univ., Ser. 2 Khim.*, **20**, 349 (1979).
14. P. Cooper, R. Fields, R. N. Haszeldine, R. N. Mictchell, H. Gordon and S. N. Nona, *J. Fluorine Chem.*, **21**, 317 (1982).
15. G. Cauquis and B. Divisia, *Bull. Soc. Chim. Fr.*, 375 (1978).
16. M. Dankowski, K. Praefcke, S. C. Nyburg and W. Wong-Ng, *Phosphorus Sulphur*, 275 (1979).
17. M. Dankowski, K. Praefcke, J.-S. Lee and S. C. Nyburg, *Phosphorus Sulphur*, 359 (1980).
18. K. Praefcke and M. Dankowski, *ACS Symp. Ser.*, No. 171, 601 (1981).
19. A. Alberti, A. Hudson, G. F. Pedulli, W. G. McGimpsey and J. K. S. Wan, *Can. J. Chem.*, **63**, 917 (1985).
20. M. Geoffroy, E. A. Lucken and C. Mazeline, *Mol. Phys.*, **28**, 839 (1974).
21. A. Alberti, D. Griller, A. S. Nazran and G. F. Pedulli, *J. Org. Chem.*, **51**, 3959 (1986).
22. S. J. Buckland and R. S. Davidson, *J. Photochem.*, **36**, 39 (1987).
23. R. M. Wilson, S. W. Wunderly, T. F. Walsh, A. K. Musser, R. Outcat, F. Geiser, S. K. Gee, W. Brabender, L. Yerino, T. T. Conrad and G. A. Tharp, *J. Am. Chem. Soc.*, **104**, 4429 (1982).
24. S. J. Buckland and R. S. Davidson, *Pestic. Sci.*, **19**, 61 (1987).
25. R. S. Davidson and M. D. Walker, *Phosphorus Sulphur*, **30**, 305 (1987).
26. J. E. Baxter, R. S. Davidson, M. D. Walker and H. J. H. Hageman, *J. Chem. Res.* (*S*), 164 (1988).
27. Monsanto, *Br. Pat.*, 1 101 334 (1968).
28. L. Maier, *Helv. Chim. Acta*, **49**, 1246 (1966).
29. E. Müller and H. G. Padeken, *Chem. Ber.*, **100**, 521 (1967).
30. J. B. Hendrickson, *J. Am. Chem. Soc.*, **86**, 4864 (1964).
31. *Landolt-Börnstein*, 6th Ed., Vol. 1I, Part 2, Molekel I, Springer, Göttingen, Heidelberg, 1951.
32. T. Emoto, R. Okazaki and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **46**, 898 (1973).
33. R. S. Davidson, R. A. Sheldon and S. Trippett, *J. Chem. Soc. C*, 722 (1966).
34. A. G. Rowley and J. R. F. Steedman, *Chem. Ind.* (*London*), 365 (1981).
35. A. G. Rowley and J. R. F. Steedman, *J. Chem. Soc., Perkin Trans. 2.*, 1113 (1983).
36. P. S. Skell and M. S. Cholod, *J. Am. Chem. Soc.*, **91**, 7131 (1969).
37. M. Eto, *Organophosphorus Pesticides, Organic and Biological Chemistry*, CRC Press, Cleveland, OH, 1974.
38. C. Worthing (Ed.), *ThePesticide Manual, a World Compendium*, 6th ed., British Crop Protection Council, Croydon, 1979.
39. R. K. Bhardwaj and R. S. Davidson, *Tetrahedron*, **43**, 4473 (1987).
40. S. Tamagaki and R. Akatsuka, *Bull. Chem. Soc. Jpn.*, **55**, 3037 (1982).
41. N. E. Kochetkova, M. K. Chmutova, I. A. Lebedev and B. F.Myasoets, *Radiokhimiya*, **23**, 420 (1981).
42. M. Reinhardt, M. Schulz, N. A. Mukmeneva, O. A. Cerkasova and M. I. Kasanovskaja, *Z. Chem.*, **28**, 442 (1988).
43. N. J. Winter, J. Fossey, B. Beccard, Y. Berchadsky, F. Vila, L. Werbelow and P. Tordo, *J. Phys. Chem.*, **90**, 6749 (1986).

44. P.-O. Samskog, S.-H. Lee, C. M. Arroyo, L. D. Kispert and M. Geoffroy, *J. Phys. Chem.*, **88**, 1804 (1984).
45. A. A. Vashman and Y. I. Savel'ev, *Radiokhimiya*, **12**, 12 (1970).
46. A. Begum, A. R. Lyons and M. C. R. Symons, *J. Chem. Soc. A.*, **14**, 2388 (1971).
47. A. Begum, and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, **69**, 43 (1973).
48. G. W. Eastland and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 833 (1977).
49. M. Geoffroy, *Helv. Chim. Acta*, **56**, 1552 (1973).
50. O. M. Aagaard, R. A. J. Janssen and H. M. Buck, *Recl. Trav. Chim. Pays-Bas*, **108**, 262 (1989).
51. R. A. J. Janssen, M. H. W. Sonnemans and H. M. Buck, *J. Chem Phys.*, **84**, 3694 (1986).
52. R. A. J. Janssen, J. A. J. M. Kingma and H. M. Buck, *J. Am. Chem. Soc.*, **110**, 3018 (1988).
53. J. C. Evans, S. P. Mishra and C. C. Rowlands, *Chem. Phys. Lett.*, **72**, 168 (1980).
54. A. R. Lyons and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1589 (1972).
55. J. E. Baxter, R. S. Davidson, H. J. Hageman, K. A. McLauchlan and D. G. Stevens, *J. Chem. Soc., Chem. Commun.*, 73 (1987).
56. J. E. Baxter and R. S. Davidson, *Makromol. Chem. Rapid Commun.*, **8**, 311 (1987).
57. W. K. Robbins and R. H. Eastman, *J. Am. Chem. Soc.*, **92**, 6077 (1970).
58. H. J. Hageman and T. Overeem, *Makromol. Chem. Rapid Commun.*, **2**, 719 (1981).
59. H. Angad Gaur, C. J. Groenenboom, H. J. Hageman, G. T. M. Hakvoort and P. Oosterhoff, T. Overeem, R. J. Polman and S. v. d. Werf, *Makromol. Chem.*, **185**, 1795 (1984).
60. J. E. Baxter, R. S. Davidson, H. J. Hageman, G. T. M. Hakvoort and T. Overeem, *Polymer*, **29**, 1575 (1988).
61. T. Sumiyoshi, and W. Schnabel, *Makromol. Chem.*, **186**, 1811 (1985).
62. T. Sumiyoshi, W. Weber and W. Schnabel, *Z. Naturforsch., Teil A*, **40**, 541 (1985).
63. J. Gimpel, V. Schwendemann, A. Henne, H.-K. Schenk, H. Spoor and H. Sander (BASF), *Deutsche Offenlegungsschrift*, 32 45 297 (1982).
64. A. Henne and P. Leuchtken, *Vortragstag. Fachgruppe Photochemie* (*Ges. Dtsch. Chem.*), 8th, 1983, p. 173.
65. M. Jacobi and A. Henne, *J. Rad. Curing*, 16 (1983).
66. M. Jacobi, A. Henne and A. Böttcher, *Adhäsion*, 6 (1986).
67. H. J. Hageman, *Prog. Org. Coatings*, **13**, 123 (1985).
68. Y. Yagci and W. Schnabel, *Makromol. Chem. Rapid Commun.*, **8**, 209 (1987).
69. J. V. Crivello, in UV Curing: Science and Technology (Ed. S. P. Pappas), Technology Marketing, Stamford, CT, 1978, p. 23.
70. Y. Yagci and W. Schnabel, *Makromol. Chem., Macromol. Symp.*, **13/14**, 161 (1988).
71. Y. Yagci, J. Borbely and W. Schnabel, *Eur. Polym. J.*, **25**, 129 (1989).
72. A. Boettcher, R. Hofmann and H. Schupp (BASF), *Deutsche Offenlegungsschrift*, 36 19 792 (1986).
73. J. E. Baxter, R. S. Davidson and H. J. Hageman, *Eur. Polym. J.*, **24**, 419 (1988).
74. J. E. Baxter, R. S. Davidson and H. J. Hageman, *Eur. Polym. J.*, **24**, 551 (1988).
75. J. E. Baxter, R. S. Davidson and H. J. Hageman, *Polymer*, **29**, 1569 (1988).
76. P. Leuchtken, I. Buethe, M. Jakobi and W. Trimborn (BASF), *Deutsche Offenlegungsschrift*, 29 09 994 (1979).
77. A. Henne and A. Hesse (BASF), *Deutsche Offenlegungsschrift*, 32 12 926 (1982).
78. H. B. Kemper (Kunststoff- & Lackfabrik Kemper), *Eur. Pat. Anm.*, 0 160 723 (1984).
79. BASF, *Deutsche Offenlegungsschrift*, 31 33 419 (1981).
80. P. Leuchtken, I. Buethe and A. Hesse (BASF), *Deutsche Offenlegungsschrift*, 28 30 927 (1978).
81. H. B. Kemper (Kunststoff- & Lackfabrik Kemper), *Eur. Pat. Anm*, 0 160 724 (1984).
82. W. Schnabel and T. Sumiyoshi, *New Trends Photochem. Polym.*, Elsevier Applied Science, Barking, 1985, p. 69.
83. W. Schnabel, *J. Radiat. Curing*, **13**, 26 (1986).
84. T. Sumiyoshi, A. Henne, P. Leuchtken and W. Schnabel, *Z. Naturforsch., Teil A*, **39**, 434 (1984).
85. T. Sumiyoshi, W. Schnabel, A. Henne and P. Leuchtken, *Polymer*, **26**, 141 (1985).
86. T. Sumiyoshi, W. Schnabel, A. Henne, *J. Photochem.*, **32**, 119 (1986).
87. T. Sumiyoshi, W. Schnabel, A. Henne, *J. Photochem.*, **32**, 191 (1986).
88. J. E. Baxter, R. S. Davidson, M. A. U. de Boer, H. J. Hageman and P. C. M. van Woerkom, *Eur. Polym. J.*, **24**, 819 (1988).
89. S. Basu, K. A. McLauchlan and A. J. D. Ritchie, *Chem. Phys.*, **79**, 905 (1983).
90. C. D. Buckley and K. A. McLauchlan, *Mol. Phys.*, **54**, 1 (1985).

91. S. Basu, K. A. McLauchlan and G. R. Sealy, *J. Phys. E*, **16**, 767 (1983).
92. R. Appel, F. Knoll and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, **20**, 731 (1981).
93. E. Niecke and D.-A. Wildbredt, *J. Chem. Soc., Chem. Commun.*, 72 (1981).
94. M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Chem. Soc., Chem. Commun.*, 862 (1983).
95. W. Disteldorf and M. Regitz, *Chem. Ber.*, **109**, 546 (1976).
96. M. Regitz, A. Heydt and B. Weber, *Angew. Chem.*, **91**, 566 (1979).
97. M. Regitz, H. Scherer and W. Anschütz, *Tetrahedron Lett.*, 753 (1970).
98. M. Regitz, *Angew. Chem.*, **87**, 259 (1975): *Angew. Chem., Int. Ed. Engl.*, **14**, 222 (1975).
99. M. Regitz, A. Liedhegener, W. Anschütz and H. Eckes, *Chem. Ber.*, **104**, 2177 (1971).
100. M. Regitz, H. Scherer, W. Illger and H. Eckes, *Andew. Chem., Int. Ed. Engl.*, **12**, 1010 (1973).
101. H. Eckes and M. Regitz, *Tetrahedron Lett.*, 447 (1975).
102. M. Regitz and H. Eckes, *Tetrahedron*, **17**, 1039 (1981).
103. M. Regitz and H. Eckes, *Chem. Ber.*, **113**, 3303 (1980).
104. M. Regitz, W. Illger and G. Maas, *Chem. Ber.*, **111**, 705 (1978).
105. G. Maas, M. Regitz, K. Urgast, M. Hufnagel and H. Eckes, *Chem. Ber.*, **115**, 669 (1982).
106. R. Gompper, A. Studeneer and W. Elser, *Trahedron Lett.*, 1019 (1968).
107. T. Kato, N. Katagiri and R. Sato, *J. Org. Chem.*, **45**, 2587 (1980).
108. T. Kato and N. Katagiri, *Chem. Pharm. Bull.*, **21**, 729 (1973).
109. T. Kato , N. Katagiri and R. Sato, *J. Chem. Soc., Perkin Trans. 1*, 525 (1979).
110. T. Kato, N. Katagiri and R. Sato, *Chem. Pharm. Bull.*, **27**, 1176 (1979).
111. M. Regitz, A. Liedhegener, W. Anschütz and H. Eckes, *Chem. Ber.*, **104**, 2177 (1971).
112. F. D. Lewis and T. A. Hilliard, *J. Am. Chem. Soc.*, **92**, 6670 (1970).
113. P. Yates and A. G. Szabo, *Tetrahedron Lett.*, 485 (1965).
114. M. Regitz, W. Anschütz, W. Bartz and A. Liedhegener, *Tetrahedron Lett.*, 3171 (1968).
115. W. Illger, A. Liedhegener and M. Regitz, *Justus Liebigs Ann. Chem.*, 760, 1 (1972).
116. J. Diekmann, *J. Org. Chem.*, **30**, 2272 (1965).
117. D. Lloyd and M. J. C. Singer, *Chem. Ind. (London)*, **118** (1967).
118. W. Ando, T. Yagihara, S. Tozune and T. Migita, *J. Am. Chem. Soc.*, **91**, 2786 (1969).
119. B. Divisia, *Tetrahedron*, **35**, 181 (1979).
120. M. Yoshifuji, J.-I. Tagawa and N. Inamoto, *Tetrahedron Lett.*, 2415 (1979).
121. O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle and H. E. Gunning, *J. Am. Chem. Soc.*, **89**, 4805 (1967).
122. F. M. Benitez and J. R. Grunwell, *Tetrahedron Lett.*, 3413 (1977).
123. Y. Tanigawa, H. Kanamaru and S.-I. Murahashi, *Tetrahedron Lett.*, 4655 (1975).
124. A. N. Hughes and C. Srivanavit, *Can. J. Chem.*, **49**, 874 (1971).
125. G. Märkl and H. Olbrich, *Angw. Chem., Int. Ed. Engl.*, **5**, 589 (1966).
126. H. Tomioka, Y. Hirano and Y. Izawa, *Tetrahedron Lett.*, 4477 (1974).
127. E. Baggiolini, E. G. Herzog, S. Iwasaki, R. Schorta and K. Schaffner, *Helv. Chim. Acta*, **50**, 297 (1967).
128. H. Tomioka, S. Takata, Y. Kato and Y. Izawa, *J. Chem. Soc., Perkin Trans. 2*, 1017 (1980).
129. H. Tomioka and Y. Izawa, *J. Org. Chem.*, **42**, 582 (1977).
130. H. Tomioka, S. Miura and Y. Izawa, *Tetrahedron Lett.*, **24**, 3353 (1983).
131. H. Tomioka and Y. Izawa, *Tetrahedron Lett.*, 5059 (1973).
132. H. Tomioka, K. Sugiura, S. Takata, Y. Hirano and Y. Izawa, *J. Org. Chem.*, **42**, 3070 (1977).
133. H. Tomioka, Y. Hirano and Y. Izawa, *Tetrahedron Lett.*, 1865 (1974).
134. J. K. Stille, J. L. Eichelberger, J. Higgins and M. E. Freeburger, *J. Am. Chem. Soc.*, **94**, 4761 (1972).
135. I. G. M. Campbell, R. C. Cookson, M. S. Hocking and A. N. Hughes, *J. Chem. Soc.*, 2184 (1965).
136. L. Horner and G. Bauer, *Tetrahedron Lett.*, 3573 (1966).
137. M. Martin, M. Regitz and G. Maas, *Justus Liebigs Ann. Chem.*, 789 (1978).
138. P. Karrer, J. Kebrle and R. M. Thakkar, *Helv. Chim. Acta*, **33**, 1711 (1950).
139. S. Holand and F. Mathey, *J. Org. Chem.*, **46**, 4386 (1981).
140. Y. Kashman, I. Wagenstein and A. Rudi, *Tetrahedron*, **32**, 2427 (1976).
141. D. G. Holah, A. N. Hughes and D, Kleemola, *J. Heterocycl. Chem.*, **14**, 705 (1977).
142. C. C. Santini, J. Fischer, F. Mathey and A. Mitschler, *J. Am. Chem. Soc.*, **102**, 5809 (1980).
143. A. Schmidpeter and H. Brecht. *Z. Naturforsch., Teil B*, **24**, 179 (1969).
144. R. Hussong, H. Heydt and M. Regitz, *Phosphorus Sulfur*, **25**, 201 (1985).

145. B. Weber and M. Regitz, *Houben Weyl, Methoden der Organischen Chemie*, Vol. E1, Georg Thieme, Stuttgart, 1982, p. 22.
146. E. Fluck, *Top. Phosphorus Chem.*, **10**, 193 (1980).
147. R. Appel, F. Knoll and I. Ruppert, *Angew. Chem.*, **93**, 771 (1981).
148. N. J. Shvetsov-Shilovskii, R.-G. Bobkova, N. P. Ignatova and N. N. Mel'nikov, *Russ. Chem. Rev.*, **46**, 514 (1977).
149. E. Niecke and O. J. Scherer, *Nachr. Chem. Tech.*, **23**, 395 (1975).
150. G. Märkl and H. Schubert, *Tetrahedron Lett.*, 1273 (1970).
151. G. Märkl, G. Daunhardt and J. Siller, *Tetrahedron Lett.*, 2979 (1979).
152. H.-J. Kleiner, J. Gersdorf and U. Bastian (Hoechst), *Eur. Pat. Anmeld.*, 0 304 782 (1988).
153. N. E. Kochetkova, M. K. Chmutova, I. A. Lebedev and B. F. Myasoedov, *Radiokhimiya*, **23**, 420 (1981).

CHAPTER **5**

Spectroscopy of phosphine chalcogenides

G. DAVIDSON

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK

I. INTRODUCTION

This chapter is concerned with UV–visible, vibrational and magnetic resonance spectroscopic results available for RR′R″PX, where R,R′ and R″ are hydrogen atoms or substituents bonded to phosphorus via a carbon atom and X = O, S, Se or Te. We shall consider the spectroscopic techniques in descending order of energies for the transitions involved, which also corresponds to increasing numbers of published papers.

II. ULTRAVIOLET AND VISIBLE (ELECTRONIC) SPECTROSCOPY

Following early reports on UV absorptions of Ph_3PO by Jaffé and Freedman[1,2] and Horner and Ödiger[3], a more detailed listing of UV absorptions for Ph_3PO and related molecules was reported by Schindlbauer[4]. These are summarized in Table 1; the band

---

The chemistry of organophosphorus compounds, Volume 2, Phosphine oxides, sulphides, selenides and tellurides
Edited by Frank R. Hartley. © 1992 John Wiley & Sons, Ltd. ISBN: 0-471-93056-3

TABLE 1. UV absorptions of some phosphine oxides (band positions in nm with log ε values in parentheses)[a]

Compound	UV absorptions			
Ph_3PO	225(4.30)	259(3.13)	264(3.22)	271(3.13)
$(PhCH_2)_3PO$	219(4.26)	255(2.67)	261(2.78)	267(2.60)
Ph_2MePO	223(4.22)	259(2.96)	264.5(3.10)	271(3.13)
$PhP(O)(CH_2CH_2CN)_2$	218(4.13)	259(2.81)	265(2.93)	272(2.86)
$PhP(O)(CH_2CH_2COOH)_2$	218(4.51)	258(2.49)	264(2.63)	271(2.56)

[a] All data refer to solutions in ethanol.

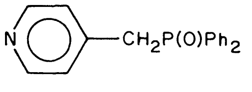
intensities were found to increase with the number of PhP units, but the band positions depended on other substituents.

UV spectra of Ph_3PO, 1,4-phenylenebisdiphenylphosphine oxide, α-naphthyldiphenylphosphine oxide and several naphthylenebisphenylphosphine oxides show that the PO group effectively 'insulates' the ligands from one another, and there is little conjugation in the molecules[5].

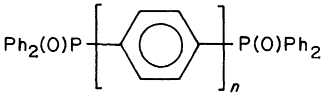
A Russian paper[6] states that curve-fitting techniques can resolve the UV absorptions of Ph_3PO into no less than ten components, but no explanation was given as to the assignment of these.

The lack of change in λ_{max} for $(p\text{-}XC_6H_4)_3PE$, where X = H, Me or MeO and E = O, or X = Me or MeO and E = S, with changing solvent was ascribed to a dominant role for the ArP^+E^- form, rather than $ArP{=}E$[7].

UV spectra of arylphosphine oxides containing electron-donating *para* substituents show progressive shifts to longer wavelength with increasing substituent electron-donor ability. This is consistent with dπ–pπ bonding between the PO group and the aromatic ring[8]. The UV absorption band of aniline is shifted to longer wavelength by *para* substituents containing phosphorus in a way typical of $^{-}$M substituents, e.g. for $p\text{-}H_2NC_6H_4P(O)Ph_2$, λ_{max} is at 267.5 nm, with $\log \varepsilon = 4.32$[9]. UV spectra of $Ph_nP(Z)(C_6H_4OMe\text{-}p)_{3-n}$, where Z = O or S and $n = 0$–2, show no dependence of the electronic effect of P on the nature of the second substituent[10]. The UV spectra of 2-, 3- and 4-picolyldiphenylphosphine oxides, such as **1**, show that they exist in that form, with no evidence for the tautomeric 4-ylidene forms[11].



(**1**)



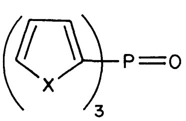
(**2**)

Small bathochromic shifts were found, due to the $Ph_2P(O)$ groups, in the UV bands of the oligophenyls in **2**, where $n = 1$–4[12]. Substitution of an NMe_2 group into the phenyl ring of bis(*p*-nitrophenylethynyl)phenylphosphine oxide gave rise to extra UV absorptions assigned to electronic transitions involving electrons delocalised through phosphorus[13].

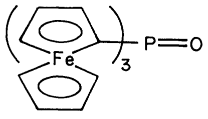
Other phosphine oxides and sulphides for which UV data have been reported are tris(*n*-methylphenyl)phosphine oxides, $n = 2$, 3 or 4 [14]; $(p\text{-}XC_6H_4)Ph_2PE$, X = H, Cl, OMe or NMe_2, E = O or S[15]; Ph_2EtPO[16]; $(p\text{-}XC_6H_4)Et_2PE$, X = H, Cl or OMe, E = O or S[17]; *cis*-4-$Ph_2P(O)C_6H_4CH{=}CHC_6H_4R$, R = 4-$Me_2N$, 3-$Me_2N$, 4-MeO-, 3-MeO or 2-MeO[18]; $R_2P(O)Ph$, $RP(O)Ph_2$, $R_2P(O)C_6H_4NMe_2\text{-}p$, $R_2P(O)Et$, R_3PO, R = $PhC{\equiv}C$-[19]; (*o*-, *m*- and *p*-$MeOC_6H_4)PhP(O)Me$[20]; $(p\text{-}CNC_6H_4)P(O)R_2$, R = Me or Ph[21]; $(2,3,5,6\text{-}Me_4C_6H)_3P(O)$ and $(2,3,5,6\text{-}Me_4C_6H)_2P(O)Ph$[22]; and $Bu^n_2P(O)CH{=}CH_2$[23].

Changes in the luminescence properties of substituted triarylphosphine oxides with the nature of the substituent have been reported [24]. The fluorescence properties of 14 tertiary phosphine oxides showed that significant fluorescence only occurred if the substituent on phosphorus was itself fluorescent, e.g. ArPhP(O)Me, where Ar = isomeric naphthyl derivatives[25]. UV data on RPh_2PO, where R = 1 = naphthyl, 9-anthryl or 1-pyrenyl, all showed intense fluorescence in the blue region[26].

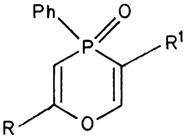
The UV spectra of **3**, where X = NR (R = H or Me), O or S, are indicative of strong $d\pi$–$p\pi$ bonding between PO and the ring[27,28]. The UV spectra of **4** and its diferrocenyl analogue show very little π-electron donation from the ferrocenyl fragment to the phosphorus[29]. $\lambda_{\max}$ values have been listed for **5**, where R, R′ = Me or Ph[30].



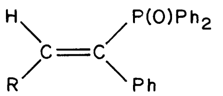
(3)



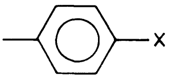
(4)



(5)



(6)



(7)

I_2, IBr and ICl complexation with phosphine oxides, sulphides and selenides was followed by shifts in characteristic UV bands of the latter compounds[31]. The UV spectra of **6**, where R = **7**, with a range of substituents X, show that the $P(O)Ph_2$ group induces a bathochromic shift in the ^1L_a and ^1L_b bands of the styrene fragment[32]. The $\lambda_{\max}$ (and log ε) values for a range of P=Se compounds have been given, including the following data for $Bu_3P{=}Se$: $\pi \rightarrow \pi^*$ 195 nm (4.18); $n \rightarrow \sigma^*$ 208 nm (4.06); $n \rightarrow \pi^*$ 238 nm (3.53)[33].

III VIBRATIONAL SPECTROSCOPY

A. Phosphine Oxides

Values of $\nu P{=}O$ in a wide range of phosphine oxides have been tabulated by Thomas[34]. The parent oxide PH_3O was prepared by red–visible photolysis of PH_3–O_3 mixtures in matrices. All its vibrational modes were seen for $H_3P^{16}O$ and most of its other isotopomers (Table 2). Normal coordinate analysis gave the following force constant values: P=O stretch, $(9.53 \pm 0.16) \times 10^2\,N\,m^{-1}$; P—H stretch, $(3.25 \pm 0.01) \times 10^2\,N\,m^{-1}$. [35]*Ab initio* SCF calculations gave calculated IR spectra of H_3PO, D_3PO and $H_3P^{18}O$ which were in good agreement with the above figures[36].

IR and Raman spectra of $Me_2P(H){=}O$ were assignable under C_s symmetry, with νPH at 2333 cm^{-1} (IR) and 2348 cm^{-1} (Raman), and $\nu P{=}O$ 1169 cm^{-1} (IR) and 1155 cm^{-1} (Raman). A normal coordinate analysis suggested that there was extensive mixing of all modes except for these two[37]. Ranges of νPH wavenumbers were listed for RR′P(H)O (2294–2380 cm^{-1}) and $R_2P(H)S$ (2288–2299 cm^{-1})[38]. IR data were listed for $CH_3(CF_3)P(H){=}O$ and $Me_2(CF_3)P{=}X$, where X = O or S[39]. νPH for (cyclo-$C_8H_{17})_2P(H)O$ showed that the P—H bond could take part in weak hydrogen bonding[40].

TABLE 2. Vibrational assignments for PH_3O (cm^{-1})

	$H_3P^{16}O$	$H_3P^{18}O$	$D_3P^{16}O$	$D_3P^{18}O$
$\nu_{as}PH$	2371.5	2371.6	—	—
$\nu_s PH$	2359.0	2367.0	1721.1	1720.0
$\nu P{=}O$	1240.2	1213.7	1217.3	1174.1
$\delta_s PH_3$	1143.5	—	843.6	840.5
$\delta_{as}PH_3$	1114.3	1114.3	—	—
δHPO	853.0	849.4	655.9	651.3

The intensity of νPH in $R_2P(H){=}O$, where R = n-C_6H_{13}, cyclo-C_6H_{11}, Ph or $PhCH_2$, correlates with the electronegativity of the phosphorus substituents[41].

A very thorough assignment of the vibrational modes of Me_3PO, Me_3PS and Me_3PSe and their perdeuteriated analogues has been made (Table 3)[42]; values of the Me torsional modes had been proposed earlier[43], and there had been several other, incomplete, studies[44–47]. There have also been a number of approximate or partial normal coordinate analyses of Me_3PO[48–54].

IR data have been collected for $Me_2P(O)CH_2X$, where X = Cl, Br or I. These show that there are equilibria between *trans* (C_s symmetry) and *gauche* (C_1) conformers in CCl_4 solution[55]. $(ClCH_2)_3PO$ has δCH_2 modes at 1391 and 1410 cm^{-1}[56]. νPO (1327 cm^{-1})

TABLE 3. Vibrational assignments (cm^{-1}) for Me_3PE, where E = O, S or Se (data for perdeuteriated analogues in parentheses)

	E		
	O	S	Se
A_1			
ν_1 νCH_3	2974(2226)	2967(2219)	2958(2218)
ν_2 νCH_3	2906(2126)	2895(2116)	2892(2117)
ν_3 δCH_3	1408(1028)	1408(1020)	1400(1016)
ν_4 δCH_3	1300(1021)	1306(1015)	1301(1016)
ν_5 ρCH_3	946(781)	951(782)	952(782)
ν_6 νPC_3	667(597)	714(648)	689(619)
ν_7 $\nu P{=}E$	1161(1165)	565(533)	441(414)
ν_8 δPC_3	320(271)	282(270)	260(232)
E			
ν_{13} νCH_3	2974(2226)	2976(2225)	2975(2230)
ν_{14} νCH_3	2974(2226)	2967(2210)	2967(2224)
ν_{15} νCH_3	2906(2126)	2895(2116)	2892(2117)
ν_{16} δCH_3	1438(1040)	1429(1043)	1425(1027)
ν_{17} δCH_3	1430(1028)	1424(1020)	1417(1023)
ν_{18} δCH_3	1282(1021)	1287(1015)	1290(1016)
ν_{19} ρCH_3	962(701)	982(647)	978(695)
ν_{20} ρCH_3	867(797)	865(822)	862(805)
ν_{21} νPC_3	741(625)	744(628)	748(627)
ν_{22} δPC_3	250(224)	282(247)	271(232)
ν_{23} ρPC_3	360(226)	229(202)	202(180)

and other modes were assigned for $(CF_3)_3PO$[57]. Detailed vibrational assignments have been proposed for $Me_2(R)P{=}O$, where R = decyl or dodecyl, which suggest that in the crystals the P=O bond is perpendicular to the plane of the hydrocarbon skeletal plane[58].

Solutions of $Ph_3P^{16}O$ and $Ph_3P^{18}O$ in CCl_4 show νPO at 1202 and 1123 cm^{-1} respectively[59]. Several other papers have discussed the vibrational spectrum of triphenylphosphine oxide, mostly relating to phenyl modes, however[60–63].

$[Me_3CC{\equiv}C]_3P{=}O$ has νP=O at 1235 and νPC_3 at 576 and 610 cm^{-1}, together with ligand modes in the expected ranges. The P=S analogue has νP=S at 689 and νPC_3 at 556 and 588 cm^{-1} [64]. νP=O assignments are summarized for $R_n(C_6F_5)_{3-n}P{=}O$, where R = Me, Et or Ph and n = 0,1 or 2, in Table 4 [65].

The νP=O wavenumbers in the IR spectra of $R^1R^2R^3PO$, where R^1,R^2 and R^3 are Ph or alkyl groups, are related by quadratic equations to the P-substituent bond energies and to the P(O)—M bond energies in their uranyl complexes[66]. The νP=O wavenumbers of $R_3P{=}O$, where R = *n*-butyl, 2-ethylhexyl, *n*-octyl or phenyl, suggest that there is no fundamental theoretical justification for equations relating νP=O to π-parameters of substituents at the phosphorus[67]. Two other reports have been made of νPO for tri-*n*-octylphosphine oxide [68,69].

A linear dependence was found between νP=X in $R_3P{=}E$, where R = alkyl and X = O, S, Se or Te, and the function $(\Sigma M/m_Pm_X)^{1/2}E_PE_X$, where M = total mass of the molecule, m_P, m_X = masses of P and X and E_P, E_X = Pauling electronegativities of P and X[70].

The IR spectra of Ph_3PX, where X = O, S or Se, suggest the following values for νP=X; 1191 (O), 637 (S) and 561 (Se) cm^{-1}. In each case $\nu_{as}PPh_3$ lay in the range 511–540 cm^{-1} [71]. νPO of R_3PO, where R = phenyl, *p*-tolyl, *o*-tolyl, 2,4-xylyl, 2,6-xylyl, mesityl or duryl, were assigned. In the *o*-tolyl and xylyl species the wavenumbers were lowered owing to interaction between the *ortho*-Me proton and the oxygen atom. Additional lowering in the last three compounds was due to further steric crowding[72]. There has been an extensive series of papers on the IR spectra of substituted triarylphosphine oxides or sulphides, in many cases proposing empirical relationships between νP=E and the electronic parameters of the substituents[73–79].

The IR intensity of νPO for Ph_3PO (1205 cm^{-1}) and other phosphoryl compounds shows no correlation with the band positions. The inductive effect of the substituents has the main influence on the intensity[80]. There has been a further report of the absolute IR intensities for the νPO band of many phosphoryl compounds, including Ph_3PO[81].

The P—Me rocking modes in (*o*-, *m*- or *p*-$MeOC_6H_4$)PhMePO were all in the range 863–902 cm^{-1} [82].

IR intensities for the ν_8 ring stretching mode (near 1600 cm^{-1}) for $(p\text{-}YC_6H_4)_3PO$, where Y = OMe, Cl, Et, Me or MeCO, and $(p\text{-}YC_6H_4)_3PS$, where Y = NMe_2, OMe, Cl, Et, Me or MeCO, suggest σ_R^0 values for PPh_2O and PPh_2S of + 0.07 and + 0.06, respectively[83]. The intensity of νCC in the IR spectra of $Ph_2P({=}O)C{\equiv}CX$, where X = H, Me, Ph or $C(OH)Me_2$, is greater than for the corresponding band in $Ph_2PC{\equiv}CX$. There was an almost linear correlation between this intensity and the Taft coefficient σ^* X for X[84].

TABLE 4. νP=O assignments for $R_n(C_6F_5)_{3-n}P{=}O$

n	νP=O (cm^{-1})		
0	1242		
1	1222 (R = Ph)	1223 (Me)	1221 (Et)
2	1201 (R = Ph)	1193 (Me)	1205 (Et)

The IR spectra of $Ph_2P(=O)CH=C=CR^1R^2$, where R^1 and $R^2 = H$ or Me, show the presence of two conformational isomers. There is therefore restricted rotation about the P—C(allene) bond. The influence of the allenic group on the P=O bond suggests that the phosphorus is conjugated with the allene system[85]. The value of νCO(aromatic) of (p-$MeOC_6H_4$)P(X)Ph_2, where X = O or S, shows that the phosphorus is acting as a proton acceptor[86].

The IR spectra of $R_3P=O$, where R = C_1–C_{16} *n*-alkyl, show that there is a dynamic equilibrium between conformers in solution. In the crystalline state only one conformer was present each time[87]. The IR spectrum of $Ph_2P(O)CH_2Ph$ shows that only the *gauche* conformation is present in the crystal. The liquid also contains a small amount of the *trans* conformer[88]. There is IR evidence for the presence of two conformers of $Ph_2P(O)CH_2C(O)NHNH_2$ in solution, in the crystal and in vitreous forms[89].

$Ph_2P(=E)P(=E)Ph_2$, where E = O or S, have νP=E at 1180 cm^{-1} (O) or 635 cm^{-1} (S)[90]. IR assignments have been made of νP=O modes for[$Ph_2P(=O)]_2CH_2$(1211, 1194 cm^{-1}) and [$Ph_2P(=O)CH_2]_2P(=O)Ph$ (1215, 1192, 1163 cm^{-1})[91]. νCC wavenumbers for $Ph_2P(X)C\equiv CP(X)Ph_2$, where X = O (2143 cm^{-1}) or S (2150 cm^{-1}) are consistent with significant X → P pπ–dπ back bonding, thereby raising the C≡C bond order by P → C dπ–pπ interaction[92]. νP=X modes were assigned for $C[CH_2P(X)Ph_2]_4$, where X = O (1187 cm^{-1}), S (625/613 cm^{-1}) or Se (588/540 cm^{-1})[93].

Shifts of νPO for a range of phosphine oxides in the presence of I_2, IBr, ICl or Br_2 show the coordination of halogen to the oxygen atom, e.g. for Bu^n_3PO, νPO decreases from 1169 to 1118 cm^{-1} in the presence of I_2 [94]. Solvent effects on the IR spectrum of (n-$C_8H_{17})_3PO$ (νPO band) show that the PO bond behaves similarly to the C=O bond in the same solvents[95]. There have been many reports on the effects of hydrogen bonding on the P=O stretching mode of phosphine oxides[96–104]. There is a linear correlation between ν_{max}(P=O) and $\Delta\delta^{31}$P for Ph_3PO in a wide range of solvents. It is therefore possible to predict NMR chemical shifts from IR results[105].

B. Phosphine Sulphides

Values of νP=S have been tabulated for a wide range of phosphine sulphides[106]. Some earlier assignments from the IR and Raman spectra of $Me_2P(H)S$[107] have been superseded by fuller data on the compound[108] and $Me_2P(D)S$[109]. The IR and Raman data were assigned in terms of C_s symmetry, with νPH and νPD at 2350 and 1714 cm^{-1}, respectively. A normal coordinate analysis showed that, apart from νPH and νCH, all of the modes were extensively mixed. Earlier references has been made to νPH assignments for $R_2P(H)S$, where R = alkyl[38].

A detailed study has been made of the IR and Raman spectra of $(CH_3)_n(CD_3)_{3-n}PS$, where $n = 0$–3[110]. Assignments for the d_0 and d_9 molecules were consistent with C_{3v} symmetry and those for the d_3 and d_6 analogues with C_s symmetry. These assignments, together with a normal coordinate analysis, complement the data referred to above[42–43]. Some approximate force constant calculations on Me_3PS were also mentioned previously[51–54]. Some partial resolution of gas-phase IR bands of Me_3PS has been achieved, with P, Q and R branches of the νPC_3 band at 575, 582 and 591 cm^{-1}, respectively[111]. Some vibrational assignments were also given for R_3PS, where R = Me or Et[112,113] or Pr^i or Ph[113]. There has been a study of the dependence of νPS in R_3PS on the electronegativity of R[70].

The IR and Raman spectra of $EtP(S)Me_2$ in the liquid phase could only be assigned on the assumption that both *gauche* and *trans* conformers were present. Only the *gauche* form persists in the solid. The vibrational spectrum of the latter was assigned completely, including a value of 110 cm^{-1} for the antisymmetric torsional mode[114]. Earlier reference was made to νCH and νCF assignments for $Me_2(CF_3)P=S$[39].

Durig *et al.*[115] have also carried out a thorough investigation of the vibrational spectra of Et_3PE, where $E = S$ or Se. In each case 60 of the 63 fundamentals were assigned, assuming C_3 symmetry. When $E = S$, but not when $E = Se$, there was strong coupling between νPE and νPC_3[115]. $\nu P{=}S$ or $\nu P{=}Se$ modes were assigned for R_3PE, $R = Me$, Pr^n, Pr^i, cyclopropyl, cyclohexyl or Ph and $E = S$ or Se. The values for $R = Pr^i$ and cyclopropyl were unusually high, presumably for steric reasons[116]. An early report listed νPS or νPSe for 15 phosphine sulphides and 13 phosphine selenides[117]. νPS values were also tabulated for $R_{3-n}(C_6F_5)_nPS$, where $R = Me$, Et or Ph and $n = 1$ or 2[118].

νPS in Ph_3PS has been assigned by a number of workers to a value of 637 cm^{-1}[71,119,120], with νPSe at 562 cm^{-1} in Ph_3PSe[120]. Other reports gave νPS in a wide range of substituted triaryl phosphine sulphides[73,74,79,83,86]. It has been suggested that νPS in R_3PS, where $R = Ph$ or Et, shows the presence of several rotamers[121].

$\nu C{\equiv}C$ in $Me_2P(S)C{\equiv}CEt$ was assigned to 2212 cm^{-1}[122]. There has been disagreement about the assignment of skeletal stretches in $Me_2P(S)P(S)Me_2$[123,124]. The more recent work suggests that $\nu_s PS$ is at 610 cm^{-1}, $\nu_{as}PS$ at 550 cm^{-1} and νPP at 510 cm^{-1}[124]. $\nu C{\equiv}C$ in $Ph_2P(S)C{\equiv}CP(S)Ph_2$ is at 2150 cm^{-1}[125].

C. Phosphine Selenides and Tellurides

A detailed assignment for Me_3PSe has already been given (Table 3)[42–43]. νPSe was also assigned for R_3PSe, where $R = alkyl$[70], or $R = Me$, Pr^n, Pr^i, cyclopropyl, cyclohexyl or Ph[116]. In Ph_3PSe, νPSe is at 561 cm^{-1}[71,120]. The equivalent mode is at 544 or 574 cm^{-1} in R_3PSe, where $R = p$- or m-MeC_6H_4, respectively[125].

A full assignment has been proposed for Me_3PTe and $(CD_3)_3PTe$, based on C_{3v} symmetry. A normal coordinate analysis suggested that there was extensive mixing of modes, with νPTe contributing significantly to bands at 226, 378 and (to a lesser extent) 674 cm^{-1}. The P–Te force constant was, as expected, smaller than that for the other PE systems[126]. The results of this work throw into considerable doubt earlier reports of νPTe modes, e.g. of values between 400 and 518 cm^{-1}, for R_3PTe, where $R = Pr^n$, Bu^n, n-C_5H_{11}, cyclo-C_6H_{11} or n-C_8H_{17}[127].

IV. MAGNETIC RESONANCE SPECTROSCOPY

The nuclei will be dealt with separately, in the following sequence: ^{31}P, ^1H, ^{13}C, ^{19}F, ^{17}O, ^{77}Se and ^{125}Te. Each paper will be referred to only once, dealing with all of the nuclei mentioned in that paper, and referring back, wherever necessary, for nuclei later in the order given above.

A. ^{31}P

An extensive list of ^{31}P chemical shifts in R_3PE, where $E = O$, S or Se, has been published[128]. These were referred to an 85% aqueous solution of H_3PO_4 as standard, as will all subsequent references, unless mentioned otherwise. The ^{31}P spectrum of $Me_2P(H){=}O$ consists of a doublet of septets, centred at -18.6 ppm, with $J_{PH} = 456$ Hz and $J_{PCH} = 14$ Hz. The ^1H spectrum contained a doublet of septuplets ($\tau 2.5$; J_{PH} 490 Hz, J_{PHCH} 3.5 Hz), due to the unique proton, and a doublet of doublets ($\tau 7.89$, J_{PCH} 14 Hz, J_{PHCH} 3.5 Hz)[129].

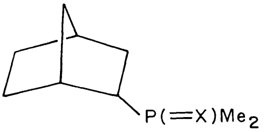
The ^{31}P spectrum of $Ph_2P(O)H$ shows a 1:1 doublet, $\delta^{31}P - 25.9$ ppm, $^1J_{PH}$ 513 Hz, while for $Ph_2P(O)D$ a 1:1:1 triplet is seen, with $\delta^{31}P - 25.7$ ppm, $^1J_{PD}$ ^{78}Hz[130]. A different report gives $^1J_{PH}$ as 493.3 Hz in $Ph_2P(O)H$[131]. CNDO/2 calculations of ^{31}P–^{13}C and ^{31}P–^1H couplings in a number of phosphine oxides and sulphides gave reasonable agreement with experiment. The results were consistent with a direct relationship between

$^1J_{PC}$ and the percentage σ-character of the phosphorus hybrid orbitals[132]. ^{31}P and ^{13}C NMR spectra of triply labelled ^{13}C forms of Me_3PO, Me_3PS and Me_3PSe oriented in a nematic phase have been recorded. The ^{31}P chemical shift tensor has a large anisotropy in all cases, but decreases in the order $O > S > Se$, consistent with decreased π-bonding in that series[133].

Ab initio M.O. calculations have been related to experimental values of $\delta^{31}P$ chemical shifts for a large number of trialkyl- and triaryl-phosphine oxides, sulphides and selenides[134–136]. Principal components of the ^{31}P chemical shift tensor were determined by ^{31}P solid-state NMR for R_3PX, where $X = O$, S or Se and $R = Me$, C_6H_{11} or Ph, $X = O$ or S and $R = Et$ or *p*-tolyl and $X = S$ and $R =$ *o*- or *m*-tolyl. The chemical shift anisotropy is greater for $X = O$ than for $X = S$ or Se[137]. The ^{31}P magnetic shielding anisotropies $(\sigma_{\parallel} - \sigma_{\perp})$ were found to $+210$ and $+127$ ppm for Me_3PO and Me_3PS respectively.[138] The calculated value for this anisotropy agrees very badly with this, however (+69 ppm)[139]. The anisotropy of the ^{31}P screening constant of Me_3PO was calculated by CNDO/2 M.O. methods. The contribution of the π-P—O bond order gave stronger shielding in the direction of the P=O bond[140]. The ^{31}P magnetic shielding anisotropies were also found for Me_3PX, where $X = O$ or S, in oriented liquid crystal media[141].

The ^{31}P spectra of Me_3PX, where $X = O$, S or Se, in liquid crystal phases gave values for the CPC angles which compared very well with those found from gas-phase electron diffraction[142]. The ^{31}P and ^1H lanthanide shifts in the NMR of MeR_2PO, where $R = Et$ or Ph, suggest that they are mainly due to a contact interaction[143]. The upfield shift of the ^{31}P NMR signal of $Me_2PhP{=}O$ in the presence of cyclodextrins in water was interpreted in terms of inclusion complex formation between cyclodextrins and the phosphine oxide. The P=O group is closer to the solvent medium than to the interior of the hydrophobic cavity of the cyclodextrins[144].

$\delta^{31}P$ values were listed for $Me_n(ClCH_2)_{3-n}PO$, i.e. $n = 0$, $+39.5$ ppm; $n = 1$, $+42.9$ ppm; and $n = 3$, $+42.6$ ppm[145]. For the species with $n = 2$, ^1H chemical shifts are $\delta(PCH_2) + 3.60$ and $\delta(PCH_3) + 1.57$ ppm. The respective $^2J_{PCH}$ coupling constants are 8.6 and 14.0 Hz[146]. ^{31}P and ^1H NMR data were listed for $(ClCH_2)_2P(Y)R$, where $Y = O$ and $R = Et$ or $Y = S$ and $R = Me$, Et or Ph[147].

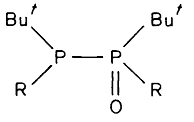


(8)

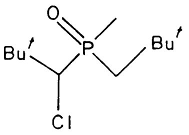
The ^{31}P chemical shifts for **8**, where $X = O$ or S, show that the *exo* species come to resonance at lower fields than the *endo* species[148]. A list has been published of ^{31}P chemical shifts for $R_2R'P(O)$, $R_2R'P(S)$ and $RR'P(S)H$, where $R, R' = Me$, Et, Pr^i or Ph[149]. The $\delta^{31}P$ values for $Ph_2P(X)C_nH_{2n+1}$, where $X = O$ or S and $n = 1$–20, show significant changes for $n = 1$–3, but then remain constant for the rest of the series. ^1H data were given on $n = 1$–4 only [150]. $\delta^{31}P$ values were listed for $(C_6F_5)_nR_{3-n}PO$, where $R = Me$, Et or Ph and $n = 1$–3[151].

$Me_2PhP{=}O$ was found to be a useful standard for setting the magic angle in ^{31}P cross-polarization magic-angle spinning (CP-MAS) NMR of solid samples[152]. Early results gave $\delta^{31}P$ for Et_3PO, Bu_3PO, Et_3PS and Et_3PSe[153]. Lanthanide-induced ^{31}P, ^1H and ^{13}C NMR shifts for Et_3PO are dominated by the pseudo-contact effect[154].

$\delta^{31}P^V$, $\delta^{31}P^{III}$ and $^1J_{P^VP^{III}}$ have been reported for **9**, where $R = Pr^i$, Bu^n, Bu^i, Bu^t and Ph, e.g. for $R = Bu^t$ $\delta^{31}P^V$ is -86.2 ppm, $\delta^{31}P^{III}$ is -49.7 ppm and $^1J_{PP}$ is 392 Hz[155]. Acceptor numbers of a wide range of alcohols were estimated from ^{31}P chemical shift changes of Bu$^n{}_3$PO in the presence of the alcohols[156]. ^{31}P chemical shifts were reported for the *R,R/S,S* and *R,S/S,R* forms of **10** and also for related systems[157]. A linear correlation was found between shifts in δ^{31}P of R$_3$PO, where R $= C_4H_9$–C_8H_{17}, on protonation and the sum of substituent constants ($\Sigma\sigma^{\Phi}$) on the phosphorus atom, and on the enthalpies of complex formation with phenol[158].



(**9**)



(**10**)

The solid-state CP-MAS ^{31}P NMR for OPPh$_3$ shows that δP is +29.2 ppm (cf. 23–27 ppm in a variety of solvents), whereas for OP(C$_{14}$H$_{29}$)$_3$ δP is + 51.5 ppm (48.5 ppm in CDCl$_3$ solution)[159]. ^{31}P, ^{1}H and ^{19}F chemical shifts and coupling constants were reported for (CHF$_2$)$_3$PO. The results show that δF is shifted upfield and δP downfield compared with the phosphine analogue, whereas J_{FCH} is about 2 Hz lower[160]. (CF$_3$)$_3$PO has δ^{31}P at -2.3 ppm and δ^{19}F at + 66.2 ppm (the latter with respect to CCl$_3$F)[161].

^{31}P chemical shifts were listed as follows: Ph$_3$PO -25, (PhC≡C)$_3$PO + 55.8, Ph$_3$PS $-$ 42.6, (PhC≡C)$_3$PS + 44.6, (PhC≡C)$_2$PhPS + 10.0 and (PhC≡C)Ph$_2$PS $-$ 18.8 ppm[162]. δ^{31}P and δ^{13}C values were listed for triphenylphosphine oxide, sulphide and selenide, together with a range of alkyl-substituted diphenylphosphine oxides. The values were consistent with the theory of competitive dπ–pπ overlap with the P═O bond[163]. ^{31}P chemical shift anisotropies were measured for Ph$_3$PX, where X = O, S or Se, oriented in liquid crystals. There was some evidence for delocalization of phosphorus electron density on to the phenyl ring[164].

δ^{31}P of Ph$_3$PX in liquid HCl shows that for X = O, protonation occurs at the oxygen, but for X = S no protonation occurs[165]. Ph$_3$P═^{17}O has δP at +28.8 ppm and δO at + 43.3 ppm (relative to H$_2{}^{17}$O), with $J(^{31}\mathrm{P}–^{17}\mathrm{O})$ at 160 ± 2.4 Hz[166]. Relaxation times (T_1) and nuclear Overhauser effect (NOE) factors (η) were measured for Ph$_3$PO at 29 and 63 °C[167]. ^{31}P chemical shifts and $^1J_{\mathrm{PH}}$ were reported for Ph(R)P(═O)H, where R = Ph, Et, Pr^i, Bu^n or Bu^s (Table 5)[168].

^{31}P, ^{1}H and ^{13}C NMR data were listed for Me$_3$CCH$_2$(Ph)P(O)Me and related species and it was suggested that the changes could be related to conformational changes[169]. It has been suggested subsequently, however, that such conclusions were erroneous[170].

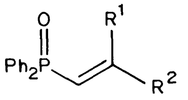
Ph$_3$P^a═CHP^b(O)Ph$_2$ has δ^{31}P values of +18.4 ppm (a) and +23.4 ppm (b), with $^2J_{\mathrm{P^aP^b}}$ of 19.0 Hz[171]. ^{31}P and ^{1}H NMR data were given for Ph$_2$P(O)CHRPPh$_2$, where R = H, Me or Pr^n, for which $\delta_{\mathrm{P=O}}$ were -27.7, -33.6 and -32.7 ppm, respectively (each

TABLE 5. ^{31}P chemical shifts and $^1J_{\mathrm{PH}}$ coupling constants for Ph(R)P(═O)H

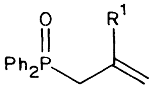
R	δ^{31}P (ppm)	$^1J_{\mathrm{PH}}$ (Hz)
Ph	-23.1	487
Et	-32.3	458
Pr^i	-36.1	458
Bu^n	-29.0	467
Bu^s[a]	$-34.3/-32.2$	457.5/458.2

[a] A mixture of diastereoisomers.

one a doublet), and for $Ph_2P(O)CHRP(O)PhR'$, where $R = H$, $R' = Et$ or $R = Me$, $R' = Ph$[172]. ^{31}P, ^{1}H and ^{13}C NMR data were also given for $Ph_2P(X)CH{=}CHR$, where $X = O$ or S and R = Me, Ph or $P(X)Ph_2$. The ^{31}P results show that the *E*-isomer comes to resonance at higher field than the *Z*-isomer[173]. Analysis of high-resolution ^{31}P and ^{1}H NMR spectra for $Ph_2P(O)CH{=}CHAr$, where Ar = phenyl, 2- or 4-pyridyl or 2- or 4-quinolyl, was able to differentiate between isomers with the P and Ar *cis* or *trans*[174]. Other diphenylphosphine oxides, sulphides or selenides for which NMR data have been given are $Ph_2P(O)CH_2CH{=}CH_2$ and $Ph_2P(O)(CH_2)_2CH{=}CH_2$ (^{31}P and ^{1}H)[175], $Ph_2P(O)CH_2CO_2H$ and $Ph_2P(S)CH_2X$ (where $X = H$ or CO_2H) (^{31}P and ^{1}H)[176], $Ph_2P(X)CH_2P(Y)Ph_2$, where X, Y = O, S, Se or electron pair (^{31}P, ^{1}H and ^{13}C)[177], $Ph_2P(O)CH{=}CHCH_2R$ (R = Pr or Bu) (^{31}P, ^{1}H and ^{13}C)[178] and $Ph_2P(O)CH_2$-$CHRP(O)Ph_2$ (R = Pr or Bu) (^{31}P) (**11** and **12**), where R^1, R^2 = Me, Ph, H, etc. (^{31}P, ^{1}H and ^{13}C)[179].



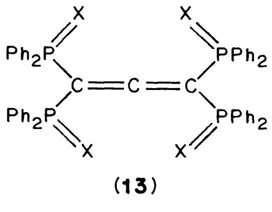
(11)



(12)

P–P nuclear spin–spin coupling was measured in $Ph_2P(Y)XP(Z)Ph_2$, where X is $=CH_2$, $=C{=}CH_2$, $-CH_2CH_2-$, *trans*-$CH{=}CH-$, *cis*-$CH{=}CH-$, $-C{\equiv}C-$ or $-CH_2CH_2CH_2-$, Y = Se or lone pair and Z = Se. $^{13}C\text{-}\{^{1}H,^{31}P\}$ and $^{31}P\text{-}\{^{1}H,^{77}Se\}$ magnetic triple resonance experiments gave the signs of these coupling constants[180]. δ_P (ppm) and $^{3}J_{PP}$(Hz) were reported for $Ph_2P(O)CH_2CH_2P(O)PhR$, where R = Me (−31.2, −36.9; 51), Et (−30.9, −40.9; 50) or Pr^i (−31.4, −46.0; 49)[181]. Phosphorus-31 and proton chemical shifts were found for $Ph_2P(X)CH_2C(OH)Ph_2$, where X = O or S. The J_{PH} coupling constants were 10.2 Hz (X = O) and 9.6 Hz (S)[182]. $\delta^{31}P$ values (ppm) were also given for $Ph_2P(O)(CH_2)_nP(O)Ph_2$, $n = 1$ (27.2) or 2 (36.7), $P(O)Ph(CH_2CH_2P(O)Ph_2)_2$ [33.4 (terminal), 42.9 (non-terminal)], $P(S)Ph(CH_2CH_2P(S)Ph_2)_2$ [42.9 (terminal), 49.9 (non-terminal)] and Ph_3PSe (33.1), and $Ph_2P(Se)(CH_2)_nP(Se)Ph_2$, where $n = 1$ (22.6), 2 (34.6) or 3 (32.5). The measured $^{1}J_{PSe}$ coupling constants were all in the range 646–694 Hz[183]. $\delta^{31}P$ values (ppm) for **13** were O 23.5, S 45.6 and Se 37.2[184].

The ^{31}P chemical shifts for $(C_6F_5)_3PE$, where E = O or S, show that there is much greater shielding of phosphorus by C_6F_5 than by C_6H_5[185]. Spin–spin coupling constants have been measured for a large number of R_3PX species, where X = O, S or Se and R = five- or six-membered heterocyclic aromatic group[186–188]. Changes in ^{31}P chemical shifts have been used to study protonation in P=O and P=S compounds.[189–190] ^{31}P and ^{13}C chemical shifts and coupling constants have been tabulated for Me_3PS and Me_3PSe (Table 6)[191]. $\delta^{31}P$ were reported for Me_3PS (−59.1 ppm), Me_2EtPS (−57.0) and Et_2PhPS (−52.0)[192].



(13)

^{31}P NMR data for *syn* and *anti* isomers of norbornene with $Me_2P(S)$ at the 7-position show deshielding of phosphorus on moving from the crowded *anti* to the less crowded

TABLE 6. ^{31}P and ^{13}C NMR data for Me_3PS and Me_3PSe

	Me_3PS	Me_3PSe
$\delta^{31}P(H_3PO_4$ ref.)(ppm)	-28.9	-87
$\delta^{13}C(CH_3COOH$ ref.)(ppm)	$+150.4$	$+150.0$
$^1J_{PC}$(Hz)	$+56.1$	$+48.5$
$^2J_{PH}$(Hz)	-13.0	-13.0
$^1J_{CH}$(Hz)	$+129.3$	$+130.5$

TABLE 7. ^{31}P chemical shifts for Me(R)-P(=S)P(=S)(R)Me (ppm from 85% aqueous H_3PO_4)

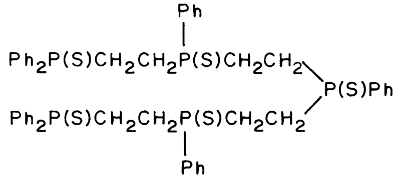
R	$\delta^{31}P$ (ppm)
Me	-34.7
Et	-42.1
Pr^n	-40.3
Ph	-37.0

syn position[193]. Proton-decoupled ^{31}P NMR spectra of cyclohexyl, *cis*- and *trans*-4-methyl- and *cis*- and *trans*-4-*tert*-butyl-cyclohexyl derivatives of $P(S)Me_2$ have been measured. The *tert*-butyl compounds are conformationally rigid, with greater shielding for the phosphorus group in the equatorial than the axial position[194].

The ^{31}P chemical shifts were measured for RR′R″PS, where R = Me, R′ = Et or Ph; R″ = Ph; R = R′ = R″ = Ph, *p*-MeC_6H_4, *o*- or *p*-ClC_6H_4[195]; and for RR′PP(S)RR′, where R = R′ = Me or Et; R = Me, R′ = Et or Ph[196]. The ^{31}P chemical shift of Et_3PS has been variously reported as -67.6[197] or -54.5 ppm[198]. For Ph_3PS the corresponding value is -42.6 ppm[199]. The ^{31}P chemical shifts for Me(R)P(=S)P(=S)(R)Me are listed in Table 7[200]. Similar data were given for $Et_2P(=S)(CH_2)_nP(=S)Et_2$, where n = 1,3 or 4[201]. ^{31}P and ^1H chemical shifts have been measured for $Ph_2P(X)CH_2P(Y)R_2$, where X, Y = S or lone pair and R = Me, Pr^i or Bu^t[202].

The ^{31}P,^1H and ^{13}C NMR data for $Ph(H)P(E)(CH_2)_n(E)P(H)Ph$, where E = S, n = 2–4 or 6; E = Se, n = 2, indicate that the ^{31}P chemical shifts show increasing differences between the *meso* and racemic forms for E = O < S < Se, for n = 2. There is little change in $\delta^{13}C$ between diastereoisomers, however. For all of the compounds the ^1H-$\{^{31}P\}$ spectra are very different for the *meso* and racemic forms[203].

Spin–lattice relaxation processes for ^{31}P in Ph_3PS and $Ph_2P(S)(CH_2)_n(S)PPh_2$, where n = 1 and 2, all operate by the chemical shift anisotropy mechanism[204]. ^{31}P NMR data for $(Ph_2P)_n[Ph_2P(S)]_{2-n}CH$, n = 0, 1 or 2, show that for n = 2 there is unhindered rotation about the P-methine C bond, but hindered rotation for n = 0 or 1[205]. ^{31}P and ^1H NMR data were listed for $[R_2P(X)][R_2P(Y)][R_2P(Z)]CH$, where X = S or Se, Y, Z = lone pair; X = Y = O, S or Se, Z = lone pair; X = S, Y = Se, Z = lone pair; X = Y = Z = S, R = Me or Ph[206]; and for $[Ph_2P(X)][R'_2P(Y)][R''_2P(Z)]CH$, where R′ = R″ = Ph, X = S, Y = Z = lone pair; X = Y = S, Z = lone pair; X = Y = Z = S; R′ = R″ = Me, X = Y = Z = S, X = Y = S, Z = O or lone pair; R′ = Ph, R″ = Me, X = Z = S, Y = lone pair[207]. ^{31}P and ^1H chemical shifts were reported for **14**[208], and one- and two-dimensional ^{31}P NMR spectra were used to disentangle the complex spectra due to a variety of sulphide derivative of the pentaphosphorus species **15**[209].



(14)

$PhP[CH_2CH(PPh_2)_2]_2$

(15)

A heteronuclear magnetic selective triple resonance technique was applied to a range of organophosphorus selenides. The results suggested that both P^+Se^- and P=Se forms contributed significantly to the bonding. The $^{31}P^{77}Se$ coupling constants were shown to be negative, and they could be interpreted in terms of the inductive effects of the substituents on the phosphorus[210]. The $^nJ_{PSe}$ coupling constants, where $n = 1$–4, were measured from proton-decoupled ^{31}P spectra of several diphosphorus selenides and diselenides[211]. The ^{31}P NMR spectrum of $Me_3P{=}Se$ oriented in liquid crystal media show that the $^1J_{PSe}$ spin–spin coupling is highly anisotropic[212]. Table 8 summarizes the ^{31}P chemical shifts and $^1J_{PSe}$ coupling constants for several alkyl- and aryl-phosphine selenides[213].

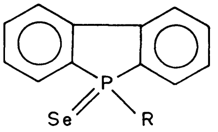
^{31}P, ^1H, ^{13}C and ^{77}Se chemical shifts and coupling constants were recorded for Bu^t_3PE, where E = Se or Te. The $^1J_{PE}$ coupling constants were found to be 711.6 Hz (Se) and 1600 Hz (Te). The $\delta^{77}Se$ value, with respect to di-*p*-tolyl diselenide, for E = Se is −890.5 ppm[214]. $\delta^{31}P$(+36 ppm), $\delta^{77}Se$ (−278 ppm, with respect to Me_2Se) and $^1J_{PSe}$ (−759 Hz) have been measured for Ph_3PSe[215]. The values of $\delta^{31}P$, $\delta^{77}Se$ and $^1J_{PSe}$ for several phosphorus(V) selenides shift in SO_2 solution in such a way as to suggest the formation of donor–acceptor complexes with the SO_2[216].

The ^{31}P–^{77}Se coupling constants in $(RC_6H_4)_3P{=}Se$, where R = *p*-Cl, H, *p*-Me, *p*-OMe, *o*-Me or *m*-Me, show a linear correlation with substituent constants, in the range 752.8 Hz (*p*-Cl) to 726.3 Hz (*m*-Me)[217]. $\delta^{31}P$ and $\delta^{77}Se$ data were listed for $R_2R'PSe$, where R and R′ = phenyl, 2- or 3-furyl, 2- or 3-thienyl or substituted aryl. Deshielding of selenium occurs on the introduction of *ortho* substituents into arylphosphine selenides, as it does on introducing 2-thienyl. The presence of 2-furyl, however, leads to increased shielding of the selenium[218].

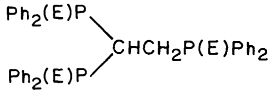
^{31}P and ^{77}Se NMR data were tabulated for **16**, where R = Me, Et, Pr^i, Ph, etc.[219–220], as were ^{31}P, ^1H, ^{13}C and ^{77}Se data for $Ph_2P(Se)(CH_2)_nPPh_2$ and $Ph_2P(Se)(CH_2)_n(Se)PPh_2$, where $n = 1$ or 2[221]. Two-dimensional ^{31}P NMR spectra of mixtures of selenides **17**, where E = lone pair or Se, led to assignments of resonances for a range of possible species[222].

TABLE 8. ^{31}P chemical shifts and $^1J_{PSe}$ coupling constants for phosphine selenides

Compound	$\delta^{31}P$ (ppm)	$^1J_{PSe}$ (Hz)
Et_3PSe	−44.2	705
Ph_3PSe	−36.1	738
$EtPh_2PSe$	−37.4	722
Et_2PhPSe	−44.6	705
MeEtPhPSe	−29.8	693
$MePr^nPhPSe$	−26.1	704
$MeBu^tPhPSe$	−47.7	702
Bu^n_3PSe	−36.4	693
$H(Bu^t)PhPSe$	−37.9	656



(**16**)



(**17**)

B. ^{1}H

Earlier reference has been made to a large number of papers containing ^{1}H NMR data on phosphorus chalcogenides: $Me_2P(H){=}O$, $Et_2P(H){=}O$[129]; $Me_n(ClCH_2)_{3-n}PO$, $n = 1$[146] or $n = 0$, 2[144]; $(ClCH_2)_2P(Y)R$, where Y = O, R = Et, Y = S, R = Me, Et or Ph[147]; $Ph_2P(X)C_nH_{2n+1}$, where X = O or S, $n = 1$–4[150]; $Et_3P{=}O$ [154]; $(CHF_2)_3PO$[160]; $Me_3CCH_2P({=}O)Ph(Me)$[169]; $Ph_2P(O)CHRPPh_2$, where R = H, Me or Pr^n; $Ph_2P(O)CHRP(O)PhR'$, where R = H, R′ = Et or R = Me, R′ = Ph[172]; $Ph_2P(X)CH{=}CHR$, where X = O or S, R = Me, Ph or $P(X)Ph_2$[173]; $Ph_2P(O)CH{=}CHAr$, where Ar = Ph, 2- or 4-pyridyl, 2- or 4-quinolyl[174]; $Ph_2P({=}O)CH_2CH{=}CH_2$, $Ph_2P({=}O)(CH_2)_2CH{=}CH_2$, $O{=}P[(CH_2)_2CH{=}CH_2]_3$[175]; $Ph_2P(O)CH_2CO_2H$, $(n\text{-}C_6H_{13})_2P(O)CH_2X$, where X = H or CO_2Me, $Ph_2P(S)CH_2X$, where X = H or CO_2H, $PhP(S)Me_2$, $PhMeP(S)CH_2CO_2H$, $(n\text{-}C_6H_{13})_2P(S)CH_2X$, where X = H or CO_2Me[176]; $Ph_2P(X)CH_2P(Y)Ph_2$, where X, Y = O, S, Se or electron pair[177]; $Ph_2P(O)CH{=}CHCH_2R$, where R = Pr or Bu, $Bu_2P(O)CH{=}CHCH_2R$, where R = Pr, Bu or C_5H_{11}[178]; vinyl- and allyldiphenylphosphine oxides[179]; $Ph_2P(X)CH_2C(OH)Ph_2$[182]; $Ph_2P(S)CH_2P(S)R_2$, where R = Me or Pr^i [202]; $Ph(H)P(E)(CH_2)_n(E)P(H)Ph$, where E = S, $n = 2$–4, 6 or E = Se, $n = 2$[203]; $[R_2P(X)][R_2P(Y)][R_2P(Z)]CH$, where X = S or Se, Y, Z = lone pair, or X = Y = O, S or Se, Z = lone pair, X = S, Y = Se, Z = lone pair, X = Y = Z = S, R = Me or Ph[206]; $[Ph_2P(X)][R'_2P(Y)][R''_2P(Z)]CH$, where R′ = R″ = Ph, X = S, Y, Z = lone pair, X = Y = S, Z = lone pair, X = Y = Z = S; R′ = R″ = Me, X = Y = Z = S, X = Y = S, Z = O or lone pair; R′ = Ph, R″ = Me, X = Z = S, Y = lone pair[207]; polytertiary phosphine sulphides[208]; $Me_nPh_{3-n}PSe$, $n = 0$–3[210]; Bu^t_3PE, where E = Se or Te[214]; and $Ph_2P(Se)(CH_2)_nPPh_2$ and $Ph_2P(Se)(CH_2)_n(Se)PPh_2$, where $n = 1$ or 2[221].

^{1}H NMR studies, including double resonance, show that for Ph(Me)P(H)O, $^1J_{PH}$ has a value of +467.8 Hz, whereas $^2J_{PCH}$ is −13.6 Hz[223]. $^1J_{PH}$ coupling constants were also measured for $Bu^n_2P(X)H$, where X = O (460 Hz) or S (431 Hz)[224]. The INDOR technique gave the following NMR parameters for Me $(Bu^t)P(S)H$: $\delta(PCH_3)$ 1.70, $\delta(PCCH_3)$ 1.21, $\delta(PH)$ 6.35, $\delta(P)$ −36.2 ppm; $^1J_{PH}$ 434.5, $^2J_{PH}$ 13.4, $^3J_{PH}$ 18.9, $^3J_{HH}$ 4.5–4.8 Hz[225].

Proton chemical shifts and coupling constants have been reported several times for Me_3PX and Et_3PX, where X = O or S[226–229]. For Me_3PO, δH was at 1.56 ppm and $^2J_{PH}$ 12.8 Hz. Laskorin *et al.*[230] have developed empirical relationships between ^{1}H NMR parameters and substituent constants for a range of P=O-containing compounds, including Me_3PO. M.O. calculations on Me_3PO and Me_3PS suggest that the dominant contribution to the proton shielding is made by the C—H bonds[231].

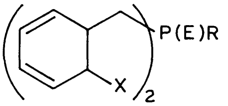
Methyl proton resonances for Me_2PhPO and Me_2PhPS are at 1.76 and 2.00 ppm, respectively. The corresponding $^2J_{PH}$ coupling constants are 13.0 and 13.2 Hz respectively.[232] pK_{BH^+} values for $Ph_nMe_{3-n}P(E)$, where $n = 1$ or 2 and E = O or S, were deduced from changes in the CH_3 ^{1}H chemical shift as a function of sulphuric acid concentration[233]. ^{1}H and ^{13}C NMR data were listed for $RR'P(O)CH_2Cl$, where R = R′ = Me or Ph; R = Me, R′ = Ph, 4-Cl-, 4-$MeOC_6H_4$ or CH_2Ph, and related systems[234]. ^{1}H chemical shifts and $^2J_{PH}$ coupling constants were given for $(RC_6H_4)P(E)Me_2$, where R = 4-MeO, 4-Me or H, 4-Cl and E = O or S, and $(RC_6H_4)_2P(E)Me$, where R = 4-Me, H or 4-Cl and E = O or S[235].

Methylene proton chemical shifts and $^2J_{PH}$ coupling constants are listed in Table 9

TABLE 9. ^{1}H NMR parameters for $(XCH_2)_3PO$

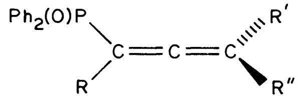
X	δCH_2 (ppm)	$^2J_{PCH}$ (Hz)
Cl	3.99	6.75
Br	3.76	6.25
I	3.58	6.87

for $(XCH_2)_3PO$, where X = Cl, Br or I. The methylene proton shielding increases with decreased electronegativity of X[236]. A more recent paper on these compounds reveals that they possess three different conformers, with characteristic $^2J_{PH}$ coupling constants[237]. ^{1}H shifts were found for a range of enantiomeric monophosphine oxides using (*R*)-(−)-*N*-(3,5-dinitrobenzoyl)-α-phenylethylamine as a chiral shift reagent[238]. Proton NMR data were listed for **18**, where X = H, R = Bu^t, E = O; X = H or Br, R = Me, E = S[239].

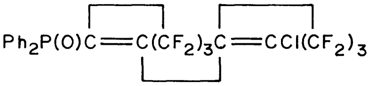


(18)

δ^1H and other NMR parameters were given for acetylenic phosphine oxides, $R_2P(O)C{\equiv}CH$, where R = Et, Bu^n, Bu^t, Ph or C≡CH[240–241] and $Ph_2P(O)C{\equiv}CR$, where R = H or Me[242–243]. ^{1}H chemical shifts and coupling constants were given for the allenic fragment in $R_2P(O)CH{=}C{=}CH_2$, where R = Et or Ph[244]. The ^{1}H data for the allenic phosphine oxides **19**, where R = H or Me; R′, R″ = H, Me or Et, reveal that the coupling constants $^2J_{PH}$ and $^2J_{PH}$ have the same sign, opposite to that of $^4J_{PH}$[245]. The phenyl proton chemical shifts for **20** are at 7.68 and 7.72 ppm (multiplets)[246].



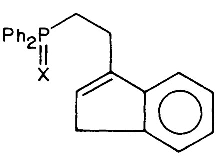
(19)



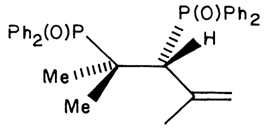
$Ph_2P(O)C{=}C(CF_2)_3C{=}CCl(CF_2)_3$

(20)

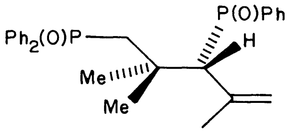
δ^1H(aliphatic) and $^2J_{PCH}$ were reported for $Ph_2P(O)CH_2X$, where X = H, OH, Cl, NMe_2, OMe, SMe, Ph, $CH{=}CH_2$ or $CH{=}C{=}CH_2$, $Ph_2P(O)CH(X)Ph$, where X = OH or Ph, and some related molecules. There was no simple explanation of the observed trends in $^2J_{PCH}$ values[247]. ^{1}H NMR data were listed and assigned for $Ph_2P(O)R$, where R = CH_2Ph, CH_2CH_2Ph, $CH_2C_6F_5$, CH_2CF_3 and $CH_2C_6H_4Cl$-*p*[248], and for **21**[249]. ^{1}H NMR spectra of **22** and **23** both show that there is severely restricted rotation about the C—C single bond[250].



(21)

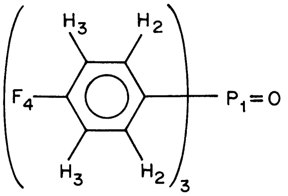


(22)



(23)

Para-substituted triarylphosphine oxides and sulphides have been the subject of very extensive ^{1}H NMR investigations[251–256]. For example, $(p\text{-}FC_6H_4)_3P{=}O$ (**24**) has J_{12}(PH) 10.87, J_{13}(PH) 2.54, J_{23}(HH) 8.97, J_{24}(HF) 5.83, J_{34}(HF) 9.03 and J_{14}(PF) 1.95 Hz and δ_2 (H) 7.70, δ_3 (H) 7.35 and δ_4 (F) 101.16 ppm. δ^1H values were listed for (*o*-, *m*- and *p*-tolyl)diphenylphosphine oxides. The *ortho* isomer gave evidence for $^4J(PCH_3)$ (ca 1 Hz). There was no evidence for analogous five- or six-bond coupling in the others[257].



(**24**)

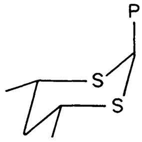
The temperature dependence of the ^{1}H NMR of $R_3P{=}X$, where X = O or S and R = 2,3,5-$Me_3C_6H_2$ or 2,3,5,6-Me_4C_6H, as used to determine free energies of activation for rotation of the rings[258]. ^{1}H NMR data were assigned for R_3PX, where X = O or S and R = furyl, thienyl or ring-substituted derivatives of these[259–263]. Double resonance experiments on the ^{1}H NMR spectrum of tris-2-pyridylphosphine oxide and sulphide gave the relative signs of $^{31}P{-}^1H$ coupling constants. Thus the two four-bond couplings have opposite signs, whereas the three- and five-bond couplings have the same sign, implying a negative sign for $^4J_{HP}$ through the nitrogen[264].

Table 10 summarizes the proton chemical shift values found for $Ph_2P({=}X)(CH_2)_n({X}{=})PPh_2$, where $n = 1$ or 2, X = O, S or Se[265]. ^{1}H NMR data were also given for $Ph_2P(O)CH_2(O)PPh_2$, $Ph_2P(X)CH_2CH_2(X)PPh_2$ and *cis*- and *trans*-$Ph_2P(X)CH{=}CH(X)PPh_2$, where X = O or S[266], and for $Ph(R)P({=}O)(CH_2)_3(O{=})O(R')Ph$, where R = Ph, R′ = Et or Bu; R = Bu, R′ = Et, Pr^n, Pr^i, n-C_5H_{11}, n-C_6H_{13}; R = Me, R′ = Et; and $Ph_2P({=}O)(CH_2)_4(O{=})P(Et)Ph$[267]. The ethylenic proton chemical shift in $Ph_2P(O)CH{=}CHP(O)Ph_2$ is at 7.30 ppm, with $^2J_{PH}$ 46 Hz[268].

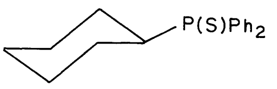
The methyl proton chemical shift in Me_3PS is at 1.78 ppm ($^2J_{PH}$ 13.10 Hz), whereas that in $Me_2P(S)P(S)Me_2$ is at 1.96 ppm[269]. The methylene proton chemical shift in $Bu^t_3P{=}S$ is a doublet at 1.48 ppm (J_{PH} 14 Hz)[270]. ^{1}H NMR data were also given for $Ph_2P(S)CH(CO_2H)C_6H_{12}$-$n$[271]. There is ^{1}H NMR evidence for the predominantly axial conformation of the $P({=}S)Ph_2$ in **25**[272]. In **26**, however, the $Ph_2P(S)$ group was shown to have a strong equatorial preference[273]. The olefinic proton in **27** gives a triplet at 8.2 ppm, with $^2J_{PH}$ 24 Hz[274].

TABLE 10. Proton chemical shifts for $Ph_2P({=}X)(CH_2)_n(X{=})PPh_2$ (ppm)

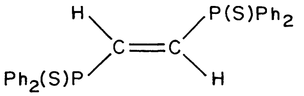
X	$n = 1$	$n = 2$
O	4.08	2.54
S	4.42	2.71
Se	4.83	2.87



(25)



(26)

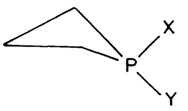


(27)

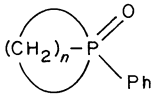
C. ^{13}C

The following earlier references have been made to ^{13}C NMR data: ($^{13}CH_3)_3PE$, where E = O, S or Se[133]; Et_3PO[154]; Ph_3PE, where E = O, S or Se; $Ph_2(R)PO$, where R = Me, Et, Pr^i, Bu^t, CH=CH$_2$, C≡CH; PhMe$_2$PO, Bu$^n_3$PE, where E = O or S[163]; Me$_3$CCH$_2$P(=O)Ph(Me)[169]; Ph$_2$P(X)CH=CHR, where X = O or S, R = Me, Ph or P(X)Ph$_2$[173]; Ph$_2$P(O)CH=CHCH$_2$R, where R=Pr or Bu; Bu$_2$P(O)CH=CHCH$_2$R, where R = Pr, Bu or C$_5$H$_{11}$[177]; vinyl- and allyl-diphenylphosphine oxides[179]; Me$_3$PS, Me$_3$PSe[191]; Ph(H)P(E)(CH$_2$)$_n$(E)P(H)Ph, where E = S, n = 2–4, 6; E = Se, n = 2[203]; Bu$^t_3$PSe[214]; Ph$_2$P(Se))(CH$_2$)$_n$PPh$_2$, Ph$_2$P(Se)(CH$_2$)$_n$(S)PPh$_2$, where n = 1 or 2[221]; RR′P(O)CH$_2$Cl, where R = R′ = Me, Ph; R = Me, R′ = Ph or 4-Cl-C$_6$H$_4$, 4-MeOC$_6$H$_4$ or CH$_2$Ph[234]; HC≡CP(O)Ph$_2$[242]; and RC≡CP(O)Ph$_2$, where R=H or Me[243]. ^{13}C chemical shifts and J_{PC} coupling constants were listed for R$_3$P=X, where R = Me or Ph, X = O or S, R = Me, X = Se. Thus, for R = Me, X = O, δ^{13}C is − 17.4 ppm and J_{CP} + 68 Hz[275].

The ^{13}C NMR spectrum of HC$_1$≡C$_2$P(O)Bu$^n_2$ shows that $\delta^{13}C_1$ is 100.4 ppm and $\delta^{13}C_2$ 111.6 ppm (CS$_2$ as standard), with $^1J(HC_1)$ 266 Hz[276]. δ^{13}C and various coupling constants were reported for (C$_8$H$_{17}$)$_2$P(=O)R, where R = Ph, C$_8$H$_{17}$ or Bu^t, and (C$_8$H$_{17}$)$_2$P(=O)R′P(=O)(C$_8$H$_{17}$)$_2$, where R′ = —(CH$_2$)$_n$—, n = 1–6[277]. ^{13}C chemical shifts and J_{CP} coupling constants were recorded for a wide range of phosphorus heterocyclic oxides and sulphides, e.g. **28**, where X, Y = O or S; Me, CH$_2$Ph,Bu^t, etc. The data are consistent with puckered conformations, which are mostly stereorigid on the NMR time scale[278]. ^{13}C chemical shifts and ^{13}C–^{31}P spin–spin coupling constants were given for **29**, where n = 3–7, and for Bu$^n_2$P(=O)Ph[279].

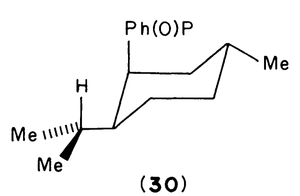


(28)

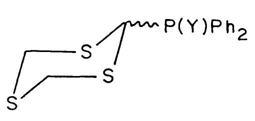


(29)

^{13}C NMR data were reported for **30**[280]. Axial preference is revealed by ^{13}C NMR to be Ph$_2$P(S) > Ph$_2$P(O) in **31** and related heterocyclic derivatives[281]. (CF$_3$)$_3$P=O has δ^{13}C at 119.50 ppm (SiMe$_4$ standard), with J_{CP} 163.3 Hz, J_{CF} 316.9 Hz and J_{CPCF}3 Hz[282]. ^{13}C NMR data for phP(O)Z$_2$ and PhP(S)Z$_2$, where Z = Me or Ph, were used to estimate substituent parameters for P(E)Z$_2$. The electron-attracting abilities are P(E)Me$_2$ > P(E)Ph$_2$ for both O and S compounds[283].



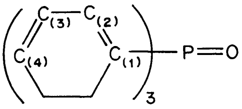
(30)



(31)

TABLE 11. ^{13}C NMR data for $Ph_3P{=}O$

	Carbon No.			
	1	2	3	4
Chemical shift (ppm)	135.56	132.28	128.76	132.25
^{13}C–^{31}P coupling constant (Hz)	104.4	9.8	12.1	2.8



(32)

^{13}C chemical shifts and ^{13}C–^{31}P nuclear spin coupling constants were obtained for $Ph_3P{=}O$ (**32**) (Table 11)[284]. The ^{13}C NMR spectra of $Ph_3P{=}X$, where X = O, S or Se, are all consistent with delocalization of π-charge from the phenyl groups to the $3d_\pi$ orbitals of the phosphorus[285]. $\delta^{13}C$ and J_{PC} were reported for unsymmetrical triarylphosphine oxides $(2,4,6\text{-}Me_3C_6H_2)_2P(O)(4\text{-}XC_6H_4)$, where X = Me, MeO or PhCOO. The results were consistent with a propeller-like arrangement of the aromatic rings and non-equivalence of the two mesityl groups[286].

^{13}C NMR data were listed for an extensive series of phosphine sulphides[287]. ^{13}C MAS NMR of solid Me_3PS shows a doublet due to $^1J_{PC}$ coupling, with a coupling constant of 54 Hz, close to the solution-state value of 56.1 Hz[288]. $\delta^{13}C$ and $^1J_{PC}$ were measured for $Bu^nP(S)RR'$, where R = R′ = Me or Bu^n; R = Me, R′ = Bu^n[289]. ^{13}C NMR data for the *cis* and *trans* isomers of *tert*-butylcyclohexane with $P(S)Me_2$ at the 4-position show that the $P(S)Me_2$ group causes considerable ring distortion in the *cis* isomer[290].

D. ^{19}F

Earlier reference was made to ^{19}F NMR data for $(CHF_2)_3PO$[160] and $(CF_3)_3PO$[161]. The ^{19}F chemical shift of $(CF_3)_2P(O)C(CH_3)_3$ is 64.7 ppm, with CCl_3F as standard. The $^2J_{FP}$ coupling constant is 84.7 Hz[291]. ^{19}F NMR data for $(XC_6H_4)(C_3F_7)_2P{=}O$, where X = H, *m*-F or *p*-F, are shown in Table 12 ($\delta^{19}F$ with respect to CF_3COOH as standard[292].

The ^{19}F NMR spectrum of **33** shows that it adopts a chiral, propeller equilibrium conformation in solution[293]. ^{19}F chemical shifts were given for several phosphine oxides and sulphides containing 3- or 4-FC_6H_4 substituents[294–298]. J_{PF} coupling constants were derived for $(C_6F_5)_nPh_{3-n}P{=}O$, where $n = 1$–3[299]. Table 13 gives the ^{19}F chemical shifts for $(C_6F_5)_3P{=}X$, where X = O or S.[300]

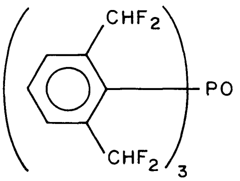
TABLE 12. ^{19}F chemical shifts for $(XC_6H_4)(C_3F_7)_2P{=}O$ (ppm)

X	$CF_2(\alpha)^a$	$CF_2(\beta)^a$	CF_3	F_{arom}
H	−39.9	−45.0	−2.4	—
m-F	−39.8	−45.1	−2.8	−30.0
p-F	−40.0	−45.2	−2.8	−20.8

[a] $PCF_2(\alpha)CF_2(\beta)CF_3$.

TABLE 13. ^{19}F chemical shifts for $(C_6F_5)_3P{=}X$ (ppm with respect to $CFCl_3$)

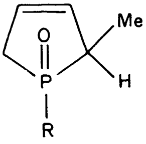
X	*o*-F	*m*-F	*p*-F
O	132.6	142.4	158.5
S	132.2	144.3	159.0



(33)

E. ^{17}O

Earlier reference was made to ^{17}O NMR data for $Ph_3P{=}^{17}O$[166]. $^1J_{PO}$ was found to be 120 ± 15 Hz from the natural abundance ^{17}O NMR spectrum of $Me_3P{=}O$. CNDO/2 FPT calculations of the analogous coupling constant in $H_3P{=}O$ gave a value of 98.5 Hz[301]. ^{17}O chemical shifts were found for a range of cyclic phosphine oxides, such as **34**, where R = Me, Ph, etc. The values were found to be very sensitive to the ring size and to the presence of γ-interactions[302]. ^{17}O NQR data were obtained for Ph_3PO: $\nu_{5/2-3/2}$ 1403 kHz, $\nu_{3/2-1/2}$ 708 KHz, e^2Qq_{zz}/h 4.683(2) MHz and η 0.085[303]. There was also evidence for substantial π-bond order in Ph_3PO and related species, in the sequence $(PhO)_3PO > Ph_2SO_2 \approx Ph_3PO > Ph_2SO$[304].



(34)

F. ^{77}Se and ^{125}Te

Data on ^{77}Se NMR have been given for $Me_nPh_{3-n}PSe$, where n = 0–3[210]; Bu^t_3PSe[214]; Ph_3PSe[215]; Ph_3PSe, $(p\text{-}MeC_6H_4)_3PSe$, Et_3PSe, $[Ph_2P(Se)]_2CH_2$, etc.[216]; $R_2R'PSe$, where R,R′ = Ph, 2-furyl or substituted analogues,[218]; RPh_2PSe, where R = Me, Et, Pr^i, Ph, etc., and related heterocyclic compounds[220]; and $Ph_2P(Se)(CH_2)_nPPh_2$ and $Ph_2P(Se)(CH_2)_n$-$(S)PPh_2$, where n = 1 or 2[221]. Heteronuclear triple resonance techniques were used to obtain δ^{77}Se for Me_3PSe (−235 ppm) and Ph_2HPSe (−349 ppm), both with respect to Me_2Se as standard. The results were consistent with contributions from both $\equiv P^+{-}Se^-$ and $\equiv P{=}Se$ to the bonding[305].

The $^1J_{TeP}$ coupling constant for Bu^n_3PTe is 1720 Hz[306]. In Bu^t_3PTe this coupling constant is 1600 Hz, with δ^{125}Te −480 ppm with respect to ditolyl telluride as standard[307].

V. REFERENCES

1. H. H. Jaffé and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 1069 (1952).
2. H. H. Jaffé, *J. Chem. Phys.*, **22**, 1430 (1954).
3. L. Horner and H. Ödiger, *Chem. Ber.*, **91**, 437 (1958).
4. H. Schindlbauer, *Monatsh. Chem.*, **94**, 99 (1963).
5. H. Schindlbauer and H. Hagen, *Monastsh. Chem.*, **96**, 285 (1965).
6. Yu. K. Tovbin, I. P. Romm, G. M. Ostrovskii and E. N. Guryanova, *Zh. Prikl. Spektrosk.*, **22**, 477 (1975).
7. V. Baliah and P. Subbarayan, *J. Org. Chem.*, **25**, 1833 (1960).
8. J. J. Monagle, J. V. Mengenhauser and D. A. Jones, Jr, *J. Org. Chem.*, **32**, 2477 (1967).
9. G. P. Schiemenz and K. Rohlk, *Chem. Ber.*, **104**, 1722 (1971).
10. G. P. Schiemenz, *Justus Liebigs Ann. Chem.*, **752**, 30 (1971).
11. A. R. Katritzky and B. Ternai, *J. Chem. Soc. B*, 631 (1966).
12. H. Schindlbauer and V. Hilzenhauser, *Monatsh. Chem.*, **98**, 1196 (1967).
13. B. I. Stepanov, L. I. Chekunina and A. I. Bokanov, *J. Gen. Chem. USSR*, **43**, 2627 (1973).
14. H. Schindlbauer, *Monatsh. Chem.*, **96**, 1793 (1965).
15. H. Goetz, F. Nerdel and K. H. Weichel, *Justus Liebigs Ann. Chem.*, **665**, 1 (1963).
16. G.Shaw, J. K. Becconsall, R. M. Canadine and R. Murray, *J. Chem. Soc., Chem. Commun.*, 425 (1966).
17. I. P. Lipatova, V. V. Moskva, T. Sh. Sitdikova, E. I. Antropova and S. A. Samartseva, *J. Gen. Chem. USSR.*, **49**, 68 (1979).
18. L. Alder, D. Gloyna, H. G. Henning, M. V. Koz'menko and M. G. Kuz'min, *Vestn. Mosk. Univ., Ser. 2 Khim.*, **20**, 248 (1979).
19. L. I. Chekunina, A. I. Bokanov and B. I. Stepanov, *J. Gen. Chem. USSR*, **42**, 985 (1972).
20. F. D. Saeva, D. R. Rayner and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4176 (1968).
21. G. V. Ratovskii, A. M. Panov, Yu. L. Sukhoverkov, O. A. Yakutina and E. N. Tsvetkov, *J. Gen. Chem. USSR*, **49**, 479 (1979).
22. G. V. Ratovskii, A. M. Panov, O. A. Yakutina, Yu. I. Sukhoverkov and E. N. Tsvetkov, *J. Gen. Chem. USSR*, **48**, 1394 (1978).
23. M. A. Weiner and G. Pasternack, *J. Org. Chem.*, **32**, 3707 (1967).
24. N. A. Rozenal'skaya, A. I. Bakanov, B. M. Uzhinov and B. I. Stepanov, *J. Gen. Chem. USSR.*, **45**, 263 (1975).
25. J. Bourson and L. Olivares, *Phosphorus Sulfur*, **26**, 75 (1986).
26. K. Akasaki, T. Suzuki, H. Ohrui and H. Meguro, *Anal. Lett.*, **20**, 731 (1987).
27. C. E. Griffin and R. A. Polsky, *J. Org. Chem.*, **26**, 4722 (1961).
28. C. E. Griffin, R. P. Peller, K. R. Martin and J. A. Peters, *J. Org. Chem.*, **30**, 97 (1965).
29. E. W. Neuse, *J. Organomet. Chem.*, **7**, 349 (1967).
30. M. Simalty and M. H. Mebazaa, *Tetrahedron*, **28**, 3343 (1972).
31. R. A. Zingora, R. E. McGlothlin and E. A. Meyers, *J. Phys. Chem.*, **66**, 2579 (1962).
32. K. G. Berndt and D. Gloyna, *Acta Chim. Acad. Sci. Hung.*, **110**, 145 (1982).
33. R. R. Shagidullin, A. V. Chernova, I. A. Nuretdinov, G. M. Dorashkina and E. V. Bayandina, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 184 (1976).
34. L. C. Thomas, *Interpretation of the Infrared Spectra of Organophosphorus Compounds*, Heyden, London, 1974.
35. R. Withnall and L. Andrews, *J. Phys. Chem.*, **91**, 784 (1987).
36. W. B. Person, J. S. Kwiatkowski and R. J. Bartlett, *J. Mol. Struct.*, **157**, 237 (1987).
37. M. A. Sarukhanov, I. A. Popova and Yu. Ya. Kharitonov, *Russ. J. Inorg. Chem.*, **29**, 957 (1984).
38. R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta*, **21**, 861 (1965).
39. A. B. Burg and D. K. Kung, *J. Am. Chem. Soc.*, **92**, 1901 (1970).
40. R. Wolf, D. Honalla and F. Mathis, *Spectrochim. Acta, Part A*, **23**, 1641 (1967).
41. M. Sanchez, R. Wolf and F. Mathis, *Spectrochim. Acta, Part A*, **23**, 2617 (1967).
42. F. Watari, E. Takayama and K. Aida, *J. Mol. Struct.*, **55**, 169 (1979).
43. H. Rojhantalab, J. W. Nibler and C. J. Wilkins, *Spectrochim. Acta, Part A*, **32**, 519 (1976).
44. J. Goubeau and W. Berger, *Z. Anorg. Allg. Chem.*, **304**, 147 (1960).
45. E. A. Robinson, *Can. J. Chem.*, **41**, 302 (1963).
46. S. H. Hunter, V. M. Langford, G. A. Rodley and C. J. Wilkins, *J. Chem. Soc. A*, 305 (1968).

47. F. Choplin and G. Kaufmann, *Spectrochim. Acta, Part A*, **26**, 2113 (1970).
48. S.-T. King and R. A. Nyquist, *Spectrochim. Acta, Part A*, **26**, 1481 (1970).
49. J. Goubeau and A. Lentz, *Spectrochim. Acta, Part A*, **27**, 1703 (1971).
50. A. K. Dublish and A. J. P. Alix, *Acta Cienc. Indica Phys.*, **13**, 97 (1987).
51. W. D. Burkhardt, E. G. Höhn and J. Goubeau, *Z. Anorg. Allg. Chem.*, **442**, 19 (1978).
52. R. Pantzer, W. D. Burkhardt, E. Walter and J. Goubeau, *Z. Anorg. Allg. Chem.*, **416**, 297 (1975).
53. R. Pantzer, W. Schmidt and J. Goubeau, *Z. Anorg. Allg. Chem.*, **395**, 262 (1973).
54. D. Köttgen, H. Stoll, R. Pantzer, A. Lentz and J. Goubeau, *Z. Anorg. Allg. Chem.*, **389**, 269 (1972).
55. A. V. Yarkov, O. A. Raevskii and T. E. Kron, *J. Gen. Chem. USSR*, **57**, 2185 (1987).
56. A. W. Frank and I. Gordon, *Can. J. Chem.*, **44**, 2593 (1966).
57. A. B. Burg and A. J. Sarkis, *J. Am. Chem. Soc.*, **87**, 238 (1965).
58. M. P. McDonald and L. D. Wilford, *Spectrochim. Acta, Part A.*, **34**, 933 (1978).
59. M. Halmann and S. Pinchas, *J. Chem. Soc.*, 3264 (1958).
60. G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, **24**, 845 (1968).
61. G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, **25**, 355 (1969).
62. S. Milićev and D. Hadži, *Inorg. Chim. Acta*, **21**, 201 (1977).
63. S. Milićev, *Spectrochim. Acta, Part A*, **30**, 255 (1974).
64. H. F. Reiff and B. C. Pant, *J. Organomet. Chem.*, **17**, 165 (1969).
65. M. Fild, I. Hollenberg and O. Glemser, *Z. Naturforsch., Teil B*, **22**, 248 (1967).
66. B. N. Laskorin, V. P. Yakshin, M. I. Tymonyuk and A. V. Romanov, *Radiokhimiya*, **26**, 161 (1984).
67. L. I. Katziu, G. W. Mason and D. F. Peppard, *Spectrochim. Acta, Part A*, **34**, 57 (1978).
68. K. W. Bagnall, D. Brown and J. G. H. du Preez, *J. Chem. Soc.*, 5217 (1965).
69. J. Kennedy and A. M. Deane, *J. Inorg. Nucl. Chem.*, **19**, 142 (1961).
70. G. N. Chremos and R. A. Zingaro, *J. Organomet. Chem.*, **22**, 647 (1970).
71. K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, **17**, 1875 (1963).
72. R. R. Shifrina, I. P. Ronin, E. N. Gur'yanova and N. A. Rozamelskaya, *Zh. Prikl. Spektrosk.*, **34**, 111 (1981).
73. G. P. Schiemenz, *Chem. Ber.*, **98**, 65 (1965).
74. G. P. Schiemenz and H. O. Siebeneick, *Chem. Ber.*, **102**, 1883 (1969).
75. J. M. Casper and E. E. Remsen, *Spectrochim. Acta, Part A*, **34**, 1 (1978).
76. A. A. Shvets, O. A. Osipov, E. G. Amarskii and O. A. Moiseeva, *J. Gen. Chem. USSR*, **42**, 821 (1972).
77. E. G. Amarskii, A. A. Shvets and O. A. Osipov, *J. Gen. Chem. USSR*, **45**, 881 (1975).
78. A. A. Shvets, E. G. Amarskii, O. A. Osipov and L. V. Goncharova, *J. Gen. Chem. USSR*, **46**, 1654 (1976).
79. R. F. de Ketelaere and G. P. van der Kelen, *J. Mol. Struct.*, **23**, 233 (1974).
80. D. Aksnes and G. Aksnes, *Acta Chem. Scand.*, **17**, 1262 (1963).
81. H. Schulze and H. Müller, *Z. Naturforsch., Teil B*, **25**, 148 (1970).
82. K. B. Mallion, F. G. Mann, B. P. Tong and V. P. Wystrych, *J. Chem. Soc.*, 1327 (1963).
83. T. B. Grindley, K. F. Johnson, H. Kaack, A. R. Katritzky, G. P. Schiemenz and R. D. Topsom, *Aust. J. Chem.*, **28**, 327 (1975).
84. R. Mathis, M. Barthelat, C. Charrier and F. Mathis, *J. Mol. Struct.*, **1**, 481 (1968).
85. R. Mathis, F. Mathis, N. Ayed, B. Baccar and C. Charrier, *Spectrochim. Acta, Part A*, **39**, 233 (1983).
86. G. P. Schiemenz, *Angew. Chem., Int. Ed. Engl.*, **5**, 731 (1966).
87. V. G. Koval, *Zh. Prikl. Spektrosk.*, **26**, 766 (1977).
88. A. B. Remizov and R. K. Ismagilov, *J. Gen. Chem. USSR.*, **53**, 2388 (1983).
89. A. B. Remizov, M. V. Alparova, R. I. Tarasova, L. P. Syrneva, V. V. Moskva, *J. Gen. Chem. USSR*, **55**, 1326 (1985).
90. W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2871 (1958).
91. P. Planinić and H. Meider, *Polyhedron*, **8**, 627 (1989).
92. A. J. Carty and A. Efraty, *J. Chem. Soc., Chem. Commun.*, 1559 (1968).
93. J. Ellermann and D. Schirmacher, *Chem. Ber.*, **100**, 2220 (1967).
94. R. A. Zingaro and R. M. Hedges, *J. Phys. Chem.*, **65**, 1132 (1961).
95. J. R. Ferraro, *Appl. Spectrosc.*, **17**, 12 (1963).
96. A. L. Geddes, *J. Phys. Chem.*, **58**, 1062 (1954).
97. G. Aksnes and P. Albriksten, *Acta Chem. Scand.*, **32**, 1866 (1968).

98. H. Stenzenberger and H. Schindlbauer, *Monatsh. Chem.*, **99**, 2474 (1968).
99. T. Gramstad and H. J. Storesund, *Spectrochim. Acta, Part A*, **26**, 426 (1970).
100. U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem.*, **106**, 1235 (1975).
101. V. G. Koval, *Zh. Prikl. Spektrosk.*, **26**, 722 (1977).
102. E. I. Matrosov abd M. I. Kabachnik, *Dokl. Chem.*, **232**, 14 (1977).
103. V. E. Bel'skii and L. Kh. Ashrafullina, *J. Gen. Chem. USSR*, **49**, 1968 (1979).
104. A. Bertoluzza, S. Bonara, G. Fini and M. A. Morelli, *Can. J. Spectrosc.*, **32**, 107 (1987).
105. M. C. R. Symons and G. Eaton, *J. Chem. Soc., Faraday Trans. 1*, **78**, 3033 (1982).
106. R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta*, **20**, 1679 (1964).
107. E. Lindner and H. Dreher, *J. Organomet. Chem.*, **104**, 331 (1976).
108. M. A. Sarukhanov, I. A. Popova and Yu. Ya. Kharitonov, *Russ. J. Inorg. Chem.*, **28**, 21 (1983).
109. I. A. Popova, M. A. Sarukhonov and Yu. Ya. Kharitonov, *Russ. J. Inorg. Chem.*, **30**, 937 (1985).
110. J. R. Durig and K. K. Chatterjee, *Inorg. Chem.*, **28**, 298 (1989).
111. A. B. Burg, *J. Am. Chem. Soc.*, **88**, 4298 (1966).
112. J. Goubeau and D. Köttgen, *Z. Anorg. Allg. Chem.*, **360**, 182 (1968).
113. J. Kincaid, K. Nakamoto, J. A. Tiethof and D. W. Meek, *Spectrochim. Acta, Part A*, **30**, 2091 (1974).
114. J. R. Durig and T. J. Hizer, *J. Mol. Struct.*, **145**, 15 (1986).
115. J. R. Durig, J. S. DiYorio and D. W. Wertz, *J. Mol. Spectrosc.*, **28**, 444 (1968).
116. A. H. Cowley and J. L. Mills, *J. Am. Chem. Soc.*, **91**, 2915 (1969).
117. R. A. Zingaro, *Inorg. Chem.*, **2**, 192 (1963).
118. M. Fild, *Z. Anorg. Allg. Chem.*, **358**, 257 (1968).
119. W. van der Veer and F. Jellinek, *Recl. Trav. Chim. Pays-Bas*, **85**, 842 (1966).
120. M. G. King and G. P. McQuillan, *J. Chem. Soc. A*, 898 (1967).
121. V. I. Katolichenko, Yu. P. Egorov, Yu. Yu. Borovikov, Yu. P. Makovetskii and N. G. Feshchenko, *Vopr. Stereokhim.*, **4**, 98 (1974).
122. A. M. Aguiar and J. R. S. Irelan, *J. Org. Chem.*, **34**, 3349 (1969).
123. J. Goubeau, H. Reinhardt and D. Bianchi, *Z. Phys. Chem. (Frankfurt)*, **12**, 387 (1957).
124. H. Gerding, D. H. Zijp, F. N. Hooge, G. Blasse and P. J. Christen, *Recl. Trav. Chim. Pays-Bas*, **84**, 1274 (1965).
125. P. Nicpon and D. W. Meek, *Inorg. Chem.*, **5**, 1297 (1966).
126. F. Watari, *Inorg. Chem.*, **20**, 1776 (1981).
127. G. N. Chremos and R. A. Zingaro, *J. Organomet. Chem.*, **22**, 637 (1970).
128. V. Mark, C. Dungan, M. Crutchfield and J. R. van Wazer, *Top. Phosphorus Chem.*, **5**, 227 (1967).
129. H. R. Hays, *J. Org. Chem.*, **33**, 3690 (1968).
130. E. Fluck and H. Binder, *Z. Naturforsch. Teil B*, **22**, 805 (1967).
131. A. A. Borisenko, N. M. Sergeev and Yu. A. Ustynyuk, *Mol. Phys.*, **22**, 715 (1971).
132. T. A. Albright, *Org. Magn. Reson.*, **8**, 489 (1976).
133. J. P. Albrand, A. Cogne and J. B. Robert, *Chem. Phys. Lett.*, **48**, 524 (1978).
134. J. H. Letcher and J. R. van Wazer, *J. Chem. Phys.*, **44**, 815 (1966).
135. J. R. van Wazer and J. H. Letcher, *Top. Phosphorus Chem.*, **5**, 169 (1967).
136. J. H. Letcher and J. R. van Wazer, *J. Chem. Phys.*, **45**, 2916 (1966).
137. J. B. Robert and L. Wiesenfeld, *Mol. Phys.*, **44**, 319 (1981).
138. J. D. Kennedy and W. McFarlane, *J. Chem. Soc., Chem. Commun.*, 666 (1976).
139. T. Weller, D. Deininger and R. Lochmann, *Z. Chem.*, **21**, 105 (1981).
140. R. Radeglia and R. Wolff, *Z. Naturforsch., Teil A*, **36**, 1177 (1981).
141. A. J. Montana, N. Zumbulyadis and B. P. Dailey, *J. Am. Chem. Soc.*, **99**, 4290 (1977).
142. J. P. Albrand and J. B. Robert, *Pure Appl. Chem.*, **52**, 1047 (1980).
143. G. A. Berkova, V. I. Zakharov, S. A. Smirnov, N. M. Morkovin and B. I. Ionin, *J. Gen. Chem. USSR*, **47**, 1315 (1977).
144. B. L. Poh and W. Saenger, *Spectrochim. Acta, Part A*, **39**, 305 (1983).
145. E. N. Tsvetkov, T. E. Kron and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 669 (1980).
146. H. H. Karsch, *Chem. Ber.*, **115**, 823 (1982).
147. L. Maier, *Helv. Chim. Acta*, **54**, 1651 (1971).
148. L. D. Quin, M. J. Gallagher, G. T. Cunkle and D. B. Chesnut, *J. Am. Chem. Soc.*, **102**, 3136 (1980).
149. L. Maier, *Helv. Chim. Acta.*, **49**, 1249 (1966).
150. J. A. Davies, J. G. Mierzowiak and R. Syed, *J. Coord. Chem.*, **17**, 25 (1988).

151. M. Fild, I. Hollenberg and O. Glemser, *Z. Naturforsch., Teil B*, **22**, 253 (1967).
152. R. C. Crosby and J. F. Haw, *J. Magn. Reson.*, **82**, 367 (1989).
153. N. Muller, P. C. Lauterbur and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956).
154. T. A. Gerken and W. M. Ritchey, *J. Magn. Reson.*, **24**, 155 (1976).
155. V. L. Foss, V. A. Solochenko, Yu. A. Verts and I. F. Lutsenko, *J. Gen. Chem. USSR*, **49**, 1510 (1979).
156. H. Elias, M. Dreher, S. Neitzel and H. Volz, *Z. Naturforsch., Teil B*, **37**, 684 (1982).
157. M. Heuschmann and H. Quast, *Chem. Ber.*, **115**, 3384 (1982).
158. V. I. Yakshin, N. M. Meshcheryakov, M. E. Ignatov, B. N. Leskorin, V. G. Yagodin and E. G. Il'in, *J. Gen. Chem. USSR*, **55**, 1266 (1985).
159. L. Bemi, H. C. Clark, J. A. Davies, C. A. Fyfe and R. E. Wasylisheen, *J. Am. Chem. Soc.*, **104**, 438 (1982).
160. A. B. Burg, *Inorg. Chem.*, **24**, 3342 (1985).
161. K. J. Packer, *J. Chem. Soc.*, 960 (1963).
162. E. Fluck and N. Seng, *Z. Anorg. Allg. Chem.*, **393**, 126 (1972).
163. T. A. Albright, W. J. Freeman and E. E. Schweizer, *J. Org. Chem.*, **40**, 3437 (1975).
164. J. B. Robert and L. Wiesenfeld, *J. Magn. Reson.* **38**, 357 (1980).
165. K. B. Dillon, T. C. Waddington and D. Younger, *J. Inorg. Nucl. Chem.*, **43**, 2665 (1981).
166. R. D. Sammons, P. A. Frey, K. Brunik and M. D. Tsai, *J. Am. Chem. Soc.*, **105**, 5455 (1983).
167. N. J. Koole, A. J. de Koning and M. J. A. de Bie, *J. Magn. Reson.*, **25**, 375 (1977).
168. S. O. Grim and L. C. Satek, *J. Inorg. Nucl. Chem.*, **39**, 499 (1977).
169. G. Singh and G. S. Reddy, *J. Org. Chem.*, **44**, 1057 (1979).
170. J. Jacobus, *J. Org. Chem.*, **44**, 3717 (1979).
171. R. Appel and U. Baumeister, *Z. Naturforsch., Teil B*, **35**, 513 (1980).
172. S. O. Grim, L. C. Satek. C. A. Tolman and J. P. Jesson, *Inorg. Chem.*, **14**, 656 (1975).
173. M. Duncan and M. J. Gallagher, *Org. Magn. Reson.*, **15**, 37 (1981).
174. H. Koppel, U. Lochmann and K. D. Schleinitz, *J. Prakt. Chem.*, **317**, 425 (1975).
175. P. W. Clark, J. L. S. Curtis, P. E. Garrou and G. E. Hartwell, *Can. J. Chem.*, **42**, 1714 (1974).
176. D. J. Peterson, *J. Org. Chem.*, **30**, 1939 (1965).
177. S. O. Grim and E. D. Walton, *Inorg. Chem.*, **19**, 1982 (1980).
178. L. A. Solovetskaya, N. M. Sergeev, R. K. Magdeeva and E. E. Nifant'ev, *J. Gen. Chem. Chem. USSR*, **55**, 1072 (1985).
179. C. Santelli-Rouvier, *Synthesis*, 64 (1988).
180. I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1915 (1982).
181. S. O. Grim, J. DelGaudio, R. P. Molenda, C. A. Tolman and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 3416 (1974).
182. D. J. Peterson, *J. Organomet. Chem.*, **8**, 199 (1967).
183. P. A. W. Dean and M. K. Hughes, *Can. J. Chem.*, **58**, 180 (1980).
184. H. Schmidbaur and T. Pollok, *Angrew. Chem., Int. Ed. Engl.*, **25**, 348 (1986).
185. H. J. Emeléus and J. M. Miller, *J. Inorg. Nucl. Chem.*, **28**, 662 (1966).
186. H. J. Jacobson, *J. Mol. Spectrosc.*, **34**, 245 (1970).
187. H. J. Jacobson and O. Menscher, *Acta Chem. Scand.*, **25**, 680 (1971).
188. H. J. Jacobson and J. A. Nielsen, *J. Mol. Spectrosc.*, **33**, 474 (1970).
189. N. K. Skvortsov, B. I. Ionin and A. A. Petrov, *J. Gen. Chem. USSR*, **44**, 209 (1974).
190. N. K. Skvortsov, G. E. Tereshchenko, B. I. Ionin and A. A. Petrov, *J. Gen. Chem. USSR*, **46**, 578 (1976).
191. W. McFarlane, *Proc. R. Soc. London, Ser. A*, **306**, 185 (1968).
192. L. Maier, *J. Inorg. Nucl. Chem.*, **24**, 1073 (1962).
193. L. B. Littlefield and L. D. Quin, *Org. Magn. Reson.*, **12**, 199 (1979).
194. M. D. Gordon and L. D. Quin, *J. Am. Chem. Soc.*, **98**, 15 (1976).
195. L. Maier, *Helv. Chim. Acta*, **47**, 120 (1964).
196. L. Maier, *J. Inorg. Nucl. Chem.*, **24**, 275 (1962)
197. R. Radeglia, J. Schulze and H. Teichmann, *Z. Chem.*, **15**, 357 (1975)
198. L. Maier, *Helv. Chim. Acta*, **47**, 27 (1964).
199. L. Maier, *Z. Anorg. Allg. Chem.*, **345**, 29 (1966).
200. L. Maier, *Chem. Ber.*, **94**, 3043 (1961).
201. L. Maier, *Helv. Chim. Acta*, **48**, 133 (1965).
202. S. O. Grim, P. H. Smith, I. J. Colquhoun and W. McFarlane, *Inorg. Chem.*, **19**, 3195 (1980).

203. G. Grossmann, B. Walther and U. Gastrock-Mey, *Phosphorus Sulfur*, **11**, 259 (1981).
204. K. Ramarajan, M. D. Herd and K. D. Berlin, *Phosphorus Sulfur*, **11**, 199 (1981).
205. I. J. Colquhoun, W. McFarlane, J. M. Bassett and S. O. Grim, *J. Chem. Soc., Dalton Trans.*, 1645 (1981).
206. S. O. Grim and E. D. Walton, *Phosphorus Sulfur*, **9**, 123 (1980).
207. S. O. Grim, L. C. Satek and J. D. Mitchell, *Z. Naturforsch., Teil B*, **35**, 832 (1980).
208. R. B. King and J. C. Cloyd, *Phosphorus*, **3**, 213 (1974).
209. J. L. Bookham and W. McFarlane, *Polyhedron*, **7**, 129 (1988).
210. W. McFarlane and D. S. Rycroft, *J. Chem. Soc., Dalton Trans.*, 2162 (1973).
211. I. J. Colquhoun, H. C. E. McFarlane, W. McFarlane, J. A. Nash, R. Keat, D. S. Rycroft and D. G. Thompson, *Org. Magn. Reson.*, **12**, 473 (1979).
212. A. Cogne, A. Grand, J. Laugier, J. R. Robert and L. Wiesnfeld, *J. Am. Chem. Soc.*, **102**, 2238 (1980).
213. W. J. Ster, A. Okruszek, B. Uznanski and J. Michalski, *Phosphorus*, **2**, 97 (1972).
214. W. W. DuMont, *Z. Naturforsch., Teil B*, **40**, 1453 (1985).
215. K. M. Emikeev, E. V. Bayandina, I. E. Ismaev, N. A. Buina, A. V. Il'yasov and I. A. Nuretdinov, *J. Gen. Chem. USSR*, **53**, 1933 (1983).
216. P. A. W. Dean, *Can. J. Chem.*, **57**, 754 (1979).
217. R. P. Pinnell, C. A. Megerle, S. L. Mannatt and P. A. Kroon, *J. Am. Chem. Soc.*, **95**, 977 (1973).
218. D. W. Allen, I. W. Nowell and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 2505 (1985).
219. D. W. Allen and B. F. Taylor, *J. Chem. Res. (S)*, 220 (1981).
220. D. W. Allen and B. F. Taylor, *J. Chem. Res. (S)*, 392 (1986).
221. S. W. Carr and R. Colton, *Austl. J. Chem.*, **34**, 35 (1981).
222. I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Commun.*, 484 (1982).
223. J. P. Albrand, D. Gagnaire and J. B. Robert, *Bull. Soc. Chim. Fr.*, 479 (1968).
224. L. I. Vinogradov, M. G. Zimin, Yu. Ya. Samitov and N. N. Pudovnik, *J. Gen. Chem. USSR*, **42**, 1712 (1972).
225. R. Kosfeld, G. Hagele and W. Kuchen, *Angew. Chem., Int. Ed. Engl.*, **7**, 814 (1968).
226. J. B. Hendrickson, M. L. Maddox, J. J. Sims and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964).
227. R. Bravo, M. Durand and J. P. Laurent, *Org. Magn. Reson.*, **5**, 357 (1973).
228. M. Durand, J. P. Laurent and P. Lepage, *J. Chim. Phys.*, **71**, 847 (1974).
229. V. Ya. Komarov, V. I. Zakharov, Yu. V. Belov and B. I. Ionin, *J. Gen. Chem. USSR*, **50**, 1020 (1980).
230. B. N. Laskorin, V. V. Yakshin and L. I. Sokal'skaya, *Dokl. Chem.*, **215**, 184 (1974).
231. R. M. Aminova, M. B. Zuev and I. D. Morozova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2255 (1985).
232. J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).
233. P. Haake, R. D. Cook and G. A. Hurst, *J. Am. Chem. Soc.*, **89**, 2650 (1967).
234. G. Matolcsy, K. Bauer, A. Pál, I. Ujvary, I. Belai, A. Gerlei, M. Kardoś, P. Sohar and I. Pelczer, *Acta Chim. Hung.*, **123**, 145 (1986).
235. A. W. Verstuyft, L. M. Cary and J. H. Nielsen, *Inorg. Chem.*, **14**, 1495 (1975).
236. O. A. Raevskii, N. G. Mumzhieva, N. A. Aleksandrova and R. G. Gainullina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 797 (1977).
237. O. A. Raevskii and N. G. Mumzhieva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1822 (1981).
238. E. Dunach and H. B. Kagan, *Tetrahedron Left.*, **26**, 2649 (1985).
239. H. P. Abicht and K. Jurkschat, *Z. Chem.*, **28**, 371 (1988).
240. W. Drenth and D. Rosenberg, *Recl. Trav. Chim. Pays-Bas*, **86**, 26 (1967).
241. D. Rosenberg and W. Drenth, *Tetrahedron*, **27**, 3893 (1971).
242. R. M. Lequan, M. J. Pouet and M. P. Simonnin, *J. Chem. Soc., Chem. Commun.*, 475 (1974).
243. R. M. Lequan, M. J. Pouet and M. P. Simonnin, *Org. Mag. Reson.*, **7**, 392 (1975).
244. C. Charrier and M. P. Simonnin, *C. R. Acad. Paris, Ser. C*, **265**, 1347 (1967).
245. M. P. Simonnin and B. Borecka, *Bull. Soc. Chim. Fr.*, 842 (1966).
246. W. R. Cullen, A. W. Wu, A. R. Davis, F. W. B. Einstein and J. D. Hazlett, *Can. J. Chem.*, **54**, 2871 (1976).
247. M. J. Gallagher, *Aust. J. Chem.*, **21**, 1197 (1968).
248. P. Sartori and G. Mosler, *Phosphorus Sulfur*, **8**, 115 (1980).
249. T. Kaufmann, K. Berghus and A. Rensing, *Chem. Ber.*, **118**, 3737 (1985).
250. D. Howells and S. Warren, *Tetrahedron Lett.*, 675 (1973).

251. C. E. Griffin, *Tetrahedron*, **20**, 2399 (1964).
252. W. McFarlane, *Org. Magn. Reson.*, **1**, 3 (1969).
253. R. Benassi, M. L. Schenetti, F. Taddei, P. Vivarelli and P. Dembech, *J. Chem. Soc., Perkin Trans. 2*, 1338 (1974).
254. R. F. de Ketelaere and G. P. van der Veken, *J. Mol. Struct.*, **27**, 25 (1975).
255. C. E. Griffin, J. J. Burke, F. E. Dickson, M. Gordon, H. H. Hsieh, R. Obrycki and M. P. Williamson, *J. Phys. Chem.*, **71**, 4558 (1967).
256. B. L. Shapiro and L. E. Mohrmann, *J. Phys. Chem. Ref. Data*, **6**, 919 (1977).
257. C. E. Griffin, R. B. Davison and M. Gordon, *Tetrahedron*, **22**, 561 (1966).
258. V. V. Negrebetskii, A. I. Bokanov, L. Ya. Bogel'fer, N. A. Rozanelskaya and B. I. Stepanov, *J. Gen. Chem. USSR*, **48**, 1196 (1978).
259. P. Dembech, G. Seconi, P. Vivarelli, M. L. Schenetti and F. Taddei, *Org. Magn. Reson.*, **4**, 185 (1972).
260. R. H. Kemp, W. A. Thomas, M. Gordon and C. E. Griffin, *J. Chem. Soc. B*, 527 (1969).
261. H. J. Jacobsen and M. Begtrup, *J. Mol. Spectrosc.*, **40**, 276 (1971).
262. H. J. Jacobsen and M. Begtrup, *J. Mol. Spectrosc.*, **35**, 158 (1970).
263. H. J. Jacobsen and J. A. Nielsen, *J. Mol. Spectrosc.*, **31**, 230 (1969).
264. C. E. Griffin and W. A. Thomas, *J. Chem. Soc. B*, 477 (1970).
265. A. J. Carty and R. K. Harris, *J. Chem. Soc., Chem. Commun.*, 234 (1967).
266. J. J. Brophy and M. J. Gallagher, *Aust. J. Chem.*, **20**, 503 (1967).
267. T. Kauffmann, E. Antfang and J. Olbrich, *Chem. Ber.*, **118**, 1022 (1985).
268. Yu. Ya. Samitov, E. A. Berdnikov, F. R. Tarantasheva, B. Ya. Margolis and E. G. Kataev, *J. Gen. Chem. USSR*, **45**, 2097 (1977).
269. R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964).
270. H. Hofmann and P. Schellenbeck, *Chem. Ber.*, **100**, 692 (1967).
271. D. J. Peterson, *J. Org. Chem.*, **31**, 950 (1966).
272. E. Juaristi, L. Valle, C. Mora-Uzeta, B. A. Valenzuela, P. Joseph-Nathan and M. F. Fredrich, *J. Org. Chem.*, **47**, 5038 (1982).
273. E. Juaristi, N. A. Lopez-Nuñez, B. Valenzuela, L. Valle, R. A. Toscano and M. Sorano-Garcia, *J. Org. Chem.*, **52**, 5185 (1987).
274. A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 5354 (1964).
275. K. A. O. Starzewski and H. tom Dieck, *Phosphorus*, **6**, 177 (1976).
276. D. Rosenberg, J. W. de Haan and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **87**, 1387 (1968).
277. N. Platzer, F. Dardoise, W. Bergeret, J. C. Gautier and S. Reynal, *Phosphorus Sulfur*, **27**, 275 (1986).
278. G. A. Gray and S. E. Cremer, *J. Org. Chem.*, **37**, 3458 (1972).
279. G. A. Gray, S. E. Cremer and K. L. Marski, *J. Am. Chem. Soc.*, **98**, 2109 (1976).
280. A. M. Aguiar, C. J. Morrow, J. D. Morrison, R. E. Burnett, W. F. Master and N. S. Bhacca, *J. Org. Chem.*, **41**, 1545 (1976).
281. M. Mikolajczyk, P. Graczyk and B. Balczewski, *Tetrahedron Lett.*, **28**, 573 (1987).
282. P. Dagnac, J. L. Virlichie and G. Jugie, *J. Chem, Soc., Dalton Trans.*, 155 (1979).
283. T. A. Modro, *Can. J. Chem.*, **55**, 3681 (1977).
284. G. A. Gray, *J. Am. Chem. Soc.*, **95**, 7736 (1973).
285. L. F. Wuyts, D. F. van de Vondel and G. P. van der Kelen, *J. Organomet. Chem.*, **129**, 163 (1977).
286. V. V. Negrebetskii, A. I. Bokanov, N. A. Rozanel'skaya and B. I. Stepanov, *J. Gen. Chem. USSR*, **49**, 1304 (1979).
287. S. R. Postle, *Phosphorus Sulfur*, **3**, 269 (1977).
288. G. E. Balimann, C. J. Groombridge, R. K. Harris, K. J. Packer, B. J. Say and S. F. Tanner, *Philos. Trans. R. Soc. London, Ser. A*, **299**, 643 (1981).
289. L. D. Quin, M. D. Gordon and S. O. Lee, *Org. Magn. Reson.*, **6**, 503 (1974).
290. M. D. Gordon and L. D. Quin, *J. Org. Chem.*, **41**, 1690 (1976).
291. R. G. Cavell, A. A. Pinkerton, W. Sim and A. J. Tomlinson, *Inorg. Chem.*, **18**, 2901 (1979).
292. L. M. Yagupol'skii, N. V. Pavlenko, N. V. Ignat'ev, G. I. Mertyushecheva and V. Ya. Semenii, *J. Gen. Chem. USSR*, **54**, 297 (1984).
293. E. E. Wille, D. S. Stephenson, P. Capriel and G. Binsch, *J. Am. Chem. Soc.*, **104**, 405 (1982).
294. H. Schindlbauer, *Chem. Ber.*, **100**, 3432 (1967).
295. H. Schindlbauer, *Chem. Ber.*, **102**, 2914 (1969).
296. W. Prikosovich and H. Schindlbauer, *Chem. Ber.*, **102**, 2922 (1969).

297. R. F. de Ketelaere and G. P. van der Kelen, *J. Mol. Struct.*, **27**, 33 (1975).
298. J. W. Rayshys, R. W. Tuft and W. A. Sheppard, *J. Am. Chem. Soc.*, **90**, 5236 (1968).
299. D. I. Nichols, *J. Chem. Soc. A*, 1471 (1969).
300. M. G. Hogben and W. A. G. Graham, *J. Am. Chem. Soc.*, **91**, 283 (1969).
301. G. A. Gray and T. A. Albright, *J. Am. Chem. Soc.*, **99**, 3243 (1977).
302. L. D. Quin, J. Szewczyk, K. Linehan and D. L. Harris, *Magn. Reson. Chem.*, **25**, 271 (1987).
303. T. L. Brown and C. P. Cheng, *Faradag Symp. Chem. Soc.*, **13**, 75 (1979).
304. C. P. Cheng and T. L. Brown, *J. Am. Chem. Soc.*, **102**, 6418 (1980).
305. W. McFarlane and D. S. Rycroft, *J. Chem. Soc., Chem. Commun.*, 902 (1972).
306. I. A. Nuretdinov and E. I. Loginova, *Bull. Acad. Sci. USSR, Chem. Sci.*, 2765 (1973).
307. W. W. DuMont and H. J. Kroth, *Z. Naturforsch., Teil B*, **36**, 332 (1981).

CHAPTER 6

Methods of preparation of phosphine chalcogenides

A. K. BHATTACHARYA
FACT Engineering and Design Organisation, New Delhi 110019, India
and
N. K. ROY
Indian Agricultural Research Institute, New Delhi 110012, India

---

The chemistry of organophosphorus compounds, Volume 2, Phosphine oxides, sulphides, selenides and tellurides
Edited by Frank R. Hartley. © 1992 John Wiley & Sons, Ltd. ISBN: 0-471-93056-3

I. INTRODUCTION

Phosphine oxides are the most stable organophosphorus compounds and belong to an important class. The oxides and sulphides find extensive use as flame retardants[1], fire-proofing agents in polyurethane foams[2], as intermediates in catalytic reactions including carbon dioxide and nitrogen fixation[3], as polydentate chelating legands[4], as catalysts[5,6], in the chlorination of carbohydrates[7,8], in surface coatings[9], as adhesives[10], as fire retardants[11], as biologically active compounds[12,13], in inhibiting the precipitation of scale-forming salts[14], as powerful sequestering agents[15,16], in the preparation of polyesters with improved properties[17], as flotation reagents for minerals[18], in the solvent extraction of precious metals[16,19] and many more. Allylic phosphine oxides have also been used as precursors[20] of dienes of defined geometry, as in the synthesis of 3-deoxy-vitamin D_2.

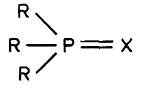
Good reviews on the subject have been published by Hays and Peterson[21], Maier[22], several by Miller[23] and others[24,25]. Older reviews include those by Maier[26], Berlin and Butler[27] and Sasse[28]. Generally these reviews are more than a decade old and the list of new organophosphorus compounds has grown tremendously in the meantime. This review attempts to cover the literature for the last 20 years or so up to June 1990. The reader is recommended to refer to the older literature and texts for the earlier references.

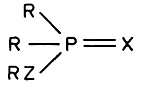
II. SCOPE AND LIMITATIONS

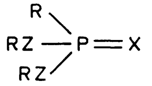
Phosphine oxides, as their name implies, are derivatives of phosphine and hence their methods of preparation necessarily include the methods of preparation of phosphines. In some cases the reactants interact to give the oxides directly, whereas in other cases they have to be synthesized through the phosphines.

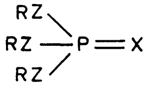
The phosphines have been dealt with in detail in the first volume of this series, including their methods of preparation. There is bound to be some overlap with the corresponding chapter of the previous volume, but the emphasis in this chapter is on the methods of preparation of the oxides and sulphides.

Organophosphorus chemistry has grown at a phenomenal rate in the last two decades or so, and a wide variety of analogous compounds are known. Thus:









R = alkyl, aryl, etc. X = O, S, Se, Te

Z = O, S, N

Phosphine oxide (1)

Phosphinate (2)

Phosphonate (3)

Phosphate (4)

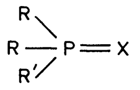
For the purpose of this Chapter, the scope will be limited to the compounds as described in **1** above, i.e. with no P—alkoxy, S—alkyl or N—alkyl linkage. This automatically excludes the compounds represented by **2**, **3** and **4** as they are discussed elsewhere in the series. However, the oxides of polyphosphines, which could have one or more P—P linkages instead of the usual P—C linkages, are included here.

III. METHODS OF PREPARATION OF PHOSPHINE OXIDES

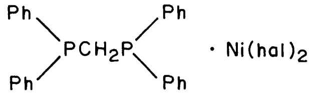
A. Reactions Involving Conversion of P^{III} to P^{V}

1. Through oxidation of phosphines

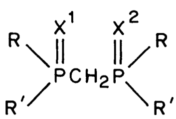
a. By air oxidation. Tertiary phosphine oxides are prepared[29] by refluxing the phosphine, **5** (R = octyl, hexyl, decyl, Ph; R′ = Ph; X = nil or O), in air. Compounds **5** in turn were prepared by treating $R'PCl_2$ with sodium powder and then Rhal (hal = halogen) in an oxygenated atmosphere. Thus 35.8 g of $PhPCl_2$ were refluxed for 6 h in xylene with sodium powder and the resulting disodium derivative was further refluxed with 1-bromooctane in air to give the oxide **5** (X = O). Nickel(II) halides form complexes **6** with diphosphines, which are stable in the solid state but decompose slowly if heated above 220 °C, undergoing air oxidation[30] to yield the diphosphine dioxide **7**($X^1 = X^2 = O$; R = R′ = Ph).



(**5**)



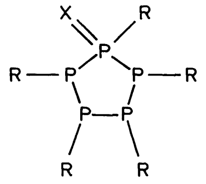
(**6**)



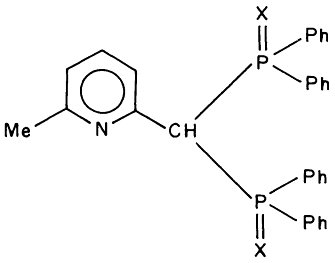
(**7**)

Phosphines on oxidation with air or oxygen in the presence of π-cyclopentadienyl- or π-indenyl-nickel catalysts give phosphine oxides in excellent yields[31], e.g. Ph_3P on stirring with nickelocene in benzene in the presence of oxygen gives Ph_3PO in 90% yield. Catalytic oxidation of phosphines using molecular oxygen has been reported[32] in the presence of $(R_2NCS_2)\cdot MoO_2$ (R = Pr, Et). Thus $R_3P{=}O$ (R = Ph, Bu) is prepared by stirring a benzene solution of R_3P (R = Ph) containing $(Pr_2NCS_2)_2{\cdot}MoO_2$ under 1 kg cm^{-2} of oxygen.

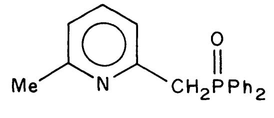
Ph_3P is reported to be converted[33] quantitatively into its oxide by treatment with oxygen in the presence of $Ph_4P^+Cl^-$, whereas in the absence of the catalyst the reaction failed. Mono-oxidation of methyl or ethyl derivatives of cyclopentaphosphine **8** is reported to occur[34] by treatment with dry atmospheric oxygen (R = Me, Et; X = nil, O). 2-Bis(diphenylphosphino)methylpyridine and its 6-methyl derivative **9** (X = nil), on aerial oxidation[35] followed by quaternization with Br_2 or warming with acetic acid, gave the monophosphine oxide **10** in 82% yield by the loss of one phosphine group, whereas oxidation with MnO_2 yielded the bisphosphine oxide **9** (X = O). Formation of **10** is unusual as $RCH(PPh_2)_2$ do not undergo similar loss of a phosphine group.



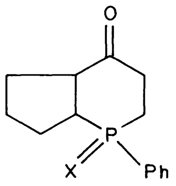
(8)



(9)



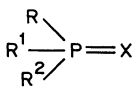
(10)



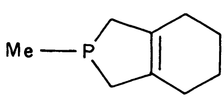
(11)

Catalytic oxidation of phosphines, e.g. Bu_3P, in the presence of $[Pd\{Ph_2P(CH_2)PPh_2\}_2]$ at 25–45 °C with dry air is found to give the oxide[36]. Il'yasov *et al.*[37] reported the oxidation of the phosphabicyclononane system **11** (X = nil) into its oxide (X = O) by reaction with oxygen. Compound **11** is prepared by reaction of β-diethylaminoethyl cyclopentenyl ketone with phenylphosphine.

Chloromethyldimethylphosphine **5** (R = Me; R′ = CH_2Cl; X = nil) is oxidized[38] by oxygen to give the phosphine oxide **5** (X = O). Likewise, acylphosphine **12** (R = Ph; R^1 = Me; R^2 = COMe; X = nil) is oxidized to **12** (X = O) on treatment[39] with dry oxygen. Halogenated acylphosphines **12** (R = R^1 = Ph; R^2 = $COCH_2Cl$, $COCH_2F$, COC_2F_5, COC_3F_7, COC_6F_5) are also similarly oxidized[40], as are the diorganyltrifluoroacetyl-



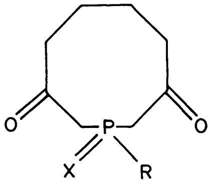
(12)



(13)

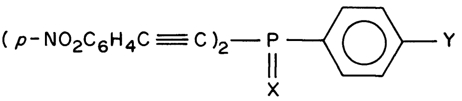
phosphines[41] **12** (R = Ph; R^1 = $PhCH_2$, cyclohexyl, Me_3C; R^2 = $COCF_3$). Aryldiphenylphosphines **5** [R = Ph; R′ = COMe, $COCF_3$, $COOMe_3$, CO-(3,5-dinitrophenyl)] are known to react[42,43] with oxygen if the latter is slowly introduced into a diethyl ether solution of the phosphine, to give the oxides **5** (X = O).

Ozone and *m*-chloroperbenzoic acid are also known[44] to oxidize phosphines and the oxidation proceeds with retention of configuration. 3-Phospholene derivatives **13** with cyclohexane or substituted cyclohexanes fused at the double bond, on ozonolysis at −78 °C, are reported[45] to offer a useful route for the synthesis of 3,8-phosphonanedione-1-oxide systems **14** (R = Me; X = O).



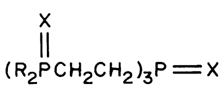
(14)

b. By peroxy compounds. Dimethylphosphine on oxidation[46] with 7% H_2O_2 at 20–30 °C in the presence of 4% HCl gives the oxide in 96% yield. The dioxide **7** is prepared[47] by oxidation of the phosphine with 100% H_2O_2 in acetone. H_2O_2 oxidation has also been used to oxidize[48] the phosphine **5** (R = *n*-octyl; R′ = *sec*-butyl). Acetylenic phosphine[49] **15** (X = nil; Y = H, Cl, OMe, etc.) and trivinylphosphine[50] are also prepared by oxidation with dilute aqueous hydrogen peroxide at less than 100 °C.



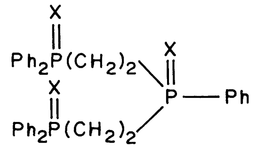
(15)

King and Heckley[51] have reported the H_2O_2 oxidation of the poly(tertiary phosphines) **16** (R = Ph; X = O) and **17** (X = nil), resulting in the oxidation of all the P^{III} present in the molecule. The preparation of poly(tertiary phosphines) is described in the literature (see Sections III.A and IV.B.1). Phosphines of the type **5** [R = CH_2OAc, $CH_2CH(Me)OH$] are also known[52,53] to give, on H_2O_2 oxidation, the corresponding oxides (X = O) in 84–95% yield. Tetraaryl(alkyl)vinylidenephosphines **18** (X = nil) have been oxidized with H_2O_2 to give the *trans* isomer in 84% yield[54]. Compound **18** was, in turn, prepared in 55% yield of the *trans* isomer, by treatment of bis-*p*-chlorophenylphosphine chloride **19** (R = *p*-ClC_6H_4; X = nil) with lithium in thf, followed by reaction with ClHC=CHCl for 1.5 h at −20 °C.

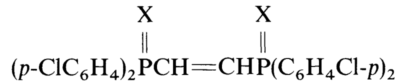


$$(R_2\overset{X}{\overset{\|}{P}}CH_2CH_2)_3P{=}X$$

(16)

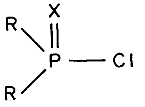


(17)

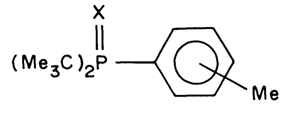


$$(p\text{-ClC}_6\text{H}_4)_2\overset{\overset{\text{X}}{\|}}{\text{P}}\text{CH}{=}\text{CH}\overset{\overset{\text{X}}{\|}}{\text{P}}(\text{C}_6\text{H}_4\text{Cl-}p)_2$$

(18)

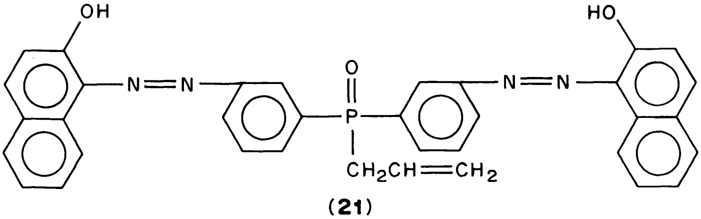


(19)



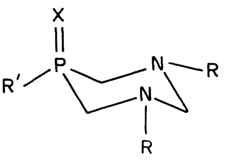
(20)

H_2O_2 oxidation of **20** (*m*-Me or *p*-Me) and **5** (R = Ph; R′ = $CH_2CH{=}CH_2$) is reported[55] to give the corresponding oxides (X = O) in 91% and 82% yields, respectively. The oxide **5** (R = Ph; R′ = $CH_2CH{=}CH_2$; X = O), obtained above, on nitration and reduction with Sn–HCl followed by diazotization and coupling with 2-naphthol, gives a phosphine oxide dye[56] (**21**).

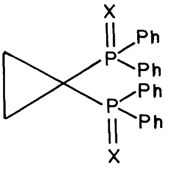


(21)

The stereochemistry of the oxidation of phosphines with H_2O_2 has been described by Leuchenbach[57].

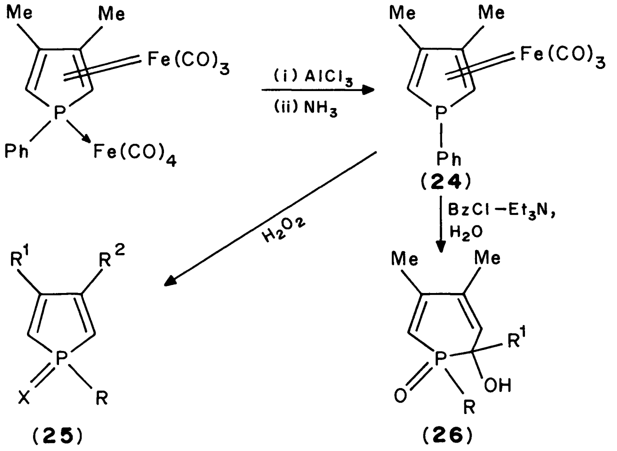


(22)



(23)

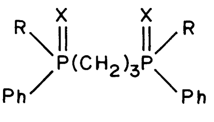
Diazaphosphorinanes **22** (R = Ph, *p*-MeC_6H_4, *p*-BrC_6H_4, H_2CPh; R′ = Ph; X = nil) are known to be oxidized[58] to 5-oxo derivatives **22** (X = O) by H_2O_2. Similarly, cyclopropylidenebis(diphenylphosphine) **23** (X = nil) is reported[59] to be prepared in 91% yield by H_2O_2 oxidation. The phosphine **23** is prepared in 26% yield by cyclopropanation of $(Ph_2P)_2C{=}CH_2$ with $Me_2SO({=}CH_2)$ and is air and moisture stable. Tertiary phosphine sulphides also, on H_2O_2 oxidation, give the corresponding phosphine oxides (see Section III.B.4 for details). Iron–phosphole complexes **24** are known[60] to be oxidized by H_2O_2 to **25** (R = Ph; $R^1 = R^2$ = Me; X = O). The decomplexed products, **24**, in turn,

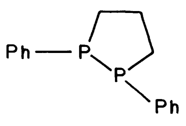


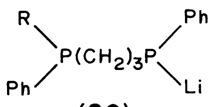
SCHEME 1. Preparation of phosphole oxides.

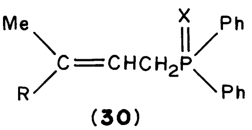
were prepared by treating the iron phosphole complex with $AlCl_3$ and then with ammonia solution. Treatment of **24** with BzCl, Et_3N and water gave the ring expanded product **26** (Scheme 1).

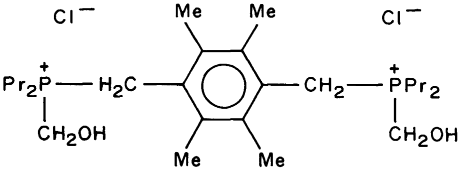
H_2O_2 oxidation of diphosphines **27** (R = Me, Bu, Ph; R′ = Et, Bu, Pr, Me_2CH, pentyl, hexyl; X = nil) are known to give[61] the oxides in 62–68% yields. Compounds **27**, in turn, are prepared by ring opening of the diphosphacyclopentanes **28** with organolithium compounds, RLi, to give **29**, followed by reaction of **29** with R′Br. Tertiary phosphines **1** (R = alkyl) on oxidation with H_2O_2 give[62] the corresponding oxides. **1**(X = nil), in turn, are prepared by treatment of RMgBr with PCl_3 in thf. Allylic phosphine oxides are likewise formed by H_2O_2 oxidation[63] of **30** (R = H, Et), prepared by reaction of Ph_2PLi in thf with $MeCR{=}CHCH_2COOC_6H_3Cl_2$-2,6. Oxidation of the phosphonium salts **31** with H_2O_2–MnO_2 is reported to give arylenebismethylenephosphine oxide[64] **32**(X = O). Compounds **31** are prepared by reaction of Pr_2PCH_2OH with arylenebis(methyl halides).


(27)

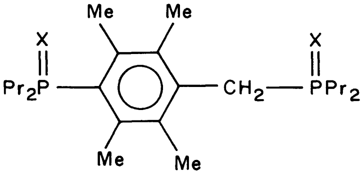

(28)


(29)


(30)

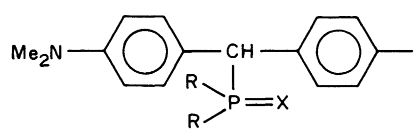


(31)

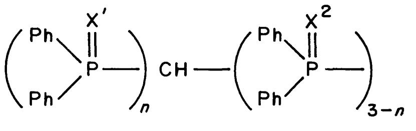


(32)

H_2O_2 is known to oxidize the leuko dyes **33** (R = Et, CMe_3, Ph; X = nil) to the phosphine oxides **33** (X = O). Polydentate ligands containing P of the type **34** (X^1 = O; X^2 = S; *n* = 1, 2, 3) are prepared[65] by H_2O_2 oxidation of **34** (X′ = nil).

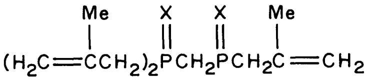


(33)



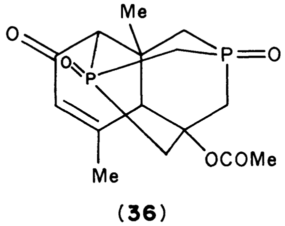
(34)

Olefinic phosphines, **35**(X = nil), on oxidation with H_2O_2, give[66] the phosphine oxides **35**(X = O). These on further oxidation with ozone followed by a multiple aldol reaction on the product, gives the phosphaheterocycle **36**. Phosphine oxide **5** (R = Ph; R^1 = 2-$MeOC_6H_4$; X = O) is prepared by H_2O_2 oxidation of the corresponding **5** (X = nil), which in turn is prepared by the reaction of Ph_2PCl with 2-$MeOC_6H_4MgBr$. Similarly, 2-XC_6H_4X' (X = X′ = halides) on reaction with 2 mol equiv. of $LiPPh_2$ in the presence of furan, followed by oxidation[68] with H_2O_2, gives **5** (R = Ph, R^1 = 2-ClC_6H_5). Likewise, 50 g of **5** (R = CO-2, 6-$Cl_2C_6H_3$; R′ = 2,5-xylyl; X = nil) in MeCN, on treatment with 150 ml of 30% H_2O_2 at 60 °C, gives[69] the corresponding oxide (X = O).



$(H_2C{=}\overset{Me}{C}CH_2)_2\overset{X}{\overset{\|}{P}}CH_2\overset{X}{\overset{\|}{P}}CH_2\overset{Me}{C}{=}CH_2$

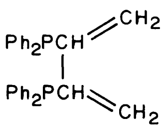
(35)



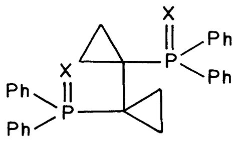
(36)

$S[OCH(CF_3)_2]_2$

(37)



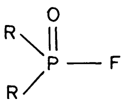
(38)



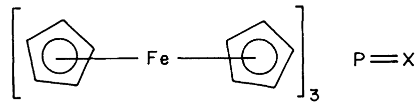
(39)

c. By oxides of sulphur. Aqueous sodium sulphite has been used to oxidize[70] the phosphine–iodine complex R_3PI_3 (see Section III.C.1). Sulphoxylate **37** is known[71] to oxidize Me_3P to its oxide. Recently Dziwok *et al.*[72] have used $Me_2S(=CH_2)O$ to convert 2,3-(bisphenylphosphinyl)buta-1,3-diene **38** by double cyclopropanation and oxidation to the phosphine oxide **39** ($X = O$). SO_2 is reported to react with Me_3P to give[37] both Me_3PO and Me_3PS. $(Me_3SiO)_2SO_2$ is known[74] to react with $PhPCl_2$ at 140 °C for 2 h to produce $(Me_3SiO)_2P(O)Ph$, Me_3SiCl and SO_2.

d. By oxides of nitrogen. Hydroxylamine hydrochloride in refluxing pyridine has been used[57] to oxidize chiral cyclic tertiary phosphines stereospecifically. Reactions of nitrosyl fluoride, FNO, with dialkylphosphines R_2PH is reported to give[75] the corresponding oxide along with the substitution of H by F. Thus 0.026 mol of dibutylphosphine, on treatment with FNO at −50 to −68 °C, gave **40** (R = Bu, Me) in 7.3% yield.



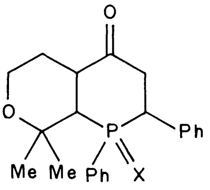
(40)



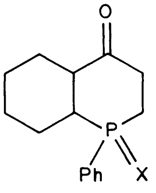
(41)

Photochemical transfer of oxygen from heterocyclic *N*-oxides to phosphine sulphide has also been reported[76] (see Section III.B.4). Enantiomeric phosphine **12** (R = Me; R′ = Ph; R^2 = Pr; X = nil) and diastereomeric phosphorinanes are thus stereospecifically oxidized[77] by tertiary amine oxides.

e. By other inorganic oxidants. Substituted phosphines and nickel halide complexes, e.g. $[(Ph_3P)_2NiX_2]$(X = Cl, Br, I) are known[78] to be quantitatively oxidized to the corresponding oxides by sodium chlorite. Use of ClO_2 as the oxidizing agent led to the preparation of $(R_3P{=}O)_2{\cdot}NiCl_2$ (R = Ph, cyclohexyl) and $[\{Ph_2P(=O)CH_2\}_2NiCl_2]$. Oxidation of triferrocenylphosphines **41** with MnO_2, $KMnO_4$ or oxygen over alumina gave the corresponding oxides[79] (X = O) in 83, 64 and 15% yields, respectively. $KMnO_4$ has also been used to oxidize[80,81] oxaphosphabicyclodecanones **42** and **43** (X = nil, O).



(42)



(43)

Mercury(II) acetate has been used to oxidize[82] Me_3P, forming a 1:1 adduct $Me_3PO{\cdot}AcOH$, which is also formed in 73–81% yield by reaction of Me_3PO with RCOOH(R = H, Me). This adduct on treatment with sodium methoxide gives $Me_3PO{\cdot}MeOH$ and sodium acetate.

Triphenylphosphine can be oxidized[83] with 2–3 mol equiv. of MnO_2 in kerosene. Thus Ph_3P (1 mol) was oxidized by MnO_2 (3 mol) in kerosene (1750 ml) at 140–150 °C for 5–6 h to give $Ph_3P{=}O$ in 80% yield. R_3P is also oxidized[84] to its oxide with $KMnO_4$ in acetone, the product being obtained by repeated extraction of the black residue with chloroform. R_3P are oxidized with FSO_2Cl at room temperature to give[85] $R_3P{=}O$.

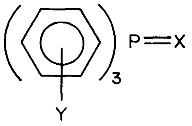
f. By miscellaneous oxidants. Tributylphosphine, on mixing with methyl pyruvate under nitrogen at 40–45 °C for 1 day, is reported[86] to give the oxide in 90% yield along with dimethylmethylene dicarboxylate. Diethyl mesoxalate also has been used as an oxidizing agent in the same reaction. A mixture of Ph_3P and ethyl pyruvate on heating for 1 h at 140 °C forms $Ph_3P{=}O$ in 58.9% yield.

The anaerobic aqueous alkaline oxidation[87] of **44**, ($w = 0$–2; $y = 3\text{-}w$) and $(p\text{-}OHC_6H_4)_3P$ gives a stoichiometric amount of hydrogen and the corresponding phosphine oxides. $(Y\text{-}C_6H_4)_3P$ reacts[88] with chloramine-T in ethanol to give **45** ($X = NSO_2C_6H_4Me\text{-}p$), which on hydrolysis with water gives the phosphine oxide **45** ($X = O$) along with $H_2NO_2SC_6H_4Me\text{-}p$, together forming a strongly hydrogen-bonded adduct **46**. $(Me_3Si)_2O$ is reported[89] to oxidize $C_6F_5PRF_3$ (**47**) to **48** ($X = O$). Compound **47** is prepared by the reaction of C_6F_5PRY ($Y = NEt_2$) with HCl or HBr, thus forming the halides ($Y = Cl$, Br), which in turn react with NaF in MeCN to give the fluoro derivative ($Y = F$). This on further reaction with AsF_3 gives **47**. $C_6F_5PRNEt_2$ was prepared by reaction of $Et_2NP(R)Cl$ ($R = Me$, Et, CMe_3, Ph) with C_6F_5MgBr.

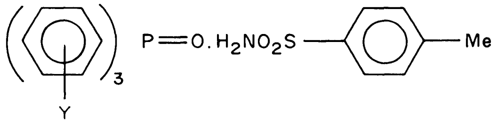
Tertiary phosphines **5** ($R = Me$, Et; $R' =$ octadecyl, octyl, dodecyl, hexadecyl, hexyl, tetradecyl; $X =$ nil) on oxidation with *tert.*-butyl peroxide give the oxides **5** ($X = O$). The phosphines **5** are prepared by treatment of dialkylphosphines with an alkene[90].

$$(Me)_wP(CH_2CH_2Z)_y$$
$$Z = COOH,\ CH_2OH,\ (CH_2)_3NH_2$$

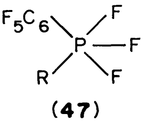
(44)



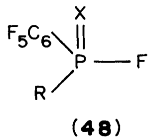
(45)



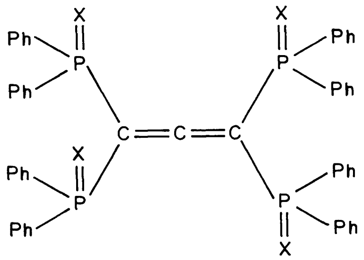
(46)



(47)



(48)

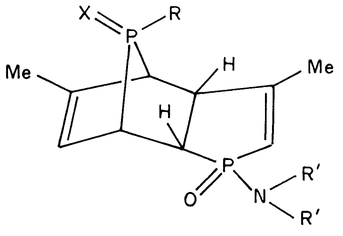


(49)

Tetrakis(diphenylphosphino)allenes **49** (X = nil) were oxidized with bistrimethylsilyl peroxide, $(Me_3SiO)_2$, to give the corresponding oxide[91,92] **49** (X = O) (see Section III.A.2.b for the preparation of the phosphine **49**).

Trimethylsilyl *tert*.-butyl peroxide, $Me_3CSiOOSiCMe_3$, is known to react[93a] with Ph_3P to give the oxide (itself being converted to $Me_3SiOCMe_3$ in the process). Bis(trimethylsilyl) peroxide is a versatile[93b] reagent for the selective generation of the oxyphosphoryl group. It oxidizes phosphines to the oxides with retention of configuration at phosphorus. It also converts the thiophosphoryl function to the oxophosphoryl function with inversion of configuration at phosphorus.

Et_3P is known to be converted into its oxide by reaction[94] with dimethylacetylene dicarboxylate in presence of water, forming dimethyl pyruvate along with other products. The tricyclic phosphine **50** (X = nil) is reported[95] to be oxidized (X = O) by treatment with Me_3COOH. Compound **50** (X = nil) was in turn prepared by the reaction of the phosphinous chloride of the phosphine **50** (R = Cl; X = nil) with PhMgBr. Haloalkylphosphine oxides are prepared[96] by oxidative halogenation of tertiary hydroxyalkyl phosphines. Thus **1** [$R = HO(CH_2)_3$; X = nil] on treatment with HCl gives **5** [$R = HO(CH_2)_3$; R′ = H; X = O).

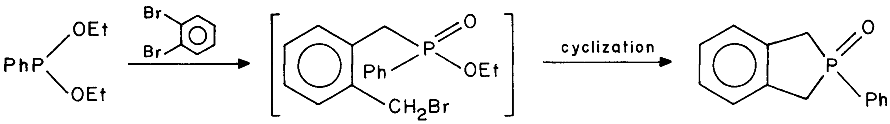


R = Ph; R′ = Me, Et

(50)

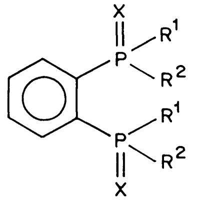
2. *Through reaction of organometallics with P^{III} compounds*

a. With P^{III} esters. 2-Phenylisophosphindoline-2-oxide (**51**) is prepared[97] by reaction of phenylphosphinic acid esters with *o*-xylene dibromide in the presence of $NaAlH_2(OCH_2CH_2CMe)_2$ through a Michaelis–Arbuzov rearrangement. The cyclization can also be brought about by treatment with $HSiCl_3$. The reaction of MeMgBr and $(EtO)_2POH$ with RI is reported[98] to give the oxide **5** [R = Me; $R' = F_3C(CF_2)_7CH_2$, $F_3C(CF_2)_5(CH_2)_2$, $F_3C(CF_2)_3(CH_2)_3$, $F_3C(CF_2)_9(CH_2)_2$]. The reaction of PhRPOH (R = Bu, $PhCH_2$, *n*-hexyl) with R′Br(R′ = Ph, *o*/*p*-tolyl, *p*-AcC_6H_4, *p*-$AcNC_6H_4$, *p*-$Me_2NC_6H_4$, *p*-PhC_6H_4, 2-naphthyl, *p*-NCC_6H_4) in the presence of $[Pd(PPh_3)_4]$ and Et_3N gives[99] phosphine oxides of the type **12** (R^2 = Ph).



(51) (1)

Biphosphine oxide ligands **52** (X = O) for transition metal complexes have been prepared[100] by reaction of *o*-difluorobenzene with $R^1R^2P(O)M^+$ (M = alkali metal). The

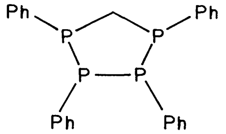


(52)

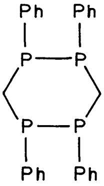
latter is prepared *in situ* by treating R^1R^2POH with an alkali metal hydride. Compound **52** (X = O) on reduction with $PhSiH_3$ at 120 °C gives the phosphine (X = nil). Tertiary phosphine oxides are prepared[101] by reaction of primary aliphatic or aromatic halides with activated sodium phosphinates, which in turn are prepared by treating dialkylphosphine oxide with complex bases $NaNH_2$-*tert*-BuONa. Ph_2POH reacts with R'hal (R' = $PhCH_2$, Et, Me_2CH, cyclohexyl, menthyl; hal = Cl, Br, I) in the presence of $NaAlH_2(OCH_2CH_2CMe)_2$ to give[102] phosphine oxides of the type **5** (R = Ph).

Alkylarylphosphine oxides of the type **5** (R = Me, R' = $CH_2C_6H_3Cl_2$-3,4) can be prepared[103] by the addition of sodium hydride to a cooled solution of 50% Me_2POH in isobutyl alcohol and 3,4-dichlorobenzyl chloride in toluene at 20–45 and 50–55 °C.

b. With P^{III} halides. PCl_3 is reported to react[104] with trialkylaluminium under nitrogen at 120–145 °C to give alkyldichlorophosphines, which on treatment with carbon in the presence of Et_3N at high temperature and pressure, followed by oxidation, give the corresponding oxides. Phenylphosphine dichloride reacts[105] with sodium acetylide to yield the phosphine, **5** (X = nil; R = —C≡CH; R' = Ph) in 52% yield, which is then oxidised (X = O) to give the oxide in 80–90% yield. Grignard reaction of arylphosphinyl halides Ph_{3-n} PCl_n with aryl halides, BrC_6H_4Et, followed by oxidation with H_2O_2 gave[19b] phosphine oxides of type **5** in 21–89% yield. As a variation of this reaction, Baudler *et al.*[106] obtained 1,2,4,5-tetraphenylcyclo-3,6-dicarba-1,2,4,5-tetraphane (**54**) in 19% yield by metallation of the phospholane **53** and subsequent reaction with CH_2Cl_2.

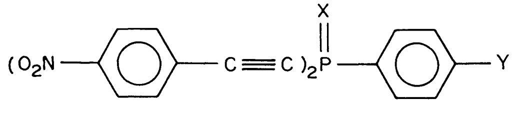


(53)



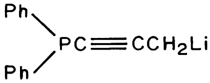
(54)

Aryl-substituted P^{III} halides on reaction[107] with aryl-substituted copper acetylides in the ratio 1:2, e.g., p-$O_2NC_6H_4C{\equiv}CCu$ in thf, containing catalytic LiCl or LiBr, gave, on oxidation with H_2O_2, the oxide **55**. A similar reaction with PCl_3 gave (p-$O_2NC_6H_4C{\equiv}C)_3P$, which polymerized during recrystallization.

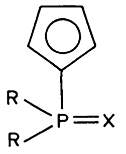


Y = H, Cl, OMe, NMe2

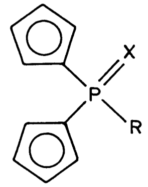
(55)



(56)



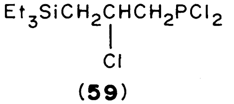
(57)



(58)

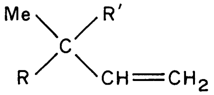
Tetrakisdiphenylphosphinoallenes **49** ($X = \text{nil}$) were prepared[91] in 56% yield by reacting the lithium derivative of the acetylenic phosphine **56** with diphenylchlorophosphine **19** ($R = Ph$; $X = \text{nil}$).

Cyclopentadienylthallium is allowed[108] to react for 1 h at room temperature with P^{III} halides such as R_2PCl or $RPCl_2$($R = Ph, Me$) in diethyl ether, yielding 40–100% $CpPR_2$ **57** ($X = \text{nil}$) and Cp_2PR **58** ($X = \text{nil}$), respectively, which on H_2O_2 oxidation gave the corresponding oxides ($X = O$). Reaction of P^{III} dihalides with organometallics has been used to prepare phosphine oxide dyes[56]. Thus reaction of **59** with PhMgBr, followed by oxidation, gives the phosphine oxide **5** ($R = Ph$; $R' = CH_2CH{=}CH_2$; $X = O$; see Section III. A. 1.b for its conversion to an azo dye, **21**). Compound **59** was prepared by the reaction of $Et_3SiCH_2CH{=}CH_2$ with PCl_5 in benzene at $-15\,°C$ when an adduct was formed which was decomposed with phosphorus and CS_2 at $-20\,°C$.



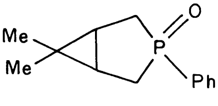
$Et_3SiCH_2CH(Cl)CH_2PCl_2$

(59)

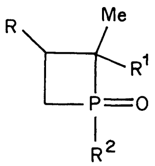


(60)

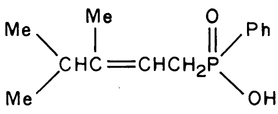
In a variation of the reaction of organometallics with P^{III} halides, phosphorus heterocycles are prepared by the reaction[109] of unsaturated compounds with a complex of a P^{III} halide with $AlCl_3$, e.g. addition of **60** ($R = CH{=}CH_2$; $R' = Me$) to the dichlorophenylphosphine.$AlCl_3$ complex in CH_2Cl_2 at room temperature followed by quenching with aqueous $NaHCO_3$ gives the phosphabicyclo[3.1.0]hexane **61** and the vinylphosphetan **62** ($R = CH{=}CH_2$; $R^1 = Me$; $R^2 = Ph$). Reaction of **60** ($R = Ph$) with $PhPCl_2.AlCl_3$ complex resulted in the formation of **62** ($R = R^2 = Ph$; $R^1 = CH{=}CH_2$), whereas with $PhPBr_2.AlCl_3$ in dichloromethane a mixture of **61** and **62** was obtained. Use of dibromomethane in the above reaction, however, resulted in the formation of the open-chain derivative **63**. A similar reaction of $MePCl_2.AlCl_3$ with camphene gave after hydrolysis the phosphetane oxide[110] **64** and the chlorophosphetane oxide **65**.



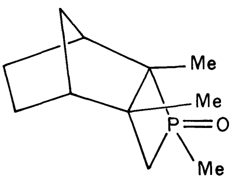
(61)



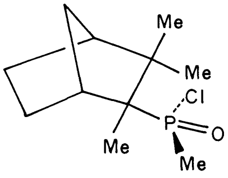
(62)



(63)



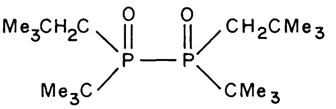
(64)



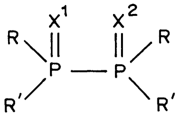
(65)

Phosphine oxides of the type **12** (R^1 and R^2 = substituted phenyl; R = *tert*.-alkyl) are prepared[111] by alkylation of the $AlCl_3$ complex of the corresponding **19** (R = aryl; X = nil) at 20–160 °C. Diaryl(tertiaryalkyl)phosphine oxide **5** (R = unsubstituted Ph; R′ = alkyl; X = O) can be prepared likwise[112,113] by reacting a complex of **19** (R = aryl; X = nil) with $AlCl_3.HCl$ and an alkylating agent in diethyl ether and heating.

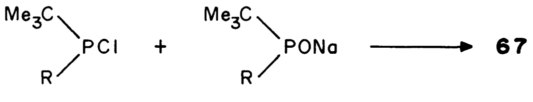
Alkoxymethylphosphine oxides are prepared in 35–80% yields by reaction[114] with Grignard reagents, e.g. $(EtOCH_2)_3P{=}O$ was prepared in 44% yield by reaction of $Cl_2P(O)CH_2OEt$ with $EtOCH_2MgCl$. Bis(*p*-chlorophenyl)methylphosphine oxide is prepared[115] by reacting *p*-chlorophenylmagnesium bromide with phosphine dichloride in thf. Alkyl(di-*tert*.-butyl)phosphine oxide **5** (R′ = Me, Et) is formed by refluxing[116] **19** (R = Me_3C; X = nil) with R′ONa in MeOH for 1 h. Tertiary phosphine oxides of the type **5** (R = R′) or **1** (R = R′ = C_{1-12}-alkyl or aryl; X = O or S) are obtained[117] by refluxing **19** with a mixture of the halo derivative of the hydrocarbon in the presence of a metal, generally magnesium. Grignard reaction of *tert*-butylphosphinic dichloride with Me_3CCH_2MgBr, followed by oxidation[118], gives oxide **5** (R = Me_3CCH_2; R′ = Me_3C; X = O) together with diphosphine dioxide **66**. The phosphine oxides **67** (R = Me_3C, Me_2CH, Me_2CHCH_2, Bu, Ph; R′ = Me_3C; X^1 = nil; X^2 = O) are prepared[119] by the reaction of Me_3CPRCl with $Me_3CPRONa$.



(66)

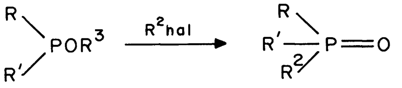


(67)



3. *Through Michaelis–Arbuzov rearrangement*

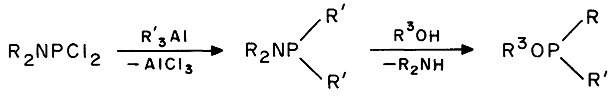
A convenient method for preparing tertiary phosphine oxides consists in the reaction of phosphinite esters **68** [(**a**) R = R′; (**b**) R ≠ R′] with alkyl halides (reaction 2). The rearrangement offers a very facile pathway for the formation of a C—P bond and has been reviewed elsewhere[120]. Compound **68** is obtained as in reaction 3. Thus methyl iodide reacts[121] vigorously with **68** (R = R′ = Et) at room temperature to yield **5** (R = Et; R′ = Me; X = O). Alkyl halides seem to be more reactive than aryl halides, in keeping with the general reluctance of the aryl groups to undergo nucleophilic substitution.



(68)

(2)

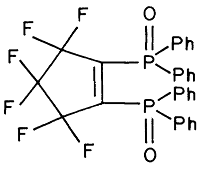
Hal = Cl, Br, I; α-halocarbonyl compounds, etc.



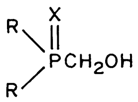
(68)

(3)

Ethyl diphenyl phosphinite reacts on refluxing[16a] with 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene to give perfluorocycloalk-1-enyl-1,2-ylenediphosphoryl compounds **69**, useful as metal extractants and sequestering agents. Some phosphinite esters undergo self-isomerization to the oxides, even in absence of any alkyl halides. Thermal isomerization is also fairly common, e.g. methylphosphine oxides can be prepared in 77.8% yield by the thermal rearrangement[122] of **70** (R = R = Me) in phenyl cyanide at 130 °C in 8 h. Toluene, xylene, octane, decalin and *o*-dichlorobenzene have also been used as solvents in the reaction.



(69)

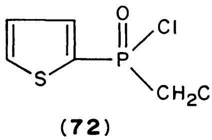


(70)

Tetramethylphosphonium halides **71** also undergo rearrangement[123] on heating at 190–200 °C in presence of HCl gas to give **70** (R = CH_2OH; R′ = Me; X = O). Me_3P or $(AcOCH_2)_3P$, on heating at 160–180 °C in the presence of HCl gas with simultaneous removal of the low-boiling products by distillation, yields[124] the phosphine oxide **5** (R = $ClCH_2$; R′ = Me; X = O). Irradiation of hydroxymethylphosphines **70** (R′ = CH_2OH; X = nil) in an inert gas is also known[125] to give the rearranged product, e.g. hydroxymethyldimethylphosphine (108 g) when irradiated for 8 h at 25 °C under nitrogen gives 79% of **70** (R = R′ = Me), which on further irradiation at 30 °C in dichloromethane for 9 h under argon gives trimethylphosphine oxide in 91.85% yield.

$(HOH_2C)_4P^+Cl^-$

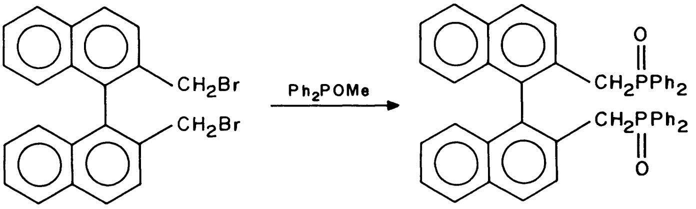
(71)



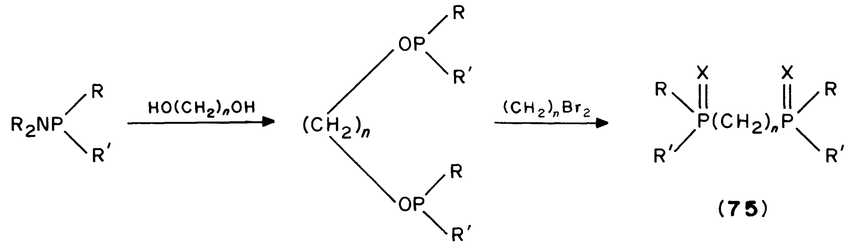
(72)

Dichlorophosphines undergo rearrangement on reaction with paraformaldehyde[126], e.g. 2-thienyldichlorophosphine on heating at 135 °C for 4 h gives **72** in 33% yield. The yield of **72** is further increased to 74.5% by heating with additional paraformaldehyde. Likewise, chlorodimethylphosphine on treatment with formaldehyde in dry benzene is known to give[127] chloromethyldimethylphosphine oxide.

Arbuzov reaction of (*S*)-(−)-2,2′-bis(bromomethyl)-1,1′-binaphthyl (**73**) with Ph_2POMe results in the formation[128] of the corresponding oxide **74**. R_2NPRR' on reaction with α,ω-alkanediols, followed by reaction with alkylene dibromide, rearranges[129] to form the phosphine oxide **75** (X = O).

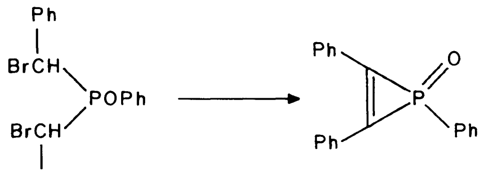


(73) **(74)**



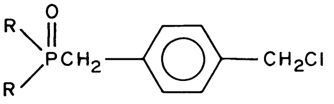
(75) (4)

Phosphine oxides containing upto four phosphorus atoms (**16**) have also been prepared[130] from the phosphinites **68** (R = R′), by reaction with trischloromethylphosphine. Triphenylphosphine oxide **76** has been synthesized[131a] starting from **68a** (R = R′ = PhCHBr; R^3 = Ph). Addition of 1,5-diazabicyclo[4.3.0]non-5-ene to a benzene solution of **68a** gave the phosphacyclopropene **76**, which at 120 °C gave PhC≡CPh. Addition of aqueous NaOH to **76** gave(*cis*-1,2-diphenylvinyl)phosphinic acid. The preparation of oxaphosphirane phosphine oxides has also been reported[131b].

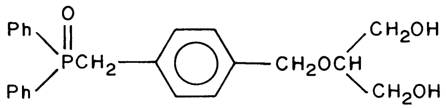


(76) (5)

Some specific phosphine oxides (**77**), useful as flame retardants in polyurethanes, are prepared[132] by reaction of phosphinite **68a** (R = R′ = Ph, tolyl; R^3 = Me, Et) with *p*-$Cl/BrCH_2C_6H_4CH_2Cl/Br$, which was further reacted with glycerol or glycols to give **78**. Thus a mixture of methyldiphenyl phosphinite (216.2 parts) and aryl halide (175.1 parts), when stirred for 1 h at 90–100 °C followed by 1 h at 120–130 °C, gives **77** (R = Ph), which on stirring with glycerin (138.1 parts) and sodium carbonate (58.0 parts) for 2 h at 100–130 °C gives **78** (440.1 parts).

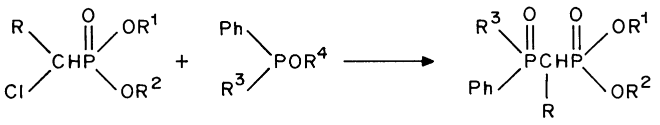


(77)



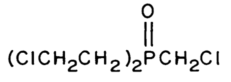
(78)

The reaction of α-halo compounds with phosphinites also leads to the formation[133] of phosphine oxides **79** ($R, R', R^2 = H, Ph; R^3 = Ph; R^4 = Et, Me_2CH$) (reaction 6). Tris(chloroethyl)phosphine oxide and **80** underwent Michaelis–Arbuzov rearrangement on heating at 170 °C with triethyl phosphite to give the oxides **81** and **82** ($R = OEt$) in high yield. Compound **80** is, in turn, prepared by the chlorination of tris(hydroxyethyl)-phosphine oxide and **5** ($R = HOCH_2CH_2; R' = CH_2OH; X = O$). Tris(chloroethyl)-phosphine oxide also undergoes an Arbuzov reaction[134] with butyldiphenyl phosphinite to give the tetra(tertiary phosphine) oxide **82** ($R = Ph; X = O$).

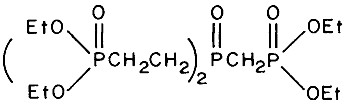


(79)

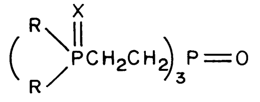
(6)



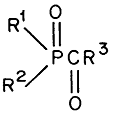
(80)



(81)

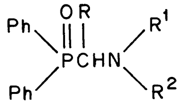


(82)



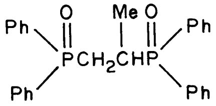
(83)

Acyl-substituted phosphine oxides **83** are prepared[135,136] by treating the phosphinite **68b** ($R = \text{aryl}; R' = C_{1-16}$-alkyl, cycloalkyl, aryl, *S*- or *N*-heterocycle) with R^2COhal ($hal = Cl, Br, I; R^2 = C_{1-16}$-alkyl, cycloalkyl) as in equation 2. Thus, 2,6-$MeOC_6H_3COCl$ is heated for 3 h at 50 °C with methyldiphenyl phosphinite to give **83** ($R' = R^2 = Ph$; $R^3 = 2$, 6-$MeOC_6H_3$). Arbuzov reaction or Mannich-type condensation of Ph_2POH with aldehydes or secondary amines results in the formation[137] of the phosphine oxides **84** ($R = H$, alkyl, Ph, CH═CHPh, CH═CHMe, SMe, SPh, cyclohexyl).



NR^1R^2 = morpholino, NMe_2,
piperidino, NMePh, $N(CH_2Ph)_2$,
$NPhCH_2Ph$

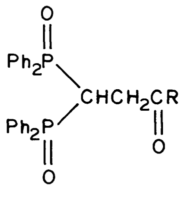
(84)



(85)

Condensation of R_2POH ($R = Et, Ph$) with unsaturated halides or 1,3-dienes, in the presence of a phase-transfer catalyst, results in the formation of a phosphine oxide containing β,γ-unsaturated groups. Thus $BrCH_2CH{=}CH_2$ reacts with Et_2POH in the presence of KOH and Katamin AB to give[138] **5** ($R = Et$; $R' = CH_2CH{=}CH_2$; $X = O$). Similarly, the alkyl(tetraphenylethylene)diphosphine dioxide **85** is prepared[139] by reaction of Ph_2POH with $CH_2{=}CHCHBr$, which gives $Ph_2P(O)CH_2CH{=}CH_2$. The latter on further reaction with Ph_2POH gives **85**.

Reaction of Ph_2POH with $Ph_2P(O)CH{=}CHCOR$ at 100–150 °C under an inert gas gives[140] the oxide **86** whereas reaction[141] with $BzCH_2CH_2NMe_2HCl$ at 100–110 °C for 3 h in MeOH gives the oxide **5** ($R = Ph$; $R' = CH_2CH_2Bz$) in 80% yield. Alkylation of R_2POH with R'hal gives[142] phosphine oxides of the type **5**. Thus, $[Me(CH_2)_7]_2POH$, on reaction with $PhCH_2Cl$ in the presence of $(Bu_4N)_2SO_4$, gives the oxide **5** [$R = Me(CH_2)_7$; $R^1 = CH_2Ph$].

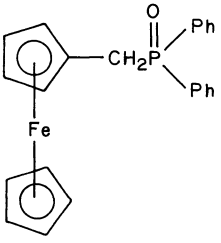


R = OMe, Ph

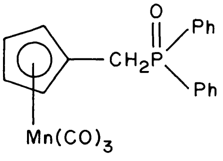
(86)

Addition of Et_2POH to p-$R^2C_6H_4N{=}CHPh$ gives **5** ($R = Et$; $R' = p$-$R^2C_6H_4$-NHCHPh, where $R^2 = COOMe/Et$; $X = O$) in 20.5% yield[143]; Et_2POH is prepared by the hydrolysis of Et_2PCl. Likewise, the reaction[144] of R_2POH (R = pentyl, hexyl, heptyl) with $hal(CH_2)_nCOOH$ (hal = Cl, Br, I; $n = 1,2$) or with $hal(CH_2)_nCOOR^2$(R' = alkyl) gives the oxide **5** [$R' = (CH_2)_nCOOR^2$, where R^2 = H or alkyl]. Reaction of $(Me_3C)_2POLi$ with Me_3CCOCl gives[145] **5** [$R = Me_3C, R' = C(O)CMe_3; X = O$].

$Ph_2P(O)CH_2Cl$, prepared from Ph_3P and $ClCH_2OMe$ in four steps, reacts[146] with cyclopentadienyllithium in benzene on refluxing for 4–5 h to give a mixture of $Ph_2P(O)CH_2R$ (R = 1- or 2-cyclopentadienyl). These oxides react with $[CpFe(CO)_2]_2$ and $[Mn_2(CO)_{10}]$ to give ferrocene and cymantrene complexes **87a** and **87b**.



(87a)

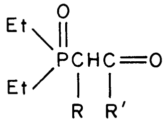


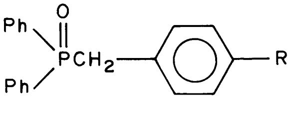
(87b)

4. *Through reactions of halophosphines*

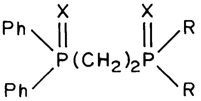
Chlorodimethylphosphine reacts with methanol at 20–30 °C with the elimination of methyl chloride, removed at 50 °C, and the mixture neutralized at 20 °C with 50% NaOH, followed by distillation, to give dimethylphosphine oxide in 90% yield[147].

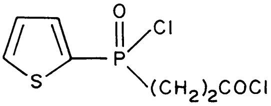
A general method for preparing tertiary phosphine oxides of the type **5** is by the reaction[148] of dimethylchlorophosphine with $Y(CH_2)_nR'$($Y = Cl$, Br; R' = alkyl, alkenyl, benzyl, functionally substituted alkyl; $n = 0$–9; X = nil), followed by treatment with an appropriate oxo or hydroxy compound. Secondary chlorophosphines **19** (X = nil) react with cyclic ketones[149] at 100–120 °C in a sealed system to give the oxide **5** (R' = cycloalkyl). Reaction of diethylchlorophosphine with α-halo ketones[150] gives **88** (R, R' = H, Me or Me, Et). Chlorodiphenylphosphine on treatment with benzyl alcohol[151] gave phosphinate esters, which rearranged to give the phosphine oxides **89** (R = H, Me, MeO, Cl).

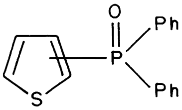

(88)

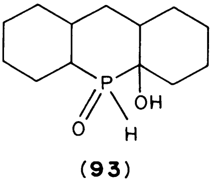

(89)

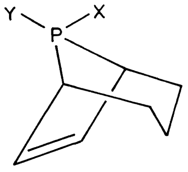
Compounds **19** (R = Ph; X = nil) are reported to react with diol ethers[152] in the presence of a tertiary amine. Thus a mixture of $(HOCH_2CH_2)_2O$ (1.2 mol) and pyridine (2.4 mol) in diethyl ether, on treatment with Ph_2PCl, gives **90** (R = Ph; X = O) in 52% yield. Treatment of a diarylphosphine halide with lithium, followed by reaction with *trans*-ClCH=CHCl for 1.5 h at −20 °C and then oxidation, gave the *trans* isomer of the phosphine[54] **18** (X = O; for details see Section III. A.1.b). Reaction of dichloro-2-thienylphosphine with acrylic acid at 60 °C for 3 h yielded[153] the corresponding oxide **91** in 74.5% yield; 2- and 3-thienylphosphine oxides **92** are also known[154]. Reaction of 2,2′-methylenebis(cyclohexanone) with PH_3 in dioxane containing HCl results in the formation[155] of the 10-oxo-10-phosphaperhydroanthracene system **93**. Addition of RPX_2 (R = Ph, Me; X = Br, Cl) to cyclohepta-1,3-diene led to the

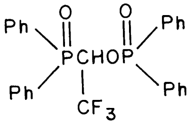

(90)


(91)

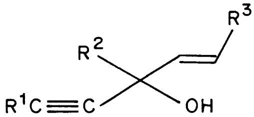

(92)

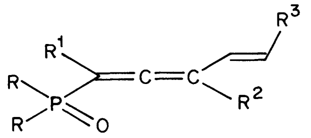

(93)


(94)


(95)

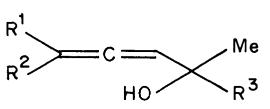
formation[156] of bicyclic phosphine oxide epimers **94** [(a) X = R; Y = O; (b) X = O; Y = R]. Reaction of **19** (R = Ph; X = nil) with trifluoroacetic acid at 160–170 °C is known to give[157] **95** in 92% yield. Reaction of **19** (R = aryl, alkyl) with enylols **96** is reported[158] to give eneallenes **97**, whereas a similar reaction with allenols **98** produces **99**, involving a [2, 3]-sigmatropic reaction at phosphorus.

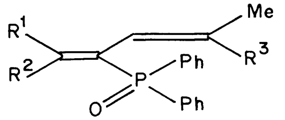




R = Ph; R^1 = H, Me, Ph; R^2 = H, Me; R^3 = H, Me

(**96**) (**97**)

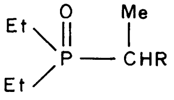




R^1 = Me, Et; R^2 = H, Me; R^3 = H, Me

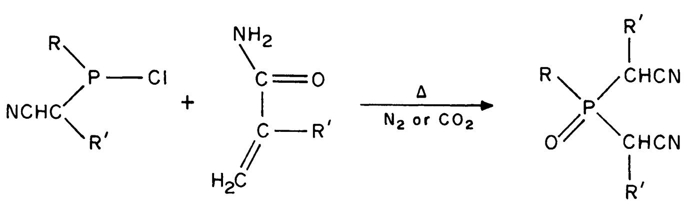
(**98**) (**99**)

Reaction of **19** with α,β-dicarbonyl compounds also gives[159] the oxide, e.g. the reaction of chlorodiethylphosphine with MeC(O)R results in the formation of **100**. Alkyl(β-cyanoalkyl)chlorophosphines, on heating at 100 °C with amides of α,β-unsaturated carbocyclic acids in an atmosphere of nitrogen or carbon dioxide, yielded[160] alkylbis(β-cyanoalkyl)phosphine oxide **101**.



R = COMe, CH$_2$COMe, CH$_2$CO$_2$Et

(**100**)

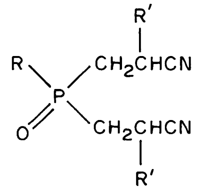


(**101**)

(7)

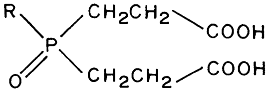
Bifunctional oxides **102** are formed in reaction 7 on heating[161] the corresponding chlorophosphine in an inert atmosphere. Compound **102** (R′ = H) on hydrolysis gave the acid **103**, which on reaction with PCl$_5$ was converted into the chloride. Pyrolysis of **103** with Ba(OH)$_2$ gave the phosphorinane **104** on cyclization.

The reaction of an olefinic phosphine with acrylic acid, followed by esterification, gives **105** by equation 9.



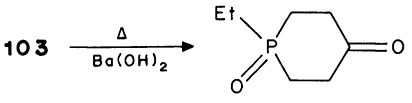
R = Me, Et; R' = H, Me

(102)



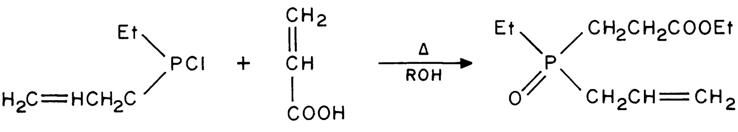
R = Et

(103)



(104)

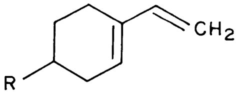
(8)



(105)

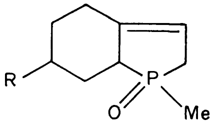
(9)

McCormack cycloaddition of dichloromethylphosphine to 1-vinylcyclohexenes, **105a**, are known to give[162] hexahydrophosphindole oxide **106** in 49.6–72.7% yield. Phosphindoline (**107**) and phosphinoline (**108**) systems have also been conveniently prepared by El-Deek *et al.*[163] in 40–70% yield in a one-step cyclization reaction of diphenylalkenylphosphine oxides **5** (R = Ph; R' = $CH_2CH{=}CH_2$) by heating at 180 °C in the presence of polyphosphoric acid.



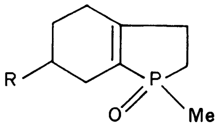
R = $O(CH_2)_2O$, OCH_2Ph

(105a)



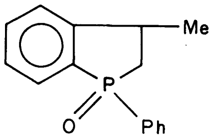
(106a)

and

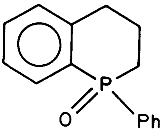


R = OCH_2Ph, OMe

(106b)

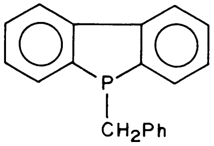


(107)

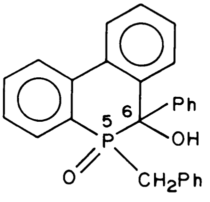


(108)

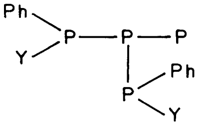
The phosphole **109**, on reaction[164] with benzyl chloride in triethylamine and water, gives 6-phenyl-5-phosphaphenanthrene (**110**) in 90% yield. Baudler and Reuschenbach[165] reported the synthesis of tetraphenylcyclotetraphosphine **112** by the cyclo-condensation of **111** with phenyl-*tert*-butylphosphine. Compound **112** (R = Ph) was unstable at room temperatures in solution and rearranged to oligomeric pentaphenylcyclopentaphosphine, whereas **112** (R = Bu^t) was remarkably stable (for oxidation[34] of **112**, see Section III.A.1.a).



(109)

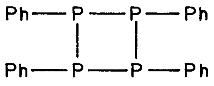


(110)



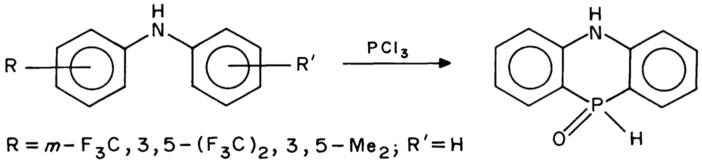
Y = K, SiMe$_3$

(111)



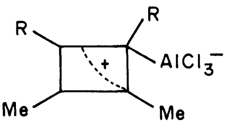
(112)

Dihydrophenophosphazines **113** are prepared[166] by the interaction of diarylamines with PCl_3, resulting in cyclization (reaction 10). Reaction of $AlCl_3$ complexes of cyclobutadienes **114** with $R'PCl_2$ (R′ = Ph,Me) in CH_2Cl_2 at −50 °C gave[167] the phospholium salts **115**, which, on aqueous NaOH work-up, gave the phosphole oxides **116** in 78% and 66% yields.

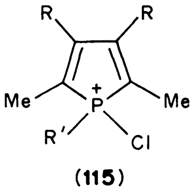


R = m-F$_3$C, 3,5-(F$_3$C)$_2$, 3,5-Me$_2$; R′ = H
R = m-Me; R′ = m-F$_3$C

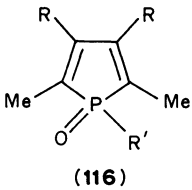
(113) (10)



(114)

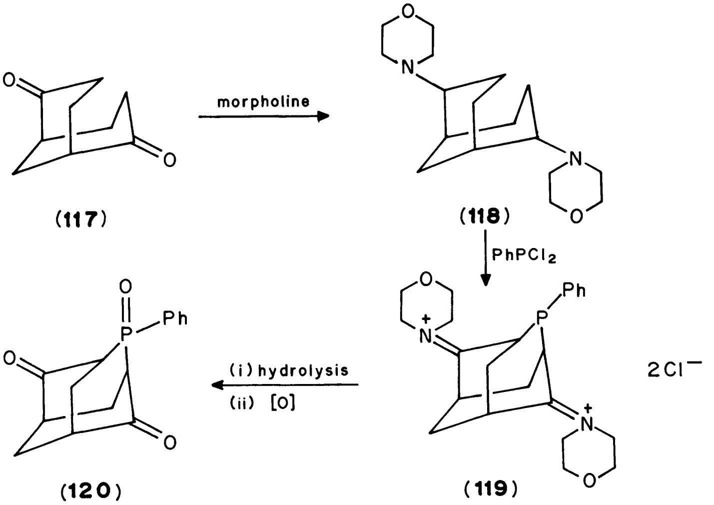


(115)

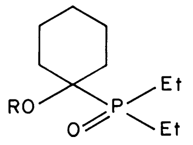


(116)

Kukhar *et al.*[168] reported the synthesis of 2-phenyl-2-phosphaadamantane-4,8-dione-2-oxide **120** in 28% yield by hydrolysing the bisiminium salt **119**, followed by its oxidation. Compound **119** in turn is prepared by treating bicyclononanedione **117** with morpholine and cyclizing the resultant bicyclononadiene **118** with dichlorophenylphosphine, followed by oxidation (Scheme 2). The reaction of **19** (R = Et; X = nil) with cyclohexanone[169] in the presence of butanol, butanethiol or AcOH gives a multi-component mixture. The reaction in the presence of butanol thus gives **121**.



SCHEME 2. Preparation of phosphaadamantane-2-oxide.

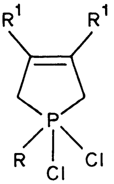


(a) R = H in 62% yield

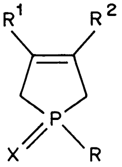
(b) R = Bu in 8% yield

(121)

Cycloaddition of dichloroalkylphosphine to butadiene and isoprene yields[170] dichlorophospholines **122**, which are hydrolysed to give phospholinones **123** in 43–95% yield. Cyclocondensation of dichlorophenylphosphine with two equivalents of enamines



(122)



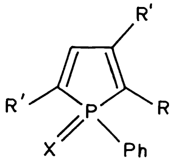
(a) R = Me ; R^1 = H

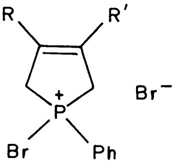
(b) R = Me , Et, Ph;

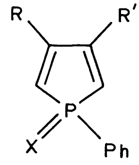
$R^1 = R^2$ = Me ; X = O

(123)

at room temperature has been reported[171] to give 2-amino-1-phenylphosphole in 30–35% yield, which on oxidation gives the oxide **124** (R = piperidino, R′ = Me, Et; R = pyrrolidino, R′ = Et; X = nil, O). Application of pressure to the cycloaddition of dibromophenylphosphine to buta-1,3-dienes reduces the reaction[172] time from days to hours, giving phospholinium bromide **125**, which readily undergoes elimination to produce phosphole **126** (X = nil) in 75–77% yield, which could be oxidized to the corresponding oxide.

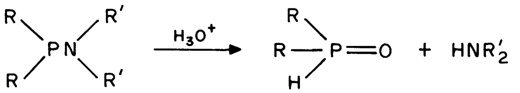

(124)


(125)

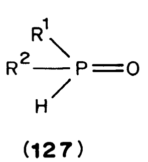

(126)

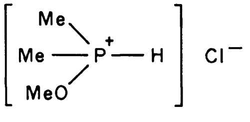
5. *Through hydrolysis of R_2PNR_2 compounds*

Secondary phosphine oxides are prepared[173] in 90–100% yield by hydrolysis of $R_2PNR'_2$ in presence of HCl, H_2SO_4 or H_3PO_4 at 30 °C (reaction 11). In a variation, dimethylphosphine oxide is prepared[174] in 80–95% yield by hydrolysis of $R_2PNR'_2$(R = Me, Et, Ph; R′ = Me, Et, H) with water in benzene at −20 to 100 °C under an atmosphere of nitrogen. In another variation[175], the hydrolysis of Me_2PR [R = Cl, OPh, NMe_2, NEt_2, $N(CHMe_2)_2$, NHPh] also yields the above phosphine oxide in 45–97.5% yield. Secondary phosphine oxides **127** (R^1 and $R^2 = C_{1-6}$-alkyl) are prepared in high yields and high purity by acidic hydrolysis[176] of dialkylchlorophosphines or their HX addition products with aqueous non-oxidizing mineral acids. Thus, **19** (R = Me; X = nil) in concentrated HCl was poured steadily at −5 °C under nitrogen into water and the mixture was adjusted to pH 6.5 with aqueous NaOH at 20–30 °C, to give the oxide in 97.5% yield.


(11)

R = Me, Et, Ph; R^1 = Me, Et, Pr^i, Bu, Ph


(127)

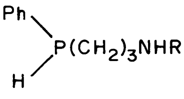

(128)

Dimethylphosphine halides are known[177] to react with sodium methoxide to give Me_2POMe, which rearranges to trimethylphosphine oxide in presence of methyl iodide or is hydrolysed to **127** ($R^1 = R^2$ = Me) via intermediate **128**.

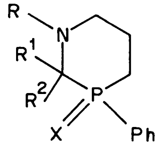
6. *Through reaction of P^{III} compounds with reactive groups*

3-Aminopropylphosphines **129** on cyclization[178] with $R^1C(O)R^2$ give 1,3-azaphosphinanes **130**. Both **130** (X = nil) and **131** (X = nil), on H_2O_2 oxidation, give the oxide

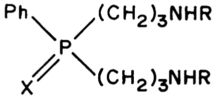
($X = O$). Compounds **130** ($X =$ nil) and **131** ($X =$ nil) are prepared by heating $PhPH_2$ and $H_2C{=}CHCH_2NHR$ in the presence of azobisisobutyronitrile (AIBN). The reaction of diarylaminomethyl-substituted tertiary phosphines with primary or secondary phosphines causes cleavage[179] of the P—C bond, to form a new P—P bond. Thus, treatment of $Ph_2PCH_2NEt_2$ with Ph_2PH yields **132** ($R = R' = Ph$) and $HNEt_2$. Similarly, reaction of $PhP(CH_2NEt_2)_2$ and $PhPH_2$ gives novel cyclic phosphines **8** and **53** ($R = Ph$; $X =$ nil), together with $HNEt_2$ and $MeNEt_2$ (see Section III.A.1.a. for oxidation of **8** and **129**).



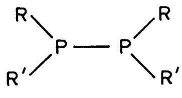
(129)



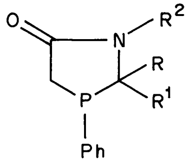
(130)



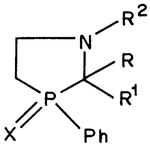
(131)



(132)



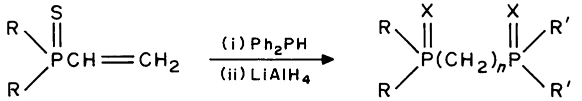
(133)



(134)

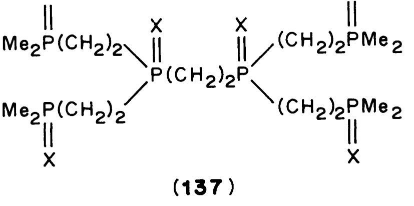
C—P bond cleavage is known in the reaction[180] of tertiary phosphine oxides substituted at the α-carbon by electronegative functional groups such as ethers, thioethers and carbonyl with BCl_3 to give high yields of secondary phsophine oxides. BF_3 and BBr_3 are also known to react but with a lower yield of the C—P bond cleavage products. Substituents with β-carbons also reacted but with a lower yield.

1,3-Azaphospholanes **134** are synthesized[181] by the addition of Schiff bases, semi- or thiosemi-carbazones, to $PhPHCH_2COOH$ followed by intramolecular condensation resulting in the formation of **133**, which on treatment with $LiAlH_4$ ($\rangle C{=}O \rightarrow \rangle CH_2$) followed by oxidation gives **134**. Base-catalysed addition of P—H bonds to vinyl double bonds has been used by King and Cloyd[182] to prepare methylated poly-tertiary phosphines **136** (reaction 11a). Thus, addition of a primary or secondary phosphine to



(135) **(136)** $n = 2$

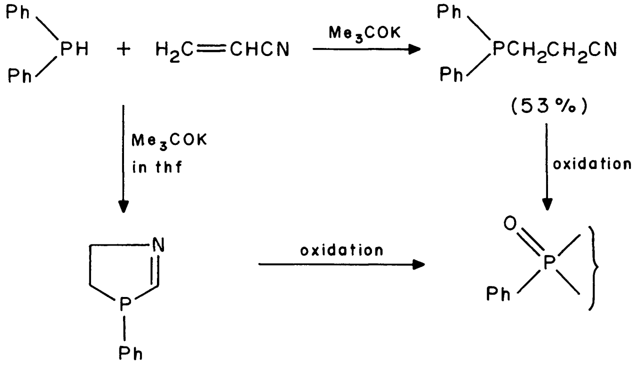
(11a)



(137)

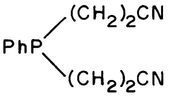
135, followed by desulphurization with $LiAlH_4$ in boiling dioxane solution, produced **136** (R = Me; R′ = Ph; X = nil) (reaction 11a). Similarly, **135** reacted with $PhPH_2$ to give **17** (X = nil). Using this method, linear P-6 polyphosphines **137** and polyphosphine oxides with up to ten phosphorus atoms have been prepared. All the phosphines **17**, **136** and **137** (X = nil) have been oxidized[51] to the corresponding phosphine oxides (X = O; see Section III.A.1.b for details). P—H bonds are reported[183] to add to the vinyl derivatives under mild conditions in presence of free radicals. Di-, tri- and tetra-(tertiary phosphines) have been synthesized by this method.

Diphenylphosphine is known to react[184] with acrylonitrile in two different ways, depending on the conditions (Scheme 3). The reaction of phenylphosphine with acrylonitrile gives[185] **139**, which on treatment with Me_3COK cyclizes to give **140**. This, on refluxing with 6M HCl followed by oxidation, gives 1-oxo-1-phenyl-4-phosphorinanone **141** (R = H).

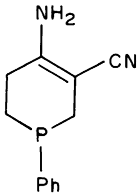


(azaphospholene; **138**)

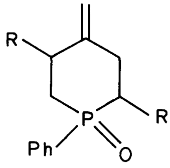
SCHEME 3. Reaction of diphenylphosphine with acrylonitrile.



(**139**)

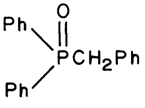


(**140**)

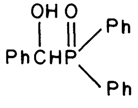


(**141**)

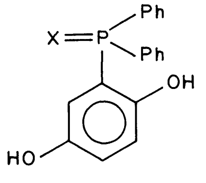
Reaction of $[Ph_2P(O)]M$ (where M = Na, MgCl or ZnCl) with aromatic carbonyl compounds gave[186] different phosphine oxides **142** or **143** depending on the metal used. Compound **142** was produced with M = Na or ZnCl, whereas with M = MgCl **143** was produced along with benzoin and benzil. Reaction of $Ph_2P(O)M$ with *p*-benzoquinone gives the phosphine oxides **144** (X = O) and **145** (X = O).



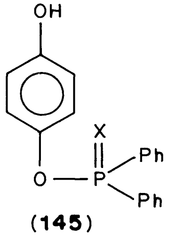
(**142**)



(**143**)

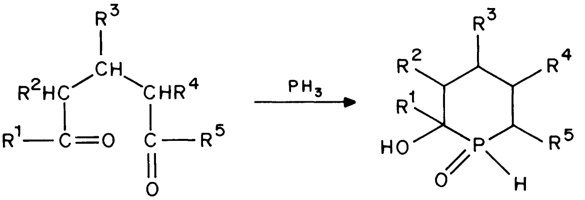


(144)



(145)

Dihydrophosphorin systems **26** are formed[187] by ring expansion of phospholes **25** (R = Ph) on reaction with R′COCl (R′ = Ph, *o*-, *m*-, *p*-MeC$_6$H$_4$, *p*-anisyl, *p*-chlorophenyl, *p*-F/NO$_2$-C$_6$H$_4$ and 2/3-thienyl) and water. Phosphorinane oxides **146** are obtained by cyclization[188] of 1,5-diketones with PH$_3$ (reaction 12). Phosphorinane ring systems **141** (R = Me) are also formed by the reaction[189] of phenylphosphine with 1,4-dienes (reaction 13). Reaction of R′P(CH$_2$OH)$_2$ with propylene oxide in triethylamine yielded[53] the phosphine oxides **5** [R = CH$_2$CH(Me)OH] in 41.6–47.8% yield (see Section III.A.1.b for their oxidation).



(146)

(12)

$R^1 = R^5 = Ph, R^2 = R^3 = R^4 = H;$

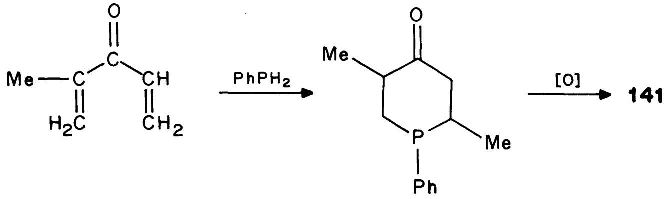
$R^1R^2 = (CH_2)_4, R^3 = R^5 = Ph, R^4 = H;$

$R^1R^2 = H_2CC(Me_2)OCH_2,\ R^3 = R^5 = Ph,\ R^4 = H;$

$R^1R^2 = (CH_2)_4,\ R^3 = R^4 = H,\ R^5 = Ph;$

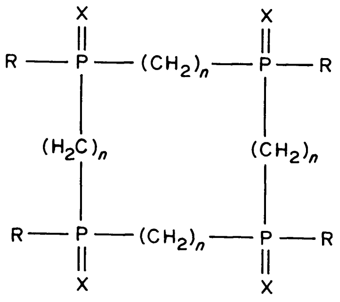
$R^1R^2 = R^4R^5 = (CH_2)_4,\ R^3 = Ph;$

$R^1R^2 = (CH_2)_4,\ R^3 = R^4 = H,\ R^5 = Ph$



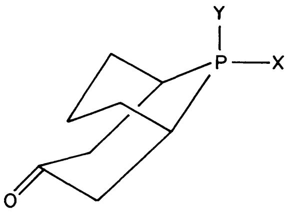
(13)

Multi-membered oligophosphacycloalkanes **147** were prepared by Horner *et al.*[190] in a five-step synthesis starting from Bz(CH$_2$)$_n$Bz and appropriate phosphorus compounds. Reaction of cycloocta-2,7-dienone with phenylphosphine, followed by oxidation, leads to the formation[191] of phosphabicyclo[3.3.1]nonan-3-one-9-oxides **148** [(a) *syn* isomer, X = O, Y = Ph; (b) *anti* isomer, X = Ph, Y = O].

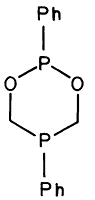


R = Ph, CH$_2$Ph; x = nil, O; n = 3, 4

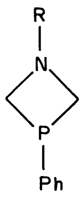
(147)



(148)

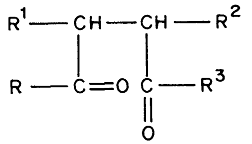


(149)

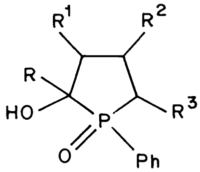


(150)

Reaction of alkenes **60** (R = R′ = Me) with phosphorus trihalides in the presence of a catalyst results in the formation[192] of a phosphetan ring, which on hydrolysis gives 1-chloro-2,2,3-trimethylphosphetane **62** (R = R′ = Me; R^2 = Cl). 1,3-Azaphosphatidine systems **150** were synthesized[193] in 20–85% yield by the reaction of **149** with RNH_2 (R = Ph,PhCH$_2$, Br/Me-C$_6$H$_4$) or in 34% yield by refluxing[193b] bis(anilinomethyl)phenylphosphine [PhP(CH$_2$NHPh)$_2$] in ethanol for 3 h. Reaction of 1,4-diketones **151** with phenyl-phosphine on cyclization gives the phospholanes[194] **152** in 23–50% yield.



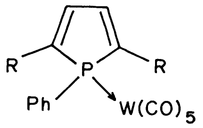
(151)



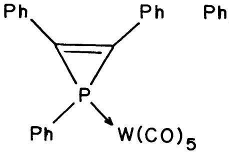
RR^1 = R^{2}R^3 = (CH$_2$)$_4$;
R = Ph, R^1 = H, R^{2}R^3 = (CH$_2$)$_4$, (CH$_2$)$_3$

(152)

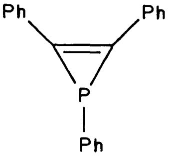
Phosphole complexes **153** (R = Ph) have been directly converted[195] into phosphirene complexes **154** by reaction with methylacetylene dicarboxylate, followed by decomplexation of **154** with iodine and *N*-methylimidazole to form **155**, which reacted with $Me_3O^+BF_4^-$ sluggishly to yield **156**. This was cleaved instantly at room temperature with neutral phosphine to give the corresponding vinyl phosphine oxide **157**. Oxaphosphabicyclodecanones (**42**; X = nil) are prepared[80] in 29% yield by cyclizing pyran **158** with phenyl phosphine, which on oxidation gave the oxide (X = O). Use of cyclohexenyl vinyl ketone **159** (in place of **158**) in ethanol containing NaOEt gave[81] **43** (X = nil) in 49% yield, which when oxidized with $KMnO_4$ in acetone gives the oxide (X = O).



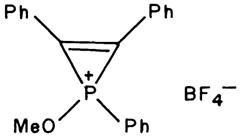
(153)



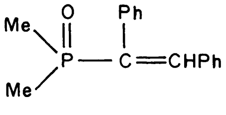
(154)



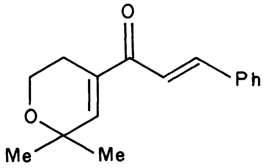
(155)



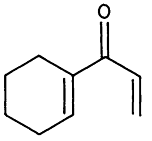
(156)



(157)

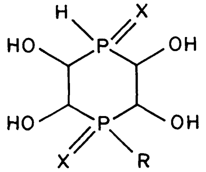


(158)



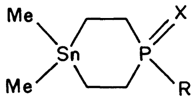
(159)

Reaction of but-2-ene and PH_3 in presence of AIBN has been reported[48] to give *sec*-butylphosphine, which is further alkylated with oct-1-ene at 80 °C in the presence of AIBN to give *sec*-butyldi-*n*-octylphosphine, oxidized by H_2O_2 to its oxide. Robertson and Gallivan[18] have synthesized 1,4-disubstituted 2,3,5,6-tetrahydroxy-1,4-diphosphorinanes **160** by reaction of propylphosphine in thf with 40% aqueous glyoxal, followed by oxidation with 30% H_2O_2. Weichmann *et al.*[196] have reported the formation of 1-organo-4,4′-dimethyl-1,4-phosphastanninanes **161** (X = O) by the hydrostannylation of the alkyldivinylphosphine RP $(CH{=}CH_2)_2$ with Me_2SnH_2, followed by oxidation.



R = C_{1-12}-alkyl, C_{5-7}-cycloalyl,
C_{8-12}-aralkyl, C_{6-12}-aryl; X = nil, O or S

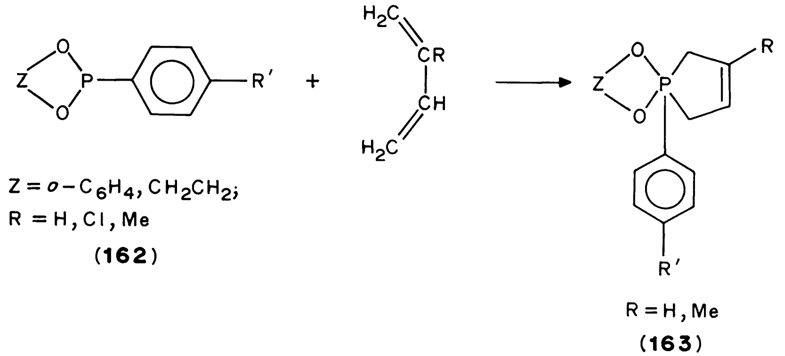
(160)



(161)

Condensation of glycollic and pyrocatecholic esters of arylphosphonous acids (**162**) with 1,3-diene hydrocarbons is reported[197] to give the phospholanes **163**. Heating **163**

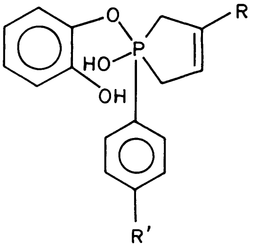
($Z = o\text{-}C_6H_4$) with water gave the partial ester **164**, which with excess of acetyl chloride gave the phospholane **165**.



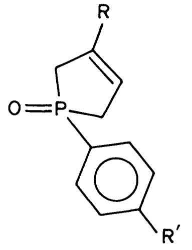
(162)

(163)

(14)



(164)

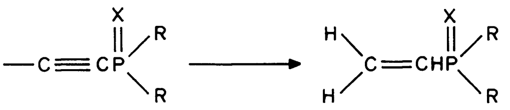


(165)

B. Reactions Involving Conversion of an Already Present P^V Nucleus

1. Through reactions of phosphine oxides.

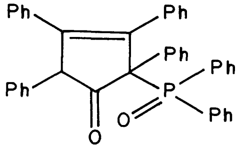
A variety of 1-(*tert*-alkynyl)-1-phosphine oxides **5** (R' = alkynyl; X = O) can be reduced[198] to *trans*-β-substituted vinylphosphine oxides, employing $NaBH_4$ as a reducing agent (reaction 15). Highly pure phosphine oxides of type **5** were prepared in high yields and short reaction times by the reaction[199a,b] of secondary phosphine oxides with α-olefins at 130–200 °C without catalytic action, with UV irradiation or in the presence of catalysts such as *tert*-butyl peroxide (TBP) or azobis(isobutyl)diacetate (ABD) under an inert atmosphere. Thus octadec-1-ene (326 g) and TBP (0.3 g) were added within 3 h to dimethylphosphine oxide at 145 °C under nitrogen and heated for 5 minutes at 160 °C to give **5** (R' = $n\text{-}C_8H_{17}$) in 94% yield. Phosphine oxides of the type **5** have recently been prepared[200] by the reaction of $R_2P(O)H$ (R = alkyl, aryl) with R'hal (R' = alkyl, alkenyl, $PhCH_2$; hal = Cl, Br, I) in the presence of alcohols R'OH at 90–210 °C.



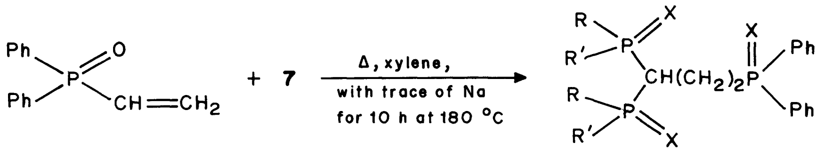
(15)

R = alkyl, aryl

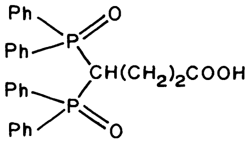
Diphenylphosphine oxide is known to react[201] with tertraphenylcyclopentadienone in the presence of dimethylamine with a 1,6-addition in which phosphorus is attached in the α-position to the carbonyl group, to give **166**. Phosphine oxides **7** (See Section III.B.3 for preparation), having an active methylene group, react[202] with unsaturated compounds to give new phosphine oxides **167** (R = R′ = Ph; X = O) (reaction 16). Similarly **7** (R = R′ = Ph; X = O) reacts with ethyl acrylate followed by alkaline hydrolysis to yield **168**.



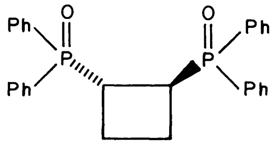
(166)



(167) (16)

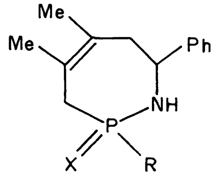


(168)

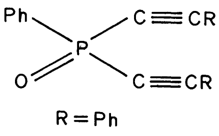


(169)

Oxidative coupling with CuCl–$CuCl_2$ of the 1,4-dicarbanions obtained from lithiation of **75** (R = R′ = Ph; X = O; $n = 4$) gives[203] (±)-*trans*-bis(1,2-diphenylphosphinyl)cyclobutane (**169**). Thus, BuLi (70 mmol) in 15% hexane is added to the phosphine oxide **75** (R = R′ = Ph; $n = 4$) (25 mmol) in thf with cooling, then CuCl (5 mmol) is added, followed by $CuCl_2$ (55 mmol), and oxygen is passed through the system to give **169** in 37% yield. These compounds are useful as ligands in metal complexes.



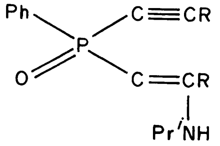
(170)



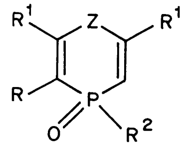
R = Ph

(171)

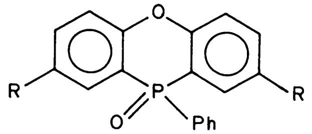
The lithium derivatives of 1-oxo-3-phospholane systems **123** ($R' = R^2 = Me$) are reported to react[204] with benzonitrile at $-70\,^\circ C$ with the formation of a seven-membered ring, which on hydrolysis yielded azaphosphepine oxide **170** ($X = O$) in 42% yield. Diacetylenic phosphine oxides **171** ($R = Ph$; $X = O$) could be converted into **172** in 82% yield by reaction[105] with isopropylamine followed by acidic hydrolysis. Addition of H_2S, H_2Se, H_2Te, H_2O or H_2NEt to **171** under nucleophilic conditions also gives rise[205] to new ring systems **173** ($R = H$; $R^1 = H$, Me, Me_3C; $R^2 = Ph$, cyclohexyl; $Z = S$, Se, Te, O or NEt) by cyclization. Compounds **172** could also be cyclized[105] with sodium methoxide to give oxaphosphorinanes **173** ($X = O$) in 86% yield. Dibenzooxaphosphorinane derivatives **174** are also known[206].



(172)

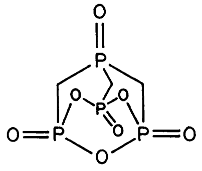


(173)

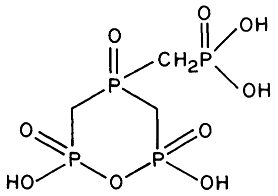


(174)

Treatment of tris(chloroethyl)phosphine oxide with tertiary amines gives trivinylphosphine oxide **1** ($R = CH{=}CH_2$) in high yields[207], whereas its reaction with **5** ($R = Ph$, $R' = Bu$; $X = O$) gives the tetraoxide **16** ($R = Ph$; $X = O$). Likewise, **5** ($R = ClCH_2CH_2$; $R' = ClCH_2$; $X = O$) on treatment with triethylamine yields[208] chloromethyldivinylphosphine oxide **5** ($R = CH{=}CH_2$, $R^1 = ClCH_2$; $X = O$). Partial anhydrides of alkylidenephosphonylphosphine oxides (**176**), used as calcium-sequestering agents, were prepared[15] from the complete anhydrides **175** by addition of sodium hydroxide solution (final pH 7.6), yielding **176** as the trisodium salt.

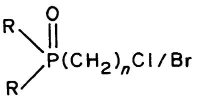


(175)



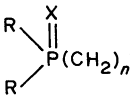
(176)

Dialkylhaloalkylphosphine oxides **177** were prepared[209] by reaction of **178** ($X = O$; $Y = OH$) with $COCl_2$ or BrCOCOBr. Thus, **178** ($R = Me$; $Y = OH$; $n = 1$) on treatment with $COCl_2$ in CH_2Cl_2 at ca $30\,^\circ C$ yielded the oxide ($Y =$ halogen; $R = Me$; $n = 1$) in 96% yield. Tris(chloromethyl)phosphine oxide **1** ($R = ClCH_2$; $X = O$) was prepared[210] by hydrolysis of tris(acetoxymethyl)phosphine oxide **1** ($R = CH_2OAc$).



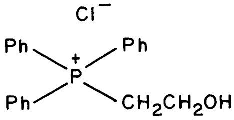
(177)

$R = Me, Et, Pr, Bu$; $n = 1, 2$



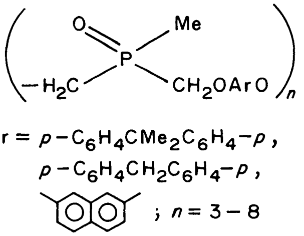
(178)

Asymmetrically substituted ethylenebis(phosphine oxides) **90** (R = Bu) were synthesized in 74% yield by reaction of the halide **178** (R = Ph; $n = 2$; Y = Cl) with dibutylphosphine oxide in the presence of butyllithium[211]. The halide **178** in turn was prepared in 88.5% yield by refluxing the hydroxyethyl compound **178** (R = Ph; $n = 2$; Y = OH) with PCl_5 for 10 min in benzene; the hydroxyethyl compound was prepared in 59.5% yield by hydrolysing the phosphonium salt **179** with KOH.



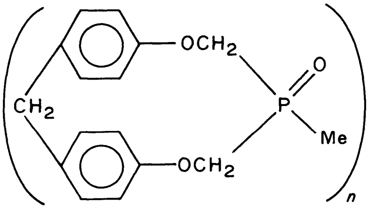
(179)

Oligomeric phosphine oxide ethers **180** or **181** are reported to be prepared[212] by polycondensation of equimolecular amounts of methyl- or ethyl-dichloromethylphosphine oxide and disodium bisphenolates in water or xylene. Phosphine oxide ethers with terminal OH groups (**182**) were obtained by using excess of bisphenolates in the above reaction.

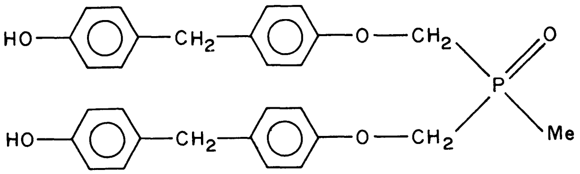


Ar = $p-C_6H_4CMe_2C_6H_4-p$, $p-C_6H_4CH_2C_6H_4-p$, ; $n = 3-8$

(180)



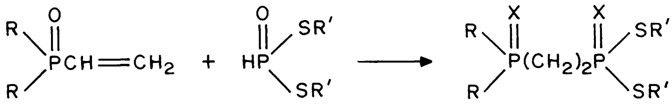
(181)



(182)

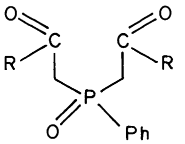
Vinyl phosphine oxides of the type **5** (R′ = CH=CH$_2$) react[213] with dithiophosphonic acids on heating at 45–75 °C in an organic solvent to give **183** (R = R′ = alkyl, aryl;

X = O) (equation 17). Heterocyclic phosphine oxides, i.e. 1,4-thiaphosphorinanes **185** (Z = S), were formed in 60–63% yields by cyclizing[214] **184** with P_2S_5.



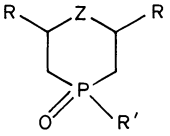
(183)

(17)



R = Me_3C, Ph

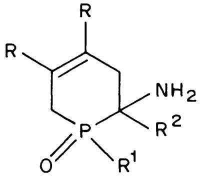
(184)



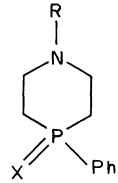
R' = Ph

(185)

3-Phospholenes **123** are reported to react[215] with RCN to give 1-aza-2-phosphacyclohepta-4,6-dienes **169** (X = O), which undergo ring contraction to **186** (R = Me, R^1 = Ph; R^2 = Ph, $C_6H_4NMe_2, C_6H_4N, Et_2$) on treatment with $HSiCl_3$. 4-Phenylperhydro-1-4-azaphosphorinane-4-oxides **187** (X = O) are synthesized[216] in almost quantitative yields by refluxing divinylphosphine oxide with a 20% excess of $MeNH_2$ or aqueous alkylamine for 6 h. Divinylphenylphosphine oxide in turn was prepared in 72% yield by the reaction of 2 mol of vinylmagnesium bromide with dichlorophenylphosphine in thf at −70 °C. Seagull *et al.*[217] have prepared dibenzophosphorins **188** (R = Ph) starting from the phosphine oxide **5** (R = Ph, R' = *o*-tolyl; X = O) (Scheme 4).

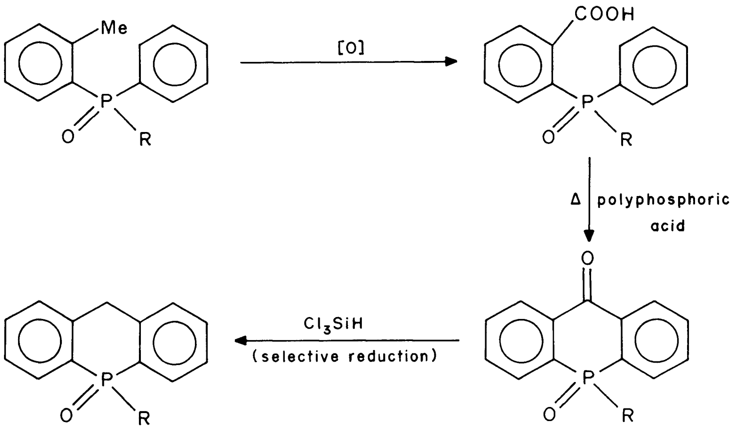


(186)



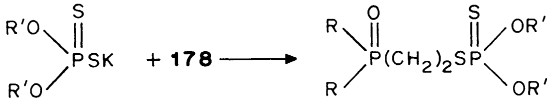
(187)

Phosphine oxides **189**, containing a dithiophosphoric acid moiety, were prepared[218] either by the reaction of alkyldithiophosphoric acid with **5** (R = alkyl; R^1 = vinyl; X = O) or by the reaction of the potassium salt of dialkyldithiophosphoric acid with **178** (R = Et, Ph; $n = 2$; Y = Cl). Bilithiation of di-3-thienylphosphine oxides **190** gave 2,2-dianions, which on treatment with esters cyclized[219] to give 1,4-dithieno-1,4-dihydrophosphorin systems **191**. Tris(trifluoroalkyl)phosphine oxides were prepared[220] by electrochemical fluorination of **1** (R = C_{5-8}-alkyl) in anhydrous hydrofluoric acid. The above phosphine oxides **1** were first brominated in HF and then electrolysed in another procedure. Thus, tri-*n*-octylphosphine oxide (145 g) in HF (40 g) and bromine (180 g) on electrolysis gave tris(*n*-perfluorooctyl)phosphine oxide[220b].



(188)

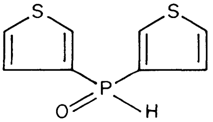
SCHEME 4. Synthesis of dibenzophosphorin-10-ones.



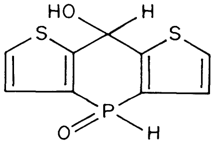
R'= Pr, Et, Ph

(189)

(18)

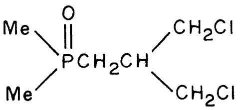


(190)

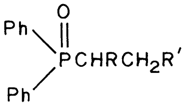


(191)

Bisphosphine oxides **136** (R = alkyl; R' = ethyl; X = O) were prepared[221] in 43–92% yields by heating the oxide **5** (R = alkyl; R' = vinyl; X = O) with diethylphosphine oxide in absolute xylene for between 1.5 and 5 h at 140 °C. Chloroalkylphosphine oxides **178** (Y = Cl; R and n = Me, 1; Me, 3; Me$_2$CH, 1) are prepared[222] by chlorination of the hydroxy derivative **178** (Y = OH) with HCl. Bis(chloromethyl)methyl- and trichloromethyl-phosphine oxides and oxide **192** were prepared similarly.

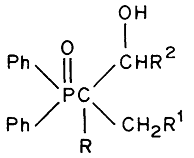


(192)

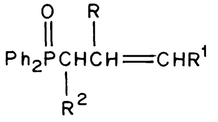


(193)

Davidson and Warren[223] used the diphenylphosphine oxide Ph$_2$P(O) group in organic synthesis by activating a series of C—C bond-forming reactions from successive carbon atoms by migration along a developing carbon framework. Thus, **193** reacted with R^2CHO in the presence of BuLi to give **194**, the tosylate of which solvolyses in carboxylic acids, with migration of the $Ph_2P(O)$ group to give **195**, which, in turn, further increases the carbon chain by reaction with BuLi and R^3CHO to give **196**.

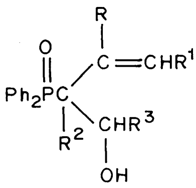


(194)



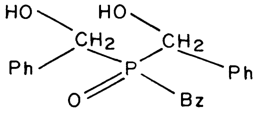
$\mathrm{Ph_2P(O)CH(R^2)C(R){=}CHR^1}$

(195)

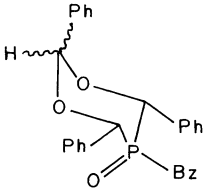


(196)

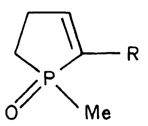
Benzylbis(α-hydroxybenzyl)phosphine oxide **197** is known to react[224] with benzaldehyde to give 5-benzyl-2,4,6-triphenyl-1,3,5-dioxophosphorinane-5-oxide (**198**) (both *dl*-and *meso*-epimers). The lithio derivative of phospholene oxides **199** (R = Li) are reported[225] to be readily carbonated to the corresponding carboxylic acid **199** (R = COOH). Dialkylphosphine oxides react with oxazolidine derivatives **200** to give[226] the tertiary phosphine oxides **201**. Thus, **200** (30 g) was added dropwise to diethylphosphine oxide (28 g) and the mixture was heated for 1 h at 50–60 °C to give **201** (R = Et) in 98% yield. Bodalski *et al.*[227] have synthesized 2-phospholene-1-oxide (**199**) derivatives by heating equimolar amounts of secondary benzylphosphine oxides with α,β-unsaturated compounds in thf. The reaction occurs via a 1,4-adduct, which rearranges to a carbonium ion, followed by cyclization to give the product.



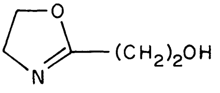
(197)



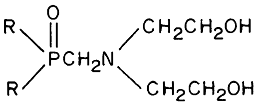
(198)



(199)

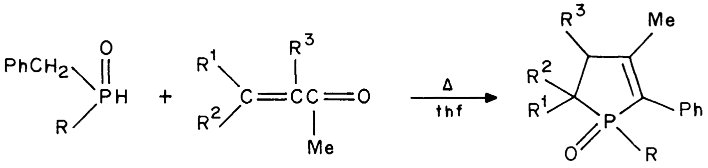


(200)

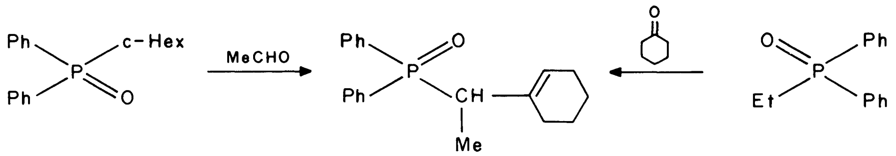


R = Et, Pr^n, Pr^i, Bu, etc.

(201)

 (19)

Cyclohexyldiphenylphosphine oxide is reported to react[228] with acetaldehyde to give **202** in which the cyclohexyl group has migrated to the carbonyl carbon, followed by elimination of water. The same product was also obtained by the reaction of **5** (R = Ph; R′ = Et; X = O) with cyclohexanone (reaction 20).



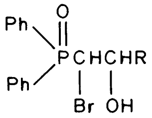
(202)

(20)

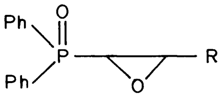
Tris(β-cyanoethyl)phosphine oxide **203** (Y = CN) is reported[229] to be hydrolysed by heating in water at 90–95 °C in the presence of strongly acidic cation exchangers, e.g. KU-1 or KU-2, giving **203** (Y = COOH). However, hydrolysis at 60–65 °C in the presence of strongly basic anion exchangers, e.g. AB-17, gave 60–80% **203** (Y = CONH$_2$) (reaction 21).

$$\begin{array}{ccccc} O=P[(CH_2)_2Y]_3 & \xleftarrow{\text{AB-17}} & O=P[(CH_2)_2Y]_3 & \xrightarrow[\text{KU-2}]{\text{KU-1 or}} & O=P[(CH_2)_2Y]_3 \\ Y=CONH_2 & & Y=CN & & Y=COOH \\ & & \textbf{(203)} & & \end{array} \qquad (21)$$

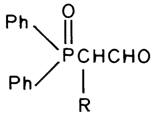
Dehydrohalogenation of **204** with KOH in hexametapol or dmf is reported[230] to give oxirenes **205** in 65–70% yields, which rearrange to **206** in presence of F$_3$CCOOH. Reaction of phosphine oxide **207** with RCHO is known[231] to give 12–50% α-phosphinyl-substituted stilbenes **208** (R = Ph, 2,4-pyridyl, 1,2,4-quinolyl) and diphenylphosphoric acid, the size of R determining whether the product is the *cis* or the *trans* isomer. Thus, with R = Ph or pyridyl the *trans* product predominates, whereas with quinolyl the *cis* isomer is the major product.



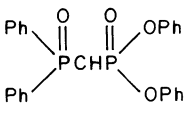
(204)



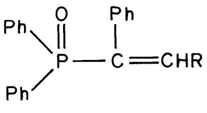
(205)



(206)

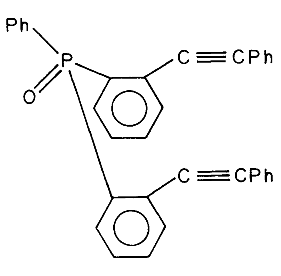


(207)

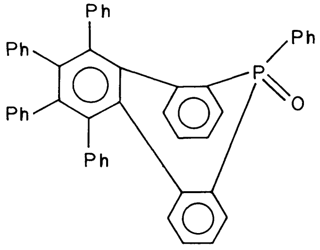


(208)

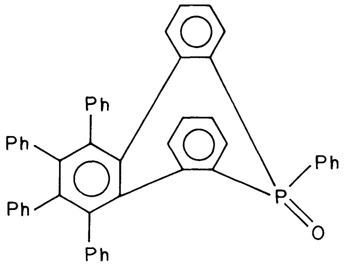
Transition metal-catalysed cyclization of **209** with tolane resulted in the formation[232] of conformationally isomeric tribenzo[*b*, *d*, *f*]phosphine oxides **210** and **211**.



(209)

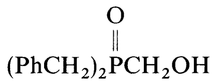


(210)



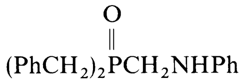
(211)

Dibenzylphosphine oxide is reported[233] to react with formaldehyde and aniline to give **212** by heating at 60–70 or 100–110 °C, the yield depending on the ratio of the reactants and the temperature. On raising the temperature to 160–170 °C, **213** was formed, which was also obtained by the reaction of aniline with **212** at 160–170 °C. Conversion of (2-hydroxyalkyl)diphenylphosphine oxides into allyl phosphine oxides by acid-catalysed migration is also known[234]. Thus, **214** on refluxing in benzene for 6 h with *p*-tolylsulphonic acid gives **215** in 90% yield.



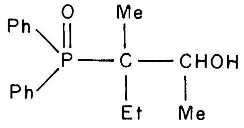
$(PhCH_2)_2\overset{O}{\overset{\|}{P}}CH_2OH$

(212)

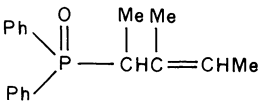


$(PhCH_2)_2\overset{O}{\overset{\|}{P}}CH_2NHPh$

(213)

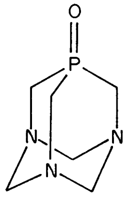


(214)

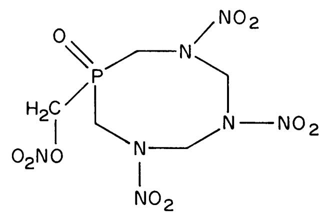


(215)

Siele[235] prepared the derivative of 1,3,5,7-triazaphosphocine (**217**) by nitration, nitrosation and acetylation of 1,3,5-triaza-7-phosphaadamantane-7-oxide (**216**). Oxidation of 3-phospholines with H_2O_2 in the presence of potassium osmate is known[236] to give the 3,4-dihydroxy derivative **218** (R = Me). The cycloaddition of **5** (R = Ph, R′ = propynyl; X = O) with diazoalkanes is known[237] to give diphenylphosphoryl-3*H*-

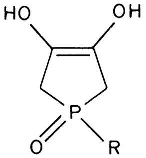


(216)

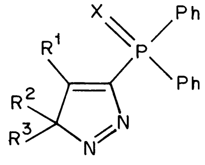


(217)

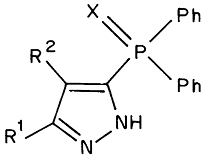
pyrazole **219** (X = O), which on heating in toluene or treating with chloroform at room temperature, rearranges to give **220** (R^1 = Me, R^2 = Ph; $R^1 = R^2$ = Ph). Cycloaddition of phenyl azide with diphenylpropenylphosphine oxide leads to the formation[238] of triazoles **221**.



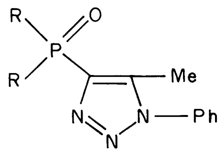
(218)



(219)



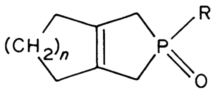
(220)



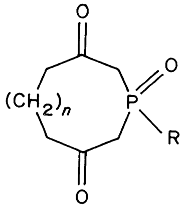
R = Et , Ph

(221)

Quin and Middlemas[239] prepared large-ring compounds by ozonolysis of 3-phospholene derivatives **222**, bearing a cyclohexane ring fused at the double bond, when 7–9-membered heterocyclic P-rings **223** (R = Me, Ph; n = 0–2) were obtained.

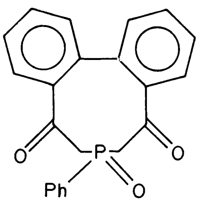


(222)

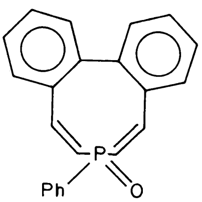


(223)

The 5,6-double bond of phenanthrene fused to a 3-phospholene oxide ring was likewise cleaved by ozone to yield a dibenzo derivative **224** of **223** (R = Ph; n = 2). This ring is non-planer and rigid. Reduction of **224**, followed by dehydration, yielded the first reported example of a phosphonin oxide, **225**.

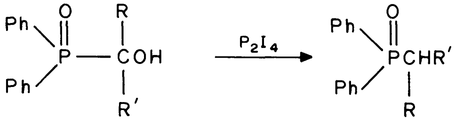


(224)



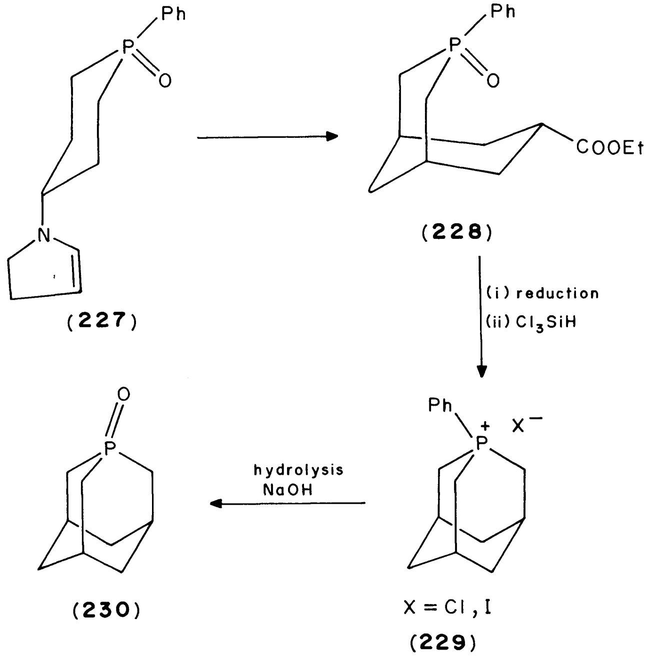
(225)

The α-hydroxy group of a phosphine oxide can be deoxygenated[240] by reaction with diphosphorus tetraiodide, giving **226** [R = H, Me; R′ = Me, Et; RR′ = $(CH_2)_5$] in



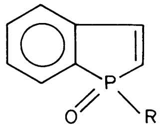
(226) (22)

73–100% yield. The annelation reaction between 1,2,3,6-tetrahydro-1-phenyl-4-(1-pyrrolidinyl)phosphorin-1-oxide (**227**) and $(BrCH_2)$ CHCOOEt resulted[241] in a mixture of two stereoisomers of the 3-phosphabicyclo[3.3.1]nonane derivative **228**. The keto function in **228** was reductively removed to give the $—CH_2OH$ group, which on cyclization followed by hydrolysis gave **230** (Scheme 5).

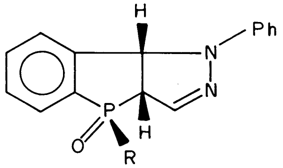


SCHEME 5. Synthesis of 1-phosphaadamantane.

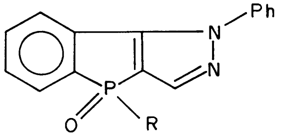
Cycloaddition of diphenylnitrilimine to phosphindole oxide **231** (R = Me, Ph) proceeds regio- and stereo-specifically to give[242] pyrazolophosphindoles **232** in 90–95% yield. Further oxidation with $CuCl_2$–LiCl gives the oxidation product **233** quantitatively. The fulvalene ylide **234** is known to undergo[243] a Stevens rearrangement on refluxing in toluene to give the spirophosphine **235** (X = nil) in almost quantitative yield. On oxidation this gave the oxide **236** (X = O). Long-chain phosphine oxides of the type **237** were prepared[244] in 80% yields by treating chloromethyldimethylphosphine oxide with the sodium salt of **70** (R = R′ = Me; X = O, n = 0–2).



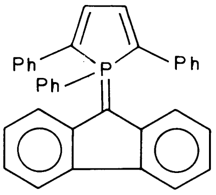
(231)



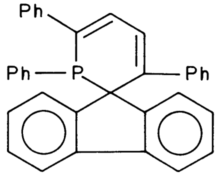
(232)



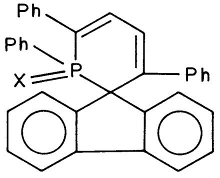
(233)



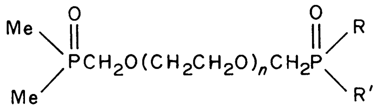
(234)



(235)

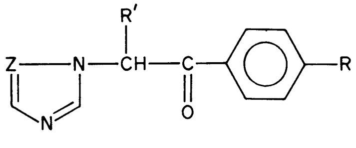


(236)



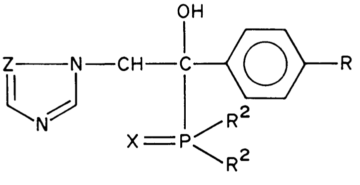
(237)

Δ^3-Phospholenes **123** (R′ = H) are known[245] to be isomerized to Δ^2-phospholenes by heating at 160–200 °C in the presence of catalytic amounts of base such as alkali or alkaline earth metal oxides, hydroxides or carbonates. Thus, **123** (R′ = Me, R^2 = H) (300 g) was heated for 4 h at 180 °C in the presence of 1.0 wt% CaO to give 54% **199** (R = COOH). Secondary phosphine oxides react with triazolyl and imidazolyl ketones **238** to give phosphorylated alcohols **239** (R^2 = Me, CH_2Ph, Ph; X = O) having fungicidal activity[13]. Reaction of dialkyl(4-methylaryl)phosphine oxide with paraformaldehyde or $CH_2(OMe)_2$ in concentrated HCl at 70–90 °C leads to the formation[246] of **5** [R = alkyl, R′ = 3-(chloromethyl)-4-methoxyaryl; X = O]. It has been shown[247] that chloromethylation is dependent on the substitutents present in the phenyl ring. β-Carboxyethylphosphine oxides are prepared by hydrolysis[248] of β-carbalkoxyethylphosphine oxides at 90–95 °C in the presence of a strongly acidic ion-exchange resin.



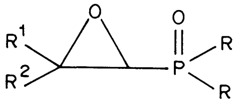
R=H,F,Cl; R′=H,Ph,1,2,4-triazolyl;
Z=N,CH

(238)



(239)

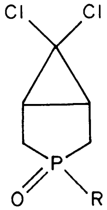
m-(Nitroaryl)dialkylphosphine oxides on reduction with $PhNHNH_2$ at 115–160 °C produce[249] **5** [R = alkyl; R′ = *m*-(aminoaryl); X = O]. Reaction of **5** (R = Ph; R′ = OMe; X = O) with acetyl chloride under a nitrogen atmosphere gives[250] the oxide **5** (R = Ph, R′ = Acetyl; X = O). Reaction of **177** (R = Bu, octyl; *n* = 1; Y = Br) with aldehydes produces[251] the α-hydroxy-substituted phosphine oxides **5** [R′ = CH(OH)Z, where Z = H, Ph or substituted phenyl]. Reaction of phosphine oxides **5** (R′ = CHBr-CR^1R^2OAc) with an alkali metal alcoholate in an aliphatic alcohol leads to the formation[252] of epoxyalkylphosphine oxides **240**.



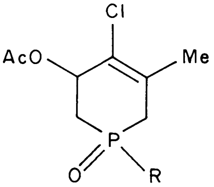
(240)

Tertiary phosphine oxides of the type **12** [R and R^1 = linear or branched C_{1-18}-alkyl, Ph; $R^2 = CH(R^3)OCH_2R^5$, where R^3 = H or CH_2R^4(R^4 = H,C_{1-11}-alkyl, Ph) and R^5 = alkyl] are obtained by reaction[253] of the phosphine oxide **12** [$R^2 = CH(R^3)OH$;R,R^1 and R^3 as above] with halomethyl derivatives in the presence of phase-transfer catalysts. Thus, reaction of dioctylphosphine oxide with HCHO in the presence of a base gives hydroxymethyldioctylphosphine oxide. Likewise, treatment with BuBr in presence of tetrabutylammonium sulphate gives dioctyl(butoxymethyl)phosphine oxide. Diarylvinylphosphine oxides **12** (R,R^1 = Ph, tolyl) are formed by dehydrochlorination[254] of **12** [R and R^1 as above; R^2 = CH(Cl)Me; X = O] with alkali at 20–100 °C, in a two-phase system containing 5–40% aqueous alkali in $CHCl_3$ or CCl_4. Similarly, oxide **5** (R = Ph, R′ = $CH{=}CR^2R^3$; X = O) can be prepared[255] by condensing **178** (R = Ph; *n* = 1; Y = Li) with R^1R^2CO($R^1 = R^2$ = Me, *p*-anisyl; R^1 = Ph, R^2 = H, Me, Ph) followed by treatment with $SOCl_2$–pyridine.

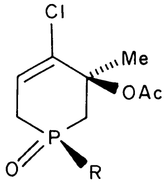
The cyclopropane ring in the dichlorocarbene adducts of alkylmethylphospholene oxides **241** (R = Me, Bu) can be opened up with mercury acetate–acetic acid[256] to form the tetrahydrophosphorin oxide diastereoisomers **242** and **243**. Dibenzophosphole-5-



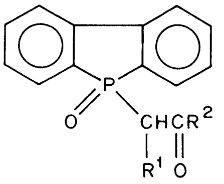
(241)



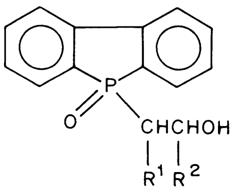
(242)



(243)

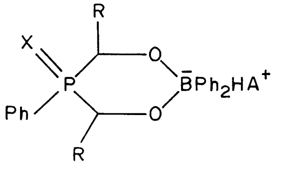


(244)

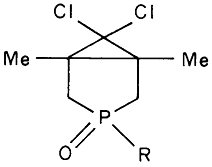


(245)

oxides containing an α-carbonyl group (**244**) [$R^1 = Me, Et, (CH_2)_2OH$; $R^1 = Me, Ph, (CH_2)_nOH$ with $n = 2, 3,5$ and $R^2 = (CH_2)_3OSiPh_2CMe_3$,2-furyl,2-pyridyl,cyclohexyl,3,4-methylene, dioxyphenyl], on reduction[257] with $NaBH_4$, give *threo*-alcohols **245**, whereas reduction with $NaBH_4$, $CeCl_3$ or $Zn(BH_4)_2$ gives the *erythro* form of **245**.

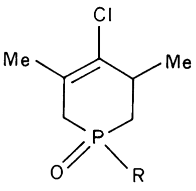


(246)

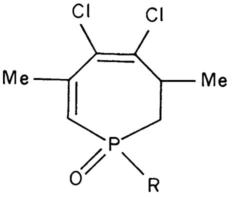


(247)

Boratadioxaphorinanes **246** (R = H; X = O) are prepared[258] by the reaction of $Ph_2BOCH_2CHMe_2$ with **5** ($R = CH_2OH, R' = Ph$; X = O) in the presence of amines A ($A = Pr_2NH$, p-MeC_6H_4,NH_2). Methylphospholene-l-oxide **123** (R = Ph, R′ = Me) reacts[259] with dichlorocarbene in the presence of triethylbenzylammonium chloride and NaOH to give dichloromethylphosphabicyclo[3.1.0]hexane-1-oxides (**247**), which react under the same conditions to give the dihydrophosphorins **248** and phosphacycloheptatrienes **249**.

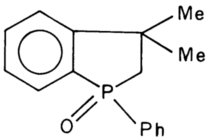


(248)

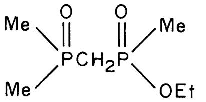


(249)

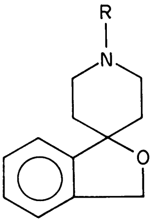
β-Hydroxyalkylphosphine oxides on acid-catalysed dehydration initially give allyl- or vinyl-phosphine oxide, which cyclise to give five- or six-membered rings. Thus, dehydration of **5** [R = Ph; $R' = CH_2C(Me)_2OH$; X = O] with H_3PO_4 (98%) initially gives the oxide **5** [R = Ph; $R' = CH_2C(Me) = CH_2$; X = O], which cyclizes[260] to give **250**. Chloromethyldimethylphosphine oxide (200 g) reacts slowly[261] at 140 °C with $MeP(OEt)_2$ (215 g) to give the dioxide **251**. Reaction of the former with the amine **252** (R = H) on heating at 100 °C for 20 h in dmf containing K_2CO_3 gives[262] the oxide **252** [$R = CH_2P(O)Me_2$].



(250)

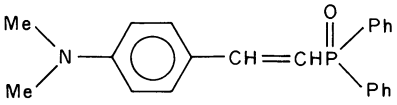


(251)

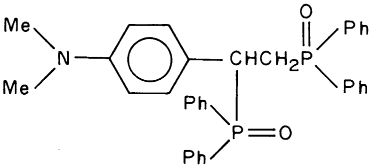


(252)

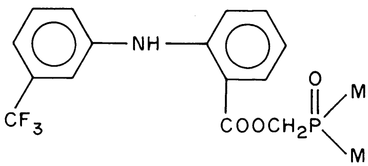
β-Nitrostyrenes react with diphenylphosphinite esters **68** (R = R′ = Ph; R^3 = Me, Et, $CHMe_2$) in MeCN below 0 °C to form 1,2-bis(phenylphosphinyl)arylethanes usually as the major product[263] together with *trans*-β-styryldiphenylphosphine oxide. Thus, *p*-$Me_2NC_6H_4CH{=}CHNO_2$ produces 0.3% *trans*-**253** and 66–85% **254**. The phosphine oxide **255**, prepared by treating chloromethyldimethylphosphine oxide with the corresponding sodium carboxylate in dmf at 150 °C, has anti-inflammatory properties[264].



(253)

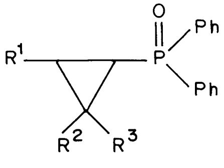


(254)

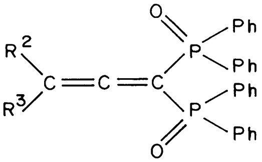


(255)

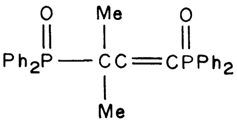
The photochemical ring opening of **219** (X = O) gives diphenylphosphorylvinylcarbenes via diazomethane intermediates[265]. These carbenes cyclize to give good yields of phosphorylated cyclopropenes **256**. Thus, **219** (R^1 = H; R^2 = R^3 = Me; X = O) produces **256** in 97% yield. Photolysis of **219** [R^1 = $P(O)Ph_2$; R^2 = Me, Ph; R^3 = Me; R^2 = R^3 = Ph) gives **257** in addition to cyclopropenes **256**, whereas when R^2 = Me and R^3 = Ph it rearranges to **258**.



(256)



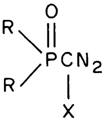
(257)



$Ph_2P(O)-C(Me)_2C{=}C\,P(O)Ph_2$

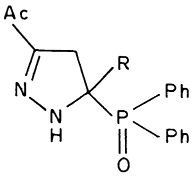
(258)

Diazomethylphosphoryl compounds **259** (R = OEt, Y = H) on lithiation give the lithiated product (Y = Li), which after acylation and silylation was transformed[266] with PhCHO and chloral into an aldol-like product **260**. Bromination or iodination of **259**



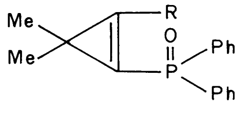
$R_2P(O)CN_2X$

(259)

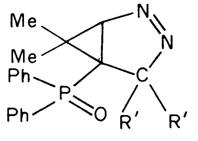


(260)

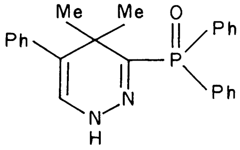
(R = alkyl, aryl; Y = Ag) with BrCN or iodine gives the halo derivative (Y = Br, Cl), which on acylation with R'COCl (R' = Me, CMe$_3$, Ph, β-anisyl, P-BrC$_6$H$_4$) gives the acyl derivative of **259** [Y = C(O)R']. Cyclopropenylphosphine oxides **261** [R = H, Me, Ph, P(O)Ph$_2$] undergo regiospecific reaction[267] with diazoalkanes R'$_2$CN$_2$ (R' = Me, Ph; R'$_2$ = 9-fluorenylidene) to give **262**. Treatment of the cycloadduct **262** with ethanolic KOH resulted in isomerization to give 1,4-dihydropyridazines **263** and **264**.



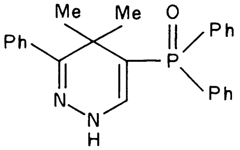
(261)



(262)

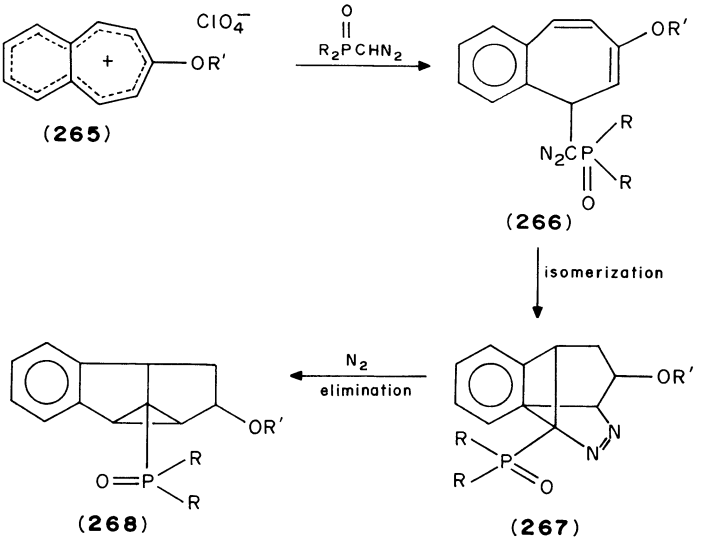


(263)



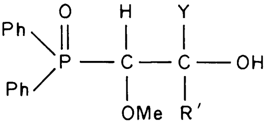
(264)

Intramolecular cycloaddition of 5-(diazomethyl)-5H-benzocycloheptenes **266** leads to their isomerization[268] to **267**, which by thermal elimination of nitrogen are converted into the tetracycles **268**. Compounds **266** are prepared by electrophilic substitution by diazoalkane of 7-alkoxybenzocycloheptenylium perchlorate **265** (R' = Me, CHMe$_2$, CH$_2$Ph) (Scheme 6).



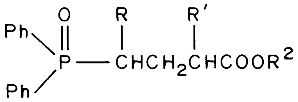
SCHEME 6. Intramolecular cycloaddition of 5-(diazomethyl)-5H-benzocycloheptenes.

Phosphine oxides **5** [R = Ph, R′ = CH(R^2)OMe, where R^2 = H, Me], on reaction with LiN(CHMe)$_2$, give the lithium derivative [R′ = C(Li)(R^2)OMe], which reacts with aldehydes and ketones to give separable diastereoisomeric adducts. Treatment of these diastereoisomers with base gives the vinyl ether geometrical isomers, e.g. reaction of **5** (R = Ph, R′ = CH$_2$OMe, X = O) with LiN(CHMe)$_2$ followed by reaction with aldehydes gives[269] the adducts **269**. Phosphine oxide **270** (R = H, Me; R^1 = H, Ph; R^2 = Me, Et, Ph, hexyl, cyclopropyl) undergoes acyl transfer[270] when treated with (Me$_2$CH)$_2$NLi to give 73–96% **271** [Y = C(O)R^2], which on reduction with NaBH$_4$ gives *threo*-alcohol **271** [Y = CH(OH)R^2]. Horner's reaction of the dioxide **272** with RC$_6$H$_4$CHO (R = H, *m*-, *p*-NMe$_2$, *o*-, *m*-, *p*-OMe) produces[271] 24–93% *trans*-oxide **273**.

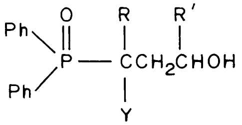


(a) R′ = (CH$_2$)$_5$Me ; Y = H
(b) R′ = H ; Y = (CH$_2$)$_5$Me

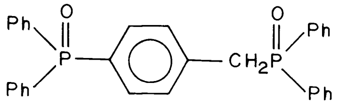
(269)



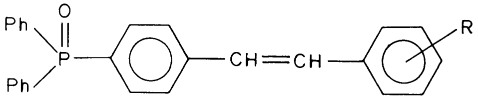
(270)



(271)



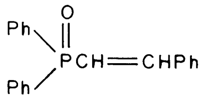
(272)



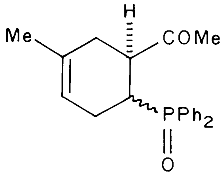
trans

(273)

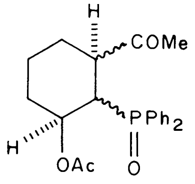
Carbonyl alkenylation of **5** [R = Ph, R′ = CH(Li)R^2, where R^2 = SnPh$_3$, PbPh$_3$, SbPh$_2$, TePh; X = O] by reaction[272] with aldehydes proceeds readily to give diphenylphosphoryl-substituted alkenes in high yields. Thus, benzaldehyde on reaction with **5** [R = Ph, R′ = CH(Li)SnPh$_3$; X = O] at −70 °C in thf gives **274** in 92% yield. Reaction of oxide **5** (R = Ph, R′ = CH=CHCOMe; X = O) with isoprene and acetic acid gives[273] adducts **275** and **276**.



(274)



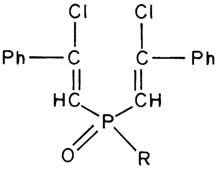
(275)



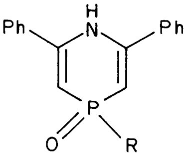
(276)

Phosphine oxides of the type **12** (R, R^1 and R^2 = hydrocarbyl; X = O, S) are prepared[274] in two steps by the reaction of dihydrocarbylphosphine oxides (or sulphides) with alkali metal (M) amides to give R(R^1)PXM, followed by treatment of the latter with organic halides R^{2}Y. Thus, reaction of dioctylphosphine oxide with NaNH$_2$–NaOCMe$_3$

followed by treatment with PhBr gives **5** (R = octyl, R′ = Ph; X = O). Triphenyl- and tribenzyl-phosphine oxides have been reported recently to react[275] with alkali metals in liquid ammonia to give diphenyl- and dibenzyl-phosphinite ions, respectively, in high yields. These react under photostimulation with aryl halides by the $S_{RN}1$ mechanism to produce aryldiphenyl- and aryldibenzyl-phosphine oxides of the type **5**. Tribenzylphosphine oxide, on consecutive debenzylation with alkali metals followed by photostimulated reaction with aryl halides, could part with all the aromatic moieties and produce unsymmetrical triarylphosphine oxides of the type **12**. 1,4-Azaphosphorin oxides **278** (R = Ph, —C≡CPh) are prepared[276] by cyclizing the halovinyl phosphine oxide **277** [R = Ph(Cl)C=CH, Ph] with ammonia in dmf.

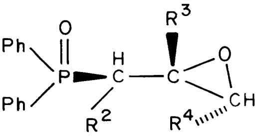


(277)

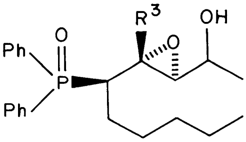


(278)

Reaction of **5** (R = Ph, R′ = Et; X = O) with BuLi and PhCHO in thf–hexane at between − 78 °C and room temperature over 24 h forms (1*RS*, 2*SR*)- and (1*RS*, 2*RS*)-oxide **5** [R = Ph; R′ = CH(Me)CH(Ph)OH], respectively[277]. Stereoselective peracid epoxidation of allylic and 6-hydroxyallylic diphenylphosphine oxides has been studied by McElroy and Warren[278]. Thus (*E*)-5-oxide [R = Ph; R′ = CH(R^2)C(R^3)=CHR^4, where R^2 = pentyl, Me, Pr; R^3 = Me, Et, H and R^4 = Me, Me_2CH] on epoxidation with *m*-chloroperbenzoic acid gives **279**. Similarly, the hydroxyallyl compound produces **280**.



(279)

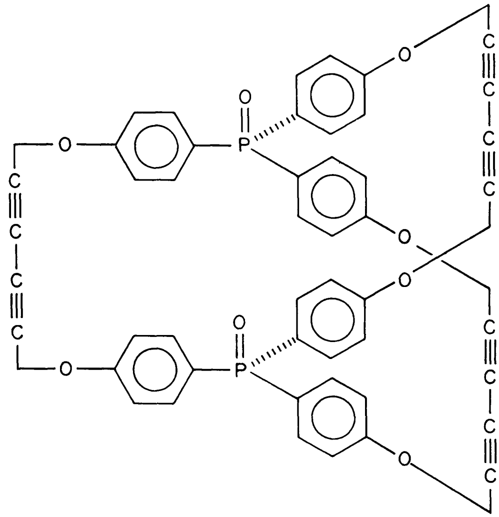


(280)

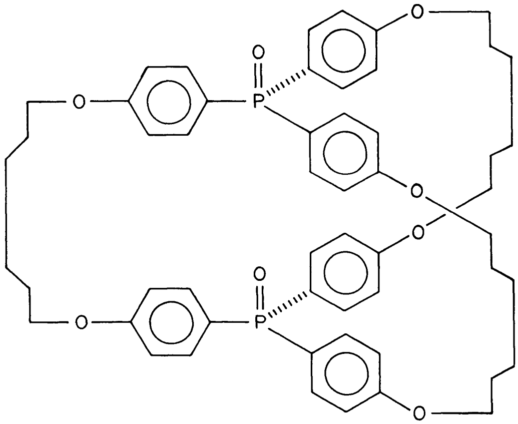
Friedrichsen and Whitlock[279] have prepared some macrocyclic phosphine oxides (**281** and **282**) starting from the reaction of tris(4-hydroxyphenyl)phosphine oxide with propargyl bromide in acetone in the presence of K_2CO_3. The tris(4-propargyloxyphenyl)phosphine oxide thus obtained cyclizes in the presence of $Cu(OAc)_2 \cdot H_2O$ in pyridine to give the macrocycle **281** together with its *exo–endo* isomer. On hydrogenation, **281** gives the macrocycle **282** in 47% yield whereas the *exo–endo* isomer of **281** gives the *exo–endo* isomer of **282** on hydrogenation in 53% yield.

2. *Through decomposition/hydrolysis of phosphonium salts*

Hexaalkyliodobis(phosphonium)pentaiodide **283a** on hydrolysis at room temperature in benzene for 1 h yields a 1:1 complex of the resultant phosphine oxide. Hydrolysis[280] for 10 h gives **283b** in 80% yield. Oxidative degradation of the phosphonium chloride **284a** with chlorine at pH 5–7 is reported[281] to give tris(hydroxyethyl)phosphine oxide,

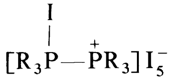


(281)



(282)

whereas at pH 1–3 **284b** is obtained.

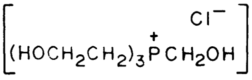


$[R_3P{-}\overset{+}{P}R_3]\,I_5^-$ with I attached to the first P

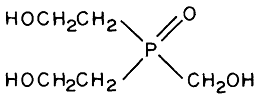
$[R_3P{=}O]_2{\cdot}HI_3$

R = octyl, cyclohexyl

(283a) **(283b)**

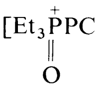


$\left[(HOCH_2CH_2)_3\overset{+}{P}CH_2OH\right]Cl^-$



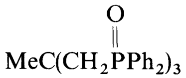
(284a) **(284b)**

$POCl_3$ reacted with triethylphosphine to give the dichlorophosphoryl phosphonium[282] salt **285** in 80–90% yield, which on alkaline or aqueous hydrolysis was converted into the triethylphosphine oxide. Compounds **75** (R′ = Ph; X = S) and **286** were similarly prepared. However, this procedure could not be applied to Ph_2PPPh_2 because of steric hindrance. The phosphonium bromide obtained by heating[283] the phosphine **123** ($R = Ph$, $R^1 = H$, $R^2 = Me$; X = nil) with alkyl bromide (R = octadecyl) at 105–115 °C for 2 h under nitrogen, on treatment with aqueous Na_2CO_3 for 5 min, yielded the oxide **12** (R = methylbutenyl, $R^1 = Ph$, R^2 = octadecyl) by cleavage of a P—C bond.



$[Et_3\overset{+}{P}(=O)PCl_2]Cl^-$

(285)

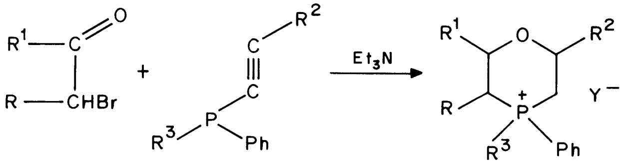


$MeC(CH_2P(=O)Ph_2)_3$

(286)

The steric course of the alkaline cleavage of phosphonium salts has been described by Luckenbach[284]. The cleavage results in more or less complete inversion of configuration at the phosphorus atom depending on the nature of the R group.

4-Phosphoniapyran salts **287** (Y = Br, ClO_4) on basic hydrolysis[285] with NaOH, Ag_2O or KOH yielded 4-oxo-4-phenyloxaphosphorin systems **173** (R = Ph, *p*-$NO_2C_6H_4$; R′ = PhC≡C, MeC≡C, Ph; R^2 = H, Me, Ph; Z = O). Compound **287**, in turn, was prepared in 55% yield by the cycloaddition[286] of diacetylenic phosphines with α-halo ketones by stirring them together for 96 h at room temperature in the presence of Et_3N (reaction 23).

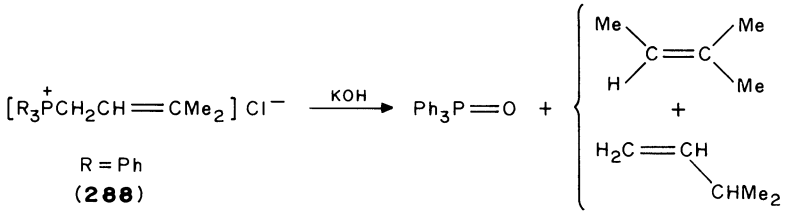


(23)

$R^3 = -C{\equiv}CPh$

(287)

Decomposition of the phosphonium salt **288** containing a γ-methylallyl or γ,γ-dimethylallyl group results in anomalous cleavage[287] yielding the phosphine oxide and isomeric alkenes, e.g. decomposition of **288** by aqueous KOH gave 65% of a mixture of alkenes and 70% of Ph_3PO. Analogous decomposition of **288** (R = Bu) gave 60%



(24)

$[R_3\overset{+}{P}R']X^-$

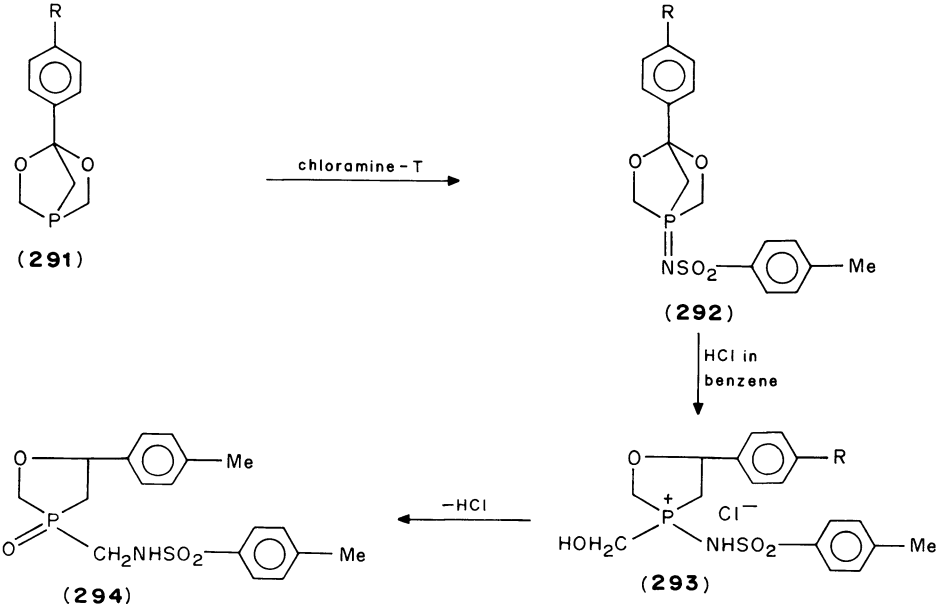
R = Ph, X = OH, Br;
R = Bu, X = OH;
$R' = CH_2CH{=}CH_2$

(289)

$R_4\overset{+}{P}Cl^-$

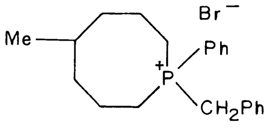
(290)

Bu_3PO and 61% of a mixture of alkenes. Similar alkaline cleavage[288] of **289** yielded trialkylphosphine oxide and propene. Hydroxymethylphosphonium chloride **290** ($R = CH_2OH$) on reaction with aniline gave[289] **290** ($R = CH_2NHPh$), which on treatment with Et_3N, followed by oxidation, yielded diazaphosphorinane oxide **22** ($R = H, R'CH_2$-NHPh; $X = O$). 1,3-Oxaphospholene oxide **294** was prepared[290] in 61–96% yield from the oxaphospholene salt **293** by dehydrochlorination (Scheme 7); **293** in turn was prepared by treating aryl dioxaphosphabicycloheptenes **291** with chloramine-T for 2 h at 20 °C, followed by treatment of the resultant **292** with 1% HCl in benzene for 24 h.

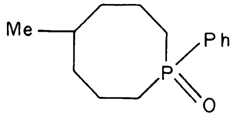


SCHEME 7. Synthesis of 1,3-oxaphospholene oxide.

The stereochemistry of the cleavage of phosphocane derivatives **295** by alkaline hydrolysis has been shown by Marsi and Burns[291] to proceed predominantly with inversion of configuration at phosphorus to give **296**.



(295)

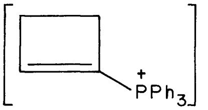


(296)

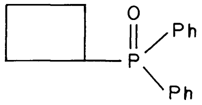
Thermal decomposition of $\{R_2\overset{+}{P}(CH_2OH)_2\}Cl^-$ is known[292] to give phosphine oxide, e.g. dimethylbis(hydroxymethyl)phosphonium chloride gave 74.3% Me_3PO. Similarly, **290** ($R = Me$) on heating in a stream of air[293a] at 80 °C gave **1** ($R = Me$; $X = O$) in 83% yield. Compound **1** ($R = Me$; $X = O$) can also be obtained[293b] by the alkaline hydrolysis of **290** ($R = Me$) with two mol equiv. of 50% aqueous NaOH. Likewise, the salts **289**

(R = Ph, Bu; R′ = OCH_2CH_2Br) on hydrolysis with water or alcohol give the corresponding[294] oxides. The phosphonium salts **289** (R = Ph; R′ = 2-pyridyl, 2-quinolyl, 2-benzothiazolyl) on hydrolysis[295] give **1**(R = Ph; X = O). Compound **289** in turn is prepared by heating Ph_3P with R′X (R′ = 2-pyridyl, 2-quinolyl, 2-benzothiazolyl, 2-benzoxazolyl; X = Br, Cl, I). Compound **289** [R = Ph; R′ = —$C(R^2){=}CHR^3$, where $R^2, R^3 = (CH_2)_n$; X = ClO_4] on hydrolysis gives[296] **5** (R = Ph, R′ = —$CR^2{=}CHR^3$; X = O).

Alkylation of the phosphine **75** (R = R′ = Ph; X = nil; $n = 1$) with $PhCH_2Br$ in toluene at 80 °C gives the phosphonium salt, which on hydrolysis with aqueous alkali produces[297] the phosphine oxide **75** (X = O). Hydrolysis of a solution of the phosphonium salt **297** (4 mmol) with NaOH (4 mmol) in MeOH-H_2O (2:3) for 5 h gave 1-cyclobutylphosphine oxide **298** in 80% yield[298].

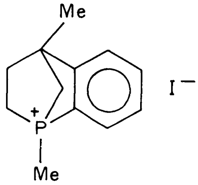


(297)

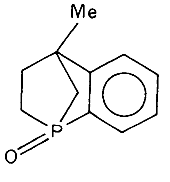


(298)

1-Phosphabicyclooctane phosphine oxides **300** are formed[299] by treatment of the methiodide of the phosphonium salt **299** with KOH. Methane is eliminated from the molecule. Owing to the constraint of the bridgehead structure, nucleophiles attack the methiodide of 3,4-benzo derivative **299** to displace the *p*-methyl group in preference to the benzylic moiety. Such displacement of a methyl group in preference to a benzylic group is very unusual and is due to the influence of the cage structure on the reactivity at phosphorus.

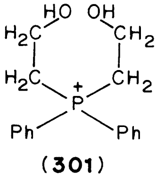


(299)

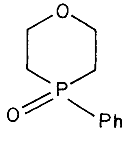


(300)

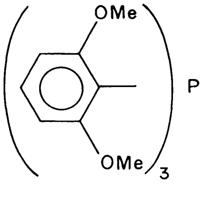
Diphenylbis(β-hydroxyethyl)phosphonium chloride (**301**) cyclizes during alkaline cleavage[300] with NaOH to give oxaphosphorinane **302** in 75% yeild. The hydroxyphosphonium salt **304**, obtained by the reaction of acids with tris(2,6- dimethoxyphenyl)-phosphine oxide **303**, is fairly stable and forms (with ClO_4^- salts) stable 1:1 adducts with various amines. An unexpected property of **303** is that it is highly soluble in water and reacts[301] with acids to give **304**. The phosphine oxide **303** is prepared by the oxidation[302] of the corresponding phosphine with H_2O_2; on treatment with $HClO_4$, **303** gives **304** (Y = ClO_4).



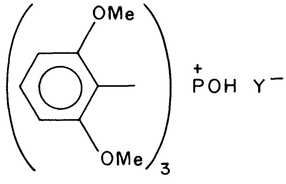
(301)



(302)



(303)

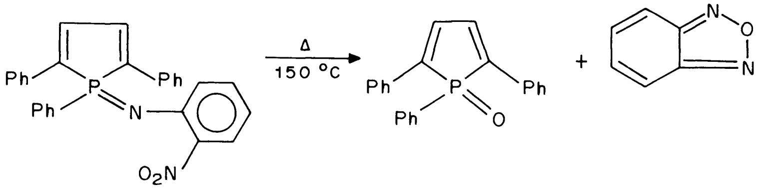


Y = ClO$_4$, BF$_3$

(304)

3. Through hydrolysis of dihalophosphoranes/imines/P=N bonds

Tetraphenylmethylenediphosphine bis(*N*-phenylimine) **7** (R = R′ = Ph; X^1, X^2 = NPh) on reaction[303] with *p*-nitrobenzaldehyde in refluxing xylene for 11 h gave the corresponding phosphine oxide **7** (X = O) in 81% yield. Thermolysis of *o*-nitroaryliminophosphole **305** at 150 °C was reported[304] to give 1,2,5-triphenylphosphole oxide **306** and the benzofuran. The *N*-phenyl derivatives **305** in turn were prepared from the corresponding phospholes.



(305) **(306)** (25)

4. Through oxidation of phosphine sulphides/selenides

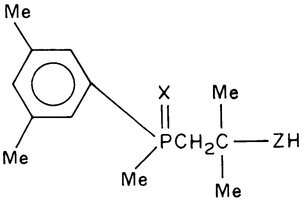
Phosphine sulphides are known[76] to be oxidized to oxides through the photochemical transfer of oxygen from heterocyclic *N*-oxides. Thus, triaryl sulphides **1** (R = *p*-R′C$_6$H$_4$, where R′ = H, Me, Cl, MeO, MeOOC; X = S) were converted into the corresponding oxides (X = O) in 29–38% yields on irradiation with 3-methylpyridazine-2-oxide in dichloromethane.

A general method for conversion of thiophosphoryl and selenophosphoryl groups into phosphoryl groups is available[305] through ozone oxidation. For example, **12** (R = R^1 = R^2 = Et, Ph; X = S, Se) is quantitatively oxidized to the oxide by ozone at −75 °C. The reaction is stereoselective and proceeds with retention of configuration at the phosphorus atom.

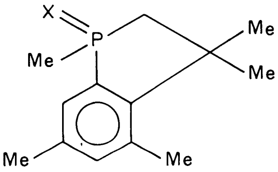
Phosphine oxides are prepared by the reaction of dimethyl sulphoxide with phosphine sulphides in acidic solution[306,307]. These conversions proceed with complete inversion of configuration at the central phosphorus atom. Thus, (*R*)-(+)-methylphenylpropylphosphine sulfide gives the (*S*)-(−)-oxide. Similarly, (*S*)-(−)-benzylmethylphenyl and (*S*)-(−)-methylphenyl-*t*-butyl phosphine sulphides yield the corresponding (*R*)-(+)-oxides. The dmso oxidation is catalysed by iodine[308]. Dimethyl selenoxide is also known[309] to oxidize the thio- and seleno-phosphoryl compounds to the phosphoryl analogues. Phosphine oxides have also been prepared by the oxidation of phosphine sulphides with H_2O_2. The oxidation is carried out[310] at 40–80 °C in at least 20–50 wt% of a C_{1-6}-carboxylic acid or anhydride. Thus, bis(*p*-(chlorophenyl)phenylphosphine sulphide (18.16 g) in acetic acid (50 ml) was treated with 35% H_2O_2 (4.51 ml) at 70 °C for 30 min to give the corresponding oxide in 97% yield. The same reaction takes 12 h in methanol. H_2O_2 oxidation of sulphides can also be carried out[311] in a solution containing 2–20 wt% of an optionally halogenated aliphatic carboxylic acid, e.g. when **12** ($R = Me$, $R^1 = Et$, $R^2 = Ph$; $X = S$) (25 g) is dissolved in methanol (50 g) and acetic acid (6.3 g) is added to the solution at 45–50 °C, subsequent treatment with 35% H_2O_2 (11.7 ml) gives the oxide **12** ($X = O$) in 90% yield.

Tertiary aryl phosphine oxides **5** ($R = p\text{-}FC_6H_4$, $R' = Ph$; $X = O$) are also prepared by the H_2O_2 oxidation[312] of the corresponding sulphides ($X = S$); see Section IV.B.2 for the preparation of **5** ($X = S$). The oxidative desulphurization by H_2O_2 is also aided by the presence of inorganic acid catalysts[313]. Thus, a refluxing mixture of phenylbis(*p*-chlorophenyl)phosphine sulphide (0.01 mol) and 32% HCl (25 ml) on treatment with 30% H_2O_2 (3.4 ml) followed by refluxing for 5 h gives the corresponding oxide in 81% yield. The stereochemistry of the oxidation of thiono- and seleno-phosphoryl compounds with H_2O_2 has been described by Stec *et al.*[314] They proceed with net retention of configuration at the phosphorus atom.

Phosphine sulphide to phosphine oxide exchange reactions are also known[315]. Thus, treatment of the sulphide **307** ($X = S, Z = O$) with polyphosphoric acid at 140–150 °C for 4 h gives the oxide **308** ($X = O$) on cyclization, in 47% yield. Under milder conditions, i.e. on reaction with $MeSO_3H$–P_2O_5 at room temperature, the sulphide alcohol **307** ($X = S$; $Z = O$) gives the oxide thiol **307** ($X = O$; $Z = S$), which cyclizes to **308** ($X = O$) on heating with polyphosphoric acid at 145 °C.



(307)



(308)

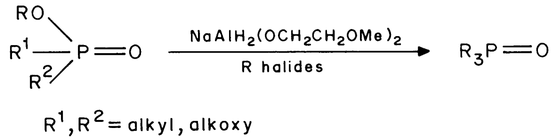
Oxidation of phosphine sulphide is also carried out using sulphuric acid or sulphonic acid at 70–200 °C in an inert aprotic solvent[316], e.g. Ph_3PS (5 g) on heating with 96% H_2SO_4 (15 ml) for 9 h at 140–150 °C and cooling, followed by extraction, gave Ph_3PO (3.8 g). Metalloporphyrins are known to catalyse[317] oxidative desulphurization/deselenation at pentavalent phosphorus. Manganese(III) mesotetraphenylporphyrin chloride in the presence of $Bu_4N^+\ IO_4^-$ helps in the oxidative desulphurization, which is further aided by the presence of imidazole. Thus, Ph_3PS reacts with periodate to give the corresponding oxide in 33% yield. Addition of the manganese(III) complex increases the yield to 59% and addition of imidazole gives Ph_3PO in 81% yield. Cumyl hydroperoxide in the presence of magnesium and iron mesotetraphenylporphyrins also have been reported[318] to catalyse the oxidative desulphurization of the phosphine sulphides.

Oxidative desulphurization/deselenation at P^V is also known to be carried out with photogenerated peroxide species[319] such as those obtained from the photooxidation of dihexyl sulphide and diphenyldiazomethane. Thus, Rose Bengal-photosensitized oxidation of dihexyl sulphide in methanol–chloroform in the presence of Ph_3PSe or Ph_3PS gave

Ph_3PO in 100% and 37% yield, respectively. Baxter *et al.*[320] have reported the oxidative desulphurization of Ph_3PS to Ph_3PO by irradiation in the presence of the photoinitiator $RC(O)P(O)R'_2$ in acetonitrile and oxygen for 10 h. Oxidative desulphurization of **1** (R = Ph, Bu; X = S) has also been carried out by reaction[321] with $COCl_2$ in MeCN for 24 h, to obtain the corresponding oxides (R = Ph, Bu) in yields of 95 and 99%, respectively. Use of $CSCl_2$ in the above reaction reduced the yields to 74 and 95%, respectively.

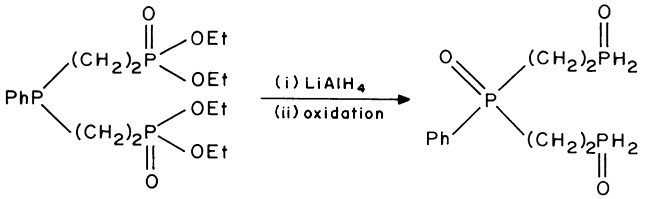
5. *Through reduction of phosphonates and phosphinates*

Phosphine oxides are reported[322] to be formed by the reduction of phosphonates, phosphinates and phosphate esters, with sodium bis(2-methoxy ethoxy)aluminium hydride, followed by the addition of either primary or secondary alkyl halides (reaction 26). Sodium aluminiumdiethyldihydride has also been used for the reduction of phosphorus esters[323], followed by reaction with alkyl halides. The yields are generally comparable to those obtained by using a Grignard reaction, but the procedures involved in reaction 26 are much simpler.



(26)

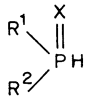
Reduction of phosphonates with $LiAlH_4$ is known[324] to give phosphines, which could be oxidized to the oxides (reaction 27).



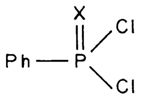
(27)

6. *Through reaction of organometallics/reactive species with P^V halides/oxyhalides*

The reaction of Grignard reagents containing tertiary aliphatic radicals with phosphonic dichlorides yields phosphine oxides **5**, **67** or **309** (X = O), depending on the nature of the reactants[325]. Tertiary phosphine oxides based on organomagnesium compounds can be prepared[326] by the reaction of organomagnesium compounds with PCl_5 or its organic derivatives at 20–80 °C in an inert solvent such as benzene, followed by treatment with aqueous NH_4Cl.

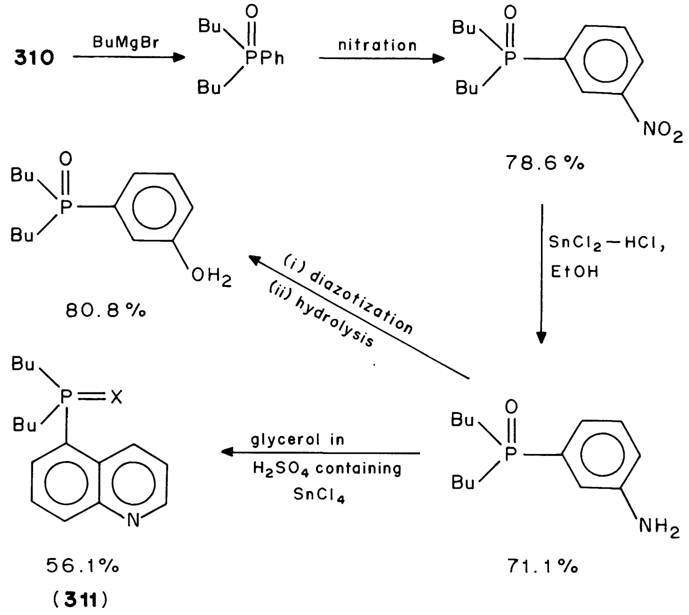


(309)



(310)

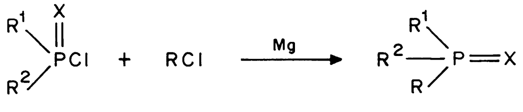
Kormachev *et al.*[327] converted dialkylaryl-, arylalkyl- and arylalkynyl-phosphine oxides **5** (X = O) into quinolinylphosphine oxide derivatives **311** (X = O) by a series of reactions involving nitration with a 26.3:71.7:2. HNO_3–H_2SO_4–H_2O mixture at 60–90 °C, followed by reduction of the nitro group to an amino group and Skraup's synthesis (Scheme 8). The starting oxide **5** in turn is prepared by the reaction of alkylmagnesium bromide with **310** ($X = O$), in 74.1% yield.



SCHEME 8. Preparation of phosphine oxides involving Skraup's synthesis.

A Grignard reaction of **312** ($R^1 = Ph; X = O$) with *o*-bromotoluene yields[328] the starting phosphine oxide (see Scheme 4: synthesis of dibenzophosphorins), which on oxidation followed by cyclization with polyphosphoric acid gives **188**. Phosphine oxides of the type **5** are prepared[117] by treating **312** ($R^1 = R^2 = C_{1-12}$-alkyl or aryl; $X = O$) with alkyl halides and metals, preferably magnesium, in a refluxing organic solvent, 80–90% (by volume) of hydrocarbon with b.p. > 110 °C and 10–20% (by volume) of ether with b.p. > 64 °C as a mixed organic solvent (reaction 28). The addition of alkyl halides and phosphorus(V) chlorides to magnesium in the organic solvent gave improved yields.

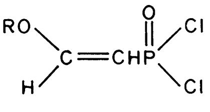
Reaction of $(BrCH_2CH_2)_2POCl$ in benzene with R'MgBr (1 mol) in diethyl ether at 0–5 °C (for $R' = Et$) or 30 °C (for $R' = Ph$) gave the oxide **5** ($R = CH_2CH_2Br; X = O$), which on heating in presence of Et_3N gave the vinyl derivative ($R = CH{=}CH_2$) by elimination of HBr from **5**, with 50–98% yield[329]. Phosphine oxides of the type **1** were prepared[19a] by Grignard reaction of $POCl_3$ with RCl or RBr [$R = C_{5-12}$-alkyl, $PhCH_2CH_2$, $Ph(CH_2)_3$, cyclohexyl]. Thus, magnesium in diethyl ether was treated with octyl chloride in xylene for more than 1 h, followed by refluxing the product with $POCl_3$ for 2.5 h and hydrolysis with water, to give trioctylphosphine oxide in 80% yield.

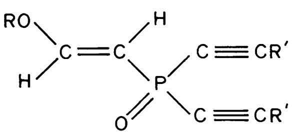


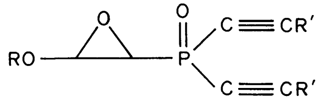
$$R^1R^2P(=X)Cl + RCl \xrightarrow{Mg} R^1R^2RP{=}X \qquad (28)$$

(312)

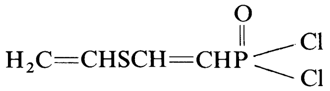
Reaction of alkylmagnesium and lithium derivatives with PCl_5 in the ratio of 3:1 has been reported[330] to give $R_3PO(R = Bu, Ph)$, whereas when they are in the ratio 1:4 the product is R_3P. Treatment of Ph_2PCl_3 with R'Li is known[331] to give $Ph_2PR'Cl_2(R' = Et, Pr, CHMe_2, Bu, CMe_3Ph,$ *p*-tolyl), which on hydrolysis yields the oxide **5**. Tertiary phosphine oxides **315** of acetylenic and diacetylenic series containing an α-epoxy ring are prepared[332] by epoxidation of **314**, which in turn is prepared by the reaction of sodium acetylide with the vinylphosphine oxide dichloride **313**.

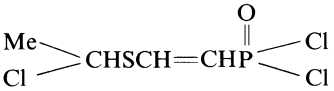

(313)

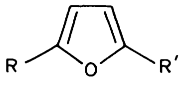

(314)

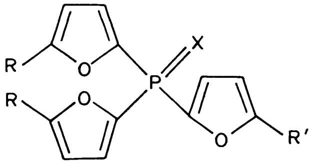

(315)

Reaction of divinyl sulphide with PCl_5 at 0–5 °C in dry benzene yielded[333] **173** ($R = R' = H; R^2 = Cl; Z = S$) in 33.6% yield as a crystalline product, together with 10.2% of **316** and 27.8% of **317**. The reaction of 2-furyllithium **318** ($R = H$, Me, NO_2; $R' = Li$) with dialkyl chlorophosphates $(RO)_2P(O)Cl$ is known to give tris(2-furyl)phosphine oxide[334] **319** ($X = O$).


$$H_2C{=}CHSCH{=}CH\overset{O}{\overset{\|}{P}}Cl_2$$
(316)


$$\begin{matrix}Me\\Cl\end{matrix}{>}CHSCH{=}CH\overset{O}{\overset{\|}{P}}Cl_2$$
(317)


(318)


(319)

C. Miscellaneous Reactions

1. Reaction of elemental phosphorus with alkyl halides

Electrochemical reduction of yellow phosphorus in the presence of alkyl halides is reported[335] to give phosphine oxides, usually mixed with other products. Thus, electrolysis of a mixture of ethyl iodide (250 g) and white phosphorus (in 150 ml of methanol) in the presence of KOH in methanol (at $60 g\ l^{-1}$ concentration) as anolyte gave 44% Et_3PO together with ethane and hydrogen. The use of sodium methoxide in place of KOH improved the yield of the oxide to 46.2%. Electrochemical reduction of phosphorus evidently occurred first, followed by reaction of the product with alkyl halide and proton.

Octyl iodide and red phosphorus is known to give[336] trioctylphosphine oxide in 89% yield in trituration with iodine followed by heating for 1.5 h at 210–215 °C, cooling and treatment with aqueous Na_2SO_3. Tris-cyclohexyl-, -hexyl-, -heptyl- and -nonylphosphine oxides were similarly prepared in 72, 81, 96 and 95% yields, respectively. Kirsanov *et al.*[337] prepared the oxides by alkylation of red phosphorus with alkyl iodides in presence of catalytic amounts of iodine, resulting in the formation of a complex $R_3P.I_3$, which was oxidized on decomposition with alcohol to give the $R_3PO.I_2$ complex. This was then decomplexed by treatment with aqueous Na_2SO_3 (see also Section III.A.1.c).

Tertiary phosphine oxides with dissimilar alkyl groups have been prepared[338] by treating white phosphorus with a mixture of metallic magnesium and alkyl iodides and (or) chlorides at 130–170 °C. When alkyl chlorides were used solutions of white phosphorus in these halides were added to a mixture of magnesium and alkyl halides. When alkyl chlorides with up to five carbon atoms were used, the reactions were carried out in the presence of 5 mol% of the corresponding alkyl iodides. Polyphosphine oxides have been prepared[339] by treating white phosphorus at 170–200 °C with a mixture of alkyl halides or alkylene dihalides and magnesium, followed by treatment of the reaction mixture with alkali at 300 °C. In another variation of the above procedure, secondary alkylphosphine oxides were prepared by treating[340] white phosphorus with the respective alkyl halides and magnesium or zinc at 120–210 °C, followed by alkaline hydrolysis at 270 °C.

Malovik *et al.*[70a] have reported details of the commercial production of the oxides **1** ($R = $ isopentyl, C_7H_{15}–C_9H_{19}, *sec*-octyl; $X = O$) by treatment of PI_3 with ROH. Treatment of alkyl iodides with phosphorus, catalysed by iodine, gave the intermediate $R_3P.I_2$, which yielded **1** ($X = O$) on treatment with Na_2CO_3. The iodine was regenerated from the aqueous solution of sodium iodide obtained from the decomposition of $R_3P.I_3$ with Na_2SO_3 in the final step of the production. This regeneration[70b] was achieved by either oxidation with $NaNO_2$ or reduction with sulphonates or methyl sulphate.

One-pot synthesis of phosphine oxides has also been carried out by Bornancini *et al.*[341] by reaction of elemental phosphorus with sodium in liquid ammonia when ionic species were formed, which reacted with alkyl halides (hal = Cl, Br, I) under irradiation to form **1** ($X = O$) by an $S_{RN}1$ mechanism, in 40–75% yield.

Trialkylphosphine oxides R_3PO ($R = C_{1-6}$-alkyl) have also been prepared[342] by the reaction of red phosphorus with alkyl iodide in presence of $[IR_3PEt_3]^+I_5^-$ or I_2 as catalyst. Thus, Et_3PO is formed[343] by heating a mixture of red phosphorus , EtI and $[IEt_3PPEt_3]^+I_5^-$ at 200 °C for 8 h. This process can be further simplified[344] by decomposing hexaalkylphosphoranephosphonium pentaiodide, with alcohol, followed by treatment with 40–50% alkali in the presence of 0.2–0.4 wt% of an inorganic oxidizing agent. Phosphorus and dimethyl ether, on reaction at 200–400 °C, are reported to produce[345] Me_3PO.

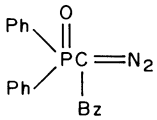
2. *Photophosphorylation reactions*

Irradiation of hydroxymethylphosphines **70** ($R' = CH_2OH$; $X = $ nil) under an inert gas is reported[125] to give phosphine oxides of the type **5** or **1** (see section III.3 for details).

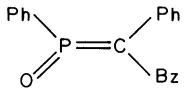
Trapping reactions[346] of α-benzoylbenzylidenephenylphosphine **321**, generated photochemically from the diazophosphine oxide **320**, with aldehydes and ketones, e.g. with benzophenones, are known to give cyclic phosphine oxide **322** formed by [4 + 2] cycloaddition, together with **323** and **324**.

1,3,4-Triphenyl-3-phospholene oxide **123** ($R = R^1 = R^2 = Ph; X = O$) on photocyclization[347] formed the phenanthrophospholene derivative **325**, which on ozonolysis[239] yielded the nine-membered ring diketone **224**. This was reduced by $NaBH_4$ to the diol and then dehydrated with $POCl_3$–pyridine to give *cis–trans*-dibenzophosphonin oxide **326**, the first known example of a phosphonin oxide.

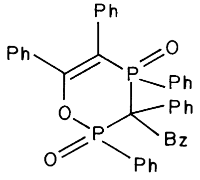
Photochemical transfer of oxygen from heterocyclic *N*-oxides to phosphine sulphides



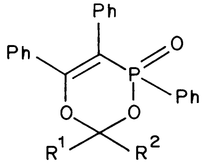
(320)



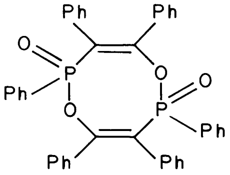
(321)



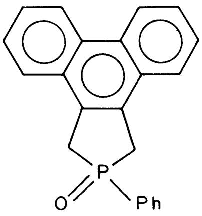
(322)



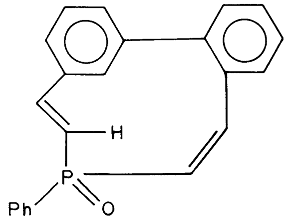
(323)



(324)

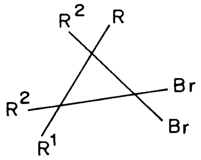


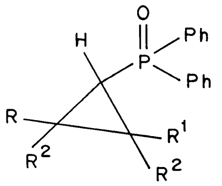
(325)



(326)

have been reported[76], e.g. the sulphides **1** (R = p-R$'$C$_6$H$_4$, where R$'$ = H, Me, Cl, MeO, MeOOC; X = S) were converted to the corresponding oxides in 29–38% yields on irradiation with 3-methylpyridazine-2-oxide in CH_2Cl_2. Diphenylphosphide ions react[348] photochemically with *gem*-dibromocyclopropanes **327** in liquid ammonia or dmso to give the phosphine oxide **328** in 38–49% yield.



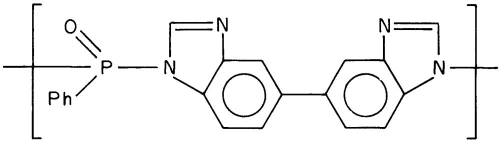


$R = R^2 = Me;\ RR^1 = (CH_2)_4;\ R^2 = H$

(327) **(328)**

3. *Polymerization of unsaturated phosphine oxides*

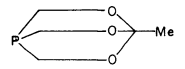
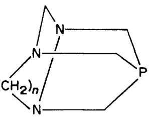
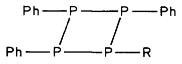
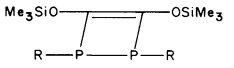
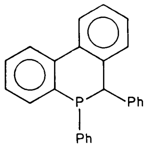
Vinylphosphine oxides **5** (R$'$ = CH═CH$_2$, R = H, Me; X = O) are polymerized[329] in the presence of an organomagnesium catalyst to give mouldable polymers[10] with high stability. Thus, **5** (R = OCH$_2$CH$_2$Cl; R$'$ = CH═CH$_2$; X = O) was polymerized under nitrogen in toluene at O °C in the presence of BuMgCl to yield a film which strongly adhered to glass. In a similar manner, **5** (R = Bu, R = CH=CH$_2$; X = O) was polymerized in the presence of EtMgCl, Bu$_2$Mg or CH$_2$CHMgCl. Similarly, **5** (R = Ph; R′ = CH=CH$_2$; X = O) and styrene react together on heating in benzene[11a] for 6 days at 60 °C in a 1:1 ratio in the presence of catalytic amounts of Me$_2$C(CN)N=N(CN)CMe$_2$ in an evacuated tube. After filteration and treatment with MeOH, a polymer was precipitated which did not burn in the open. A dark-coloured solid polymeric product with unit formula (**329**) was prepared[9] by treating 5,5′-bisbenzimidazole with diimidazole-1-ylphenylphosphine oxide or dipyrrol-1-ylphenylphosphine oxide. These polymers are good adhesives, giving tough surface coatings. The synthesis of oligomers and polymers from phosphine oxides has been reviewed by Borisov *et al.*[349].



(**329**)

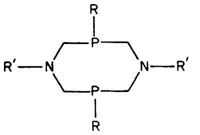
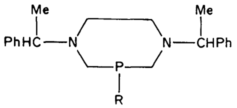
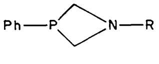
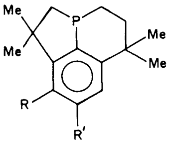
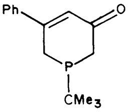
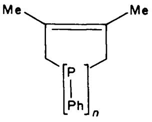
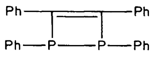
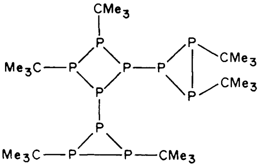
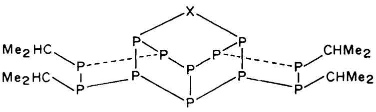
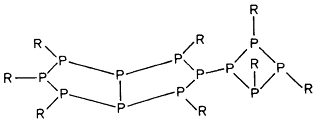
Some heterocyclic phosphines are mentioned in the literature for which the corresponding phosphine oxides have not been reported. These phosphines are listed in Table 1. They should give the oxides on oxidation.

TABLE 1. Some phosphines, the oxides of which have not been reported

Name	Structure	Reference
Bicyclic phosphine		350
Phosphor-III adamantane	 (n = 0,1,2,6)	351
Tetraphenylcyclotetraphosphine	 R = (a)Ph; (b)Bu^t	165
1,2-Diphosphacyclobut-3-ene		352
6-Phenyl-5-phosphaphenanthrene		164

(continued)

TABLE 1. (*continued*)

Name	Structure	Reference
1,5-Diaza-3,7-diphosphacyclooctane		353
1,5-Diaza-3-phosphacycloheptane		354
Azaphosphetane		193
Bicyclic C–P heterocycles		355
3-Keto-5-phenylphosphabenzenes		356
Phospha-heterocycle	 	357
1,2-Bis(di-*tert*-butylcyclotriphosphinyl)-3,4-di-*tert*-butylcyclotetraphosphine-$P_{10}R_6$ type		358
Polyphosphine-$P_{12}R_4$ and-$P_{13}R_5$ structure type		359
Octa-*tert*-butyldodecaphosphine(8)-$P_{12}R_8$ structure type	 R = *tert*-butyl	360

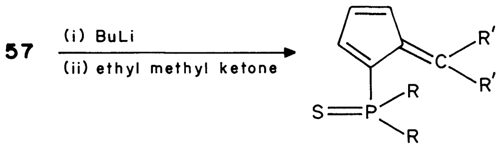
IV. METHODS OF PREPARATION OF PHOSPHINE SULPHIDES

This subject has been reviewed previously[21–24]. Many of the general methods of preparation are common with those used to prepare the oxides. Usually the sulphides are produced more easily.

A. Reactions Involving the Conversion of P^{III} to P^{V}

1. Through sulphurization of phosphines

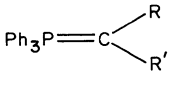
a. Through addition of sulphur. Poly(tertiary phosphine) sulphide **16** and **17** (X = S; see Section III.A.1.b) are prepared[51] by reacting the phosphines **16** and **17** (X = nil) with sulphur in boiling benzene. Mathey and Lampin[108] prepared the diarylcyclopentadienylphosphine sulphide **57** (X = S; R = Ph) by boiling the corresponding phosphine **57** (X = nil; see Section III.A.2.c) with sulphur in a suitable solvent. The sulphide, on treatment with BuLi followed by treatment with ethyl methyl ketone, yielded the corresponding fulvene **330** in 20–70% yield (reaction 28a).



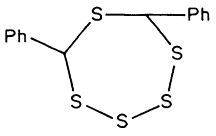
(330)

(28a)

Some phosphines react with sulphur to produce the sulphide, as shown in Table 2. Incidentally, these phosphines, on oxidation, give phosphine oxides also. Reaction of alkylidenetriphenylphosphoranes **331** with sulphur is known[364] to give the phosphine sulphides. When R = H and R′ = Ph in **331**, reaction with sulphur gave the triphosphine sulphide and 1,2,3,4,6-pentathiepane (**332**).

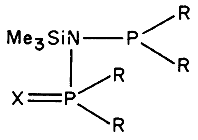


(331)



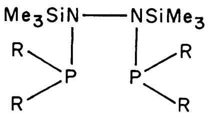
(332)

Reaction of silylated iminodiphosphanes **333** (X = nil) with sulphur[365] yielded the sulphide **333** (X = S), which, on hydrolysis gave the secondary phosphine sulphide **309** (X = S; $R^1 = R^2$) and R_2POONH_4. Compounds **333** (X = nil) were prepared by the reaction of **67** (R = R′; $X^1 = X^2$ = nil) with Me_3SiN_3 together with **334**.



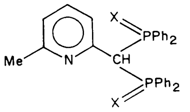
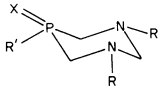
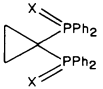
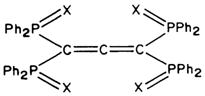
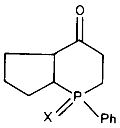
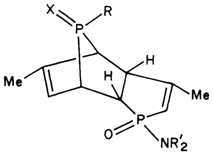
R=Me,Et,Pr,Bu

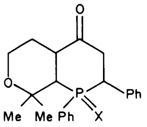
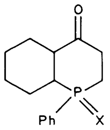
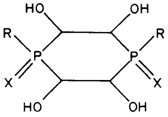
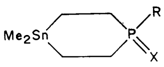
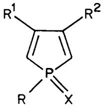
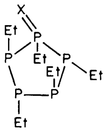
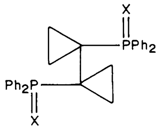
(333)



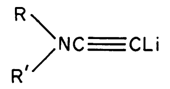
(334)

TABLE 2. List of phosphines sulphurated by reaction with sulphur

Name	Structure of the phosphine (X = nil), sulphide (X = S)	Formula No. in text	Section in text	References	Remarks
2-Bis(diphenylphosphino)methyl-pyridine		**9**	III.A.1.a	35	
N,*N*-Disubstituted-5-phenyl-diazaphosphorinane		**22**	III.A.1.b	58	
Cyclopropylidenebis(diphenyl-phosphine)		**23**	III.A.1.b	59	Sulphide obtained in 88% yield
Tetrakis(diphenylphosphino)allene		**49**	III.A.1.f	91,92	
2-Phenyl-2-phosphabicyclo[4.3.0]-nonan-5-one		**11**	III.A.1.a	37,36	Reaction at 40–60 °C with sulphur
Tricyclic phosphine		**50**	III.A.1.f	95	

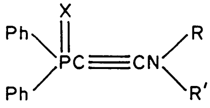
Oxaphosphabicyclodecanone	 	**42,43**	III.A.6	80,81	
1,4-Diphosphorinane		**160**	III.A.6	18	
1,4-Phosphastanninane		**161**	III.A.6	196	
3,4-Dialkylphosphole		**116**	III.A.5	167	
Tris(trichloromethyl)phosphine	$(ClCH_2)_3P{=}X$	**1**	III.A.3	362	Heating with S at 60–80 °C in the presence of 0.2–0.6% of active carbon
Pentaethylcyclopentaphosphine		**8**	III.A.1.a	363	
1,1-Bis(diphenylphosphino)-bicyclopropyl		**39**	III.A.1.c	72	The oxide (X = 0) on reduction with $HSiCl_3$–NEt_3 gives the phosphine (X = nil) which on treatment with sulphur gives the sulphide (X = S)

Reaction of acetylenic phosphines **336** (X = nil) with sulphur leads to the formation[366] of the sulphides **366** (X = S); **336** (X = nil) in turn were prepared in 33–57% yield by the reaction of chlorodiphenyl phosphines **312** (R′ = R^2 = Ph; X = nil) with the lithium derivative **335** at −10 °C in diethyl ether under nitrogen. Reaction of **336** with R^2SOON_3 in chloroform led to the formation of a crystalline equilibrium mixture of **337** and **338** (X = S) by diazo group transfer.

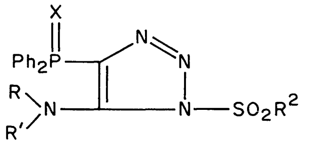


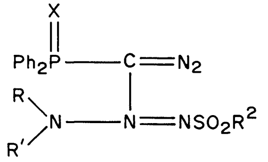
R = Et, Me, CH_2Ph, Ph ;
R′ = Et, Ph

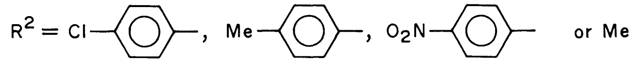
(335)



(336)



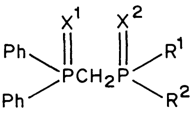




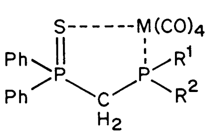
(337)

(338)

(Phosphinomethyl)phosphine sulphides **339** (X^1 = S; X^2 = nil) on reaction[367] with sulphur give the disulphide **339** ($X^1 = X^2$ = S; R^1, R^2 = Me, Et, Ph, $PhCH_2$). The sulphide **339** (X^1 = S, X^2 = nil), on reaction with Group VI metal carbonyls, gives a complex **340** (M = Mo, Cr, W), with phosphorus and sulphur bonded to the metal in a six-membered chelate ring. On heating, the sulphur transfers to the more basic phosphorus atom, forming **339** (X^1 = nil, X^2 = S). Disecondary phosphine sulphides **75** (R = Ph; R′ = H; *n* = 2, 4 and 6; X = S) were prepared[368] by treating the corresponding bisphosphine **75** (X = nil) with sulphur. The disulphide **75** (n = 1; X = S; R = R′ = Me) on treatment with lithium gave the lithium derivative, which on reaction with dimethylthiophosphoryl chloride **19** (R = Me; X = S) gave a novel mesomeric stabilized carbanion[369], the tris(dimethyl thiophosphinyl)methanide **341**. Diastereoisomerically pure (−)-(Rp)-*O*-menthyl methyl phenylphosphinite and *O*-methyl ethyl phenylphosphinite underwent stereospecific alkylation with alkyllithium (R = Pr) to give chiral tertiary phosphines with very high optical purity. These phosphines on sulphuration[370] with S_8 gave(−)-S-methyl propyl phenylphosphine sulphides. Similar sulphuration was obtained with other chiral phosphines. Reaction of adamantylphosphine **342** (X = nil) with sulphur

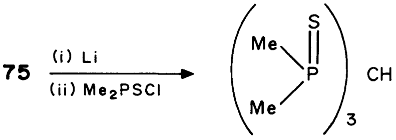


(339)



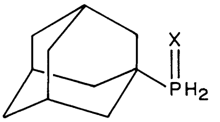
(340)

at 85–90 °C gives the corresponding sulphide[371] **342** (X = S). Acylphosphine sulphides **343** (X = S), used as photoinitiators, are formed by the reaction[372] of sulphur with the phosphine **343** (X = nil; R = MeO; R′ = H).

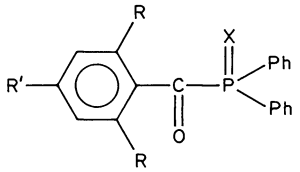


(29)

(341)

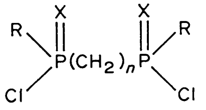


(342)

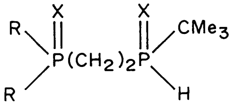


(343)

1-*tert*-Butylphosphinoethane derivative **345** (R, R′ = Ph; X = nil) and bis-*tert*-butylphosphinoethane **345** (R = Bu^t; R′ = H; X = nil) on reaction[373] with sulphur give the corresponding sulphides **345** (X = S). The bisphosphine **345** (R = Bu^t; R′ = H; X = nil) is prepared by the reaction of *tert*-butylmagnesium chloride with halophosphine **344** (R′ = Cl; *n* = 2; X = nil), when one chlorine on each phosphorus is replaced by a CMe_3 group. This on reduction gives **345** (X = nil; R = CMe_3; R′ = H). The diphenylphosphinoethane derivative **345** (R = R′ = Ph; X = nil) is prepared by treatment of the lithium derivative of the *tert*-butylphosphine $LiP(H)CMe_3$ with **178** (x = nil; R = Ph; *n* = 2; Y = Cl).



(344)



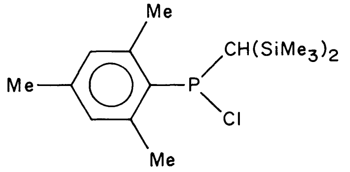
(345)

The sulphides **346** (X = S), produced in 53–59% yield by reaction of sulphur on the phosphine **346** (X = nil), showed triad thiophosphorylmercapto ylide tautomerism (S═P—CH⇌HS—P═C) on reaction[374] with halogen acids HY (Y = Cl, Br), yielding the corresponding phosphonium salt. The above tautomerism is dependent on the nature of the substituents on the central carbon atom.

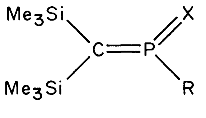
R = Bu, Ph; R′ = —$O_2SC_6H_4Me$-*p*, COOMe

(346)

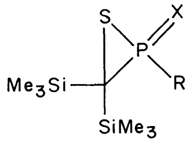
The methylene phosphine **348** (X = nil) is smoothly oxidized[375] by elemental sulphur to the three-membered ring sulphide **349** (X = S). The phosphine **348** (X = nil) is prepared[376] by dehydrohalogenation of **347** (R = mesityl) with 1,8-diazabicyclo[5.4.0]-undec-7-ene. Alcaraj and Mathey[377] prepared a bicyclic C–P heterocyclic phosphine sulphide (**351**) by the reaction of 2-phenyl-4,5-dimethylphosphorin (**350**) with S_8, followed by cycloaddition with 2,3-dimethylbutadiene.



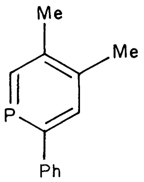
(347)



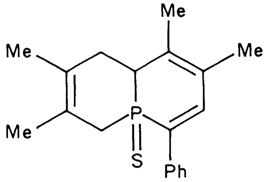
(348)



(349)

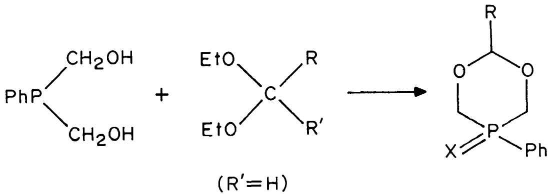


(350)



(351)

5-Phenyl-1,3-dioxaphosphorinane systems **352** (X = nil), on reaction with sulphur[378], gave the 5-thio derivatives **352** (X = S). The phosphines **352** (X = nil; R = furyl, Me, Ph) were prepared in 7.3–41% yield[379] according to equation 30. Alkyl bis(trifluoromethyl)-phosphine sulphides of the type **5** (R = CF_3; X = S), used as reference standards in gas chromatography, are prepared by sulphuration[380] of the corresponding phosphines (R = CF_3; R′ = C_{1-30}-alkyl; X = nil). These in turn may be prepared by the reaction of halobis(trifluoromethyl)phosphine with RMgBr.

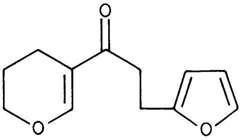


(352)

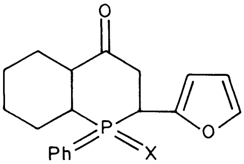
(30)

2-Thio-2-phosphabicyclo[4.4.0]decanone sulphide **354** (X = S) is formed[381] by reaction of the phosphine **354** (X = nil) with sulphur. The phosphine in turn is prepared by cycloaddition of phenylphosphine with furan derivative **353**. Progressive reaction of bis2,2-bis(diphenylphosphino)ethylphenylphosphine **356** (X = nil) with sulphur gives[382] the corresponding sulphide **356** (X = S). The phosphine, in turn, is prepared in 85% yield, through the potassium *tert*-butoxide-catalysed reaction of the phosphine **355** with phenylphosphine. 1,4-Dihydroazaphosphinine sulphides **358** (X = S) are formed on reaction of S_8 with the phosphinines **358** (X = nil). These in turn are synthesized[383] in

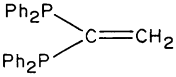
75–85% yield by the cyclocondensation of dichlorophenylphosphines with 2-aza-1,3-dienes **357** (R′ = Ph; R^2 = Me, Et, Pr) in hexane followed by hydrolysis. Thus, reaction of **357** (R′ = Ph; R = Me) with $PhPCl_2$ in the presence of Et_3N gave 1,4-dihydro-^{3}-azaphosphinines **358** (X = nil).



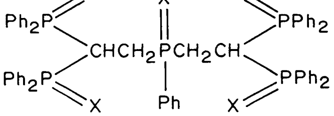
(353)



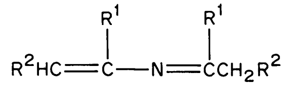
(354)



(355)

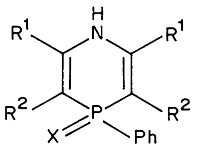


(356)



$$R^2HC{=}\overset{\displaystyle R^1}{\overset{|}{C}}{-}N{=}\overset{\displaystyle R^1}{\overset{|}{C}}CH_2R^2$$

(357)



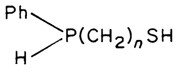
(358)

b. Through addition of sulphides/SO_2. Chan and Goldwhite[384] reported the formation of trimethyl sulphide from the corresponding phosphine by reaction with SO_2. However, some phosphine oxide is also produced in the reaction. Generally, fully oxidized acid is formed when the primary and secondary phosphines react with SO_2. Thus, phenyl- and diphenyl-phosphines give $PhP(O)(OH)_2$ and $Ph_2P(O)OH$, respectively.

$POCl_3$ adducts of R_3PO (R = alkyl, aryl), on reaction with Ag_2S at 120–150 °C, give the corresponding tertiary phosphine sulphides[385]. The adducts are formed by reaction of $POCl_3$ with R_3PO in the molar ratio 1:2–3.

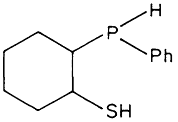
c. Through sulphur transfer agants. Trialkyl- and triaryl-phosphines **1** (R = Et, Ph; X = nil) and bisphosphines **75** (n = 0, 1,2; R′ = Ph; X = nil) are known to be converted[282] into the corresponding sulphides (X = S) in yields of 70–90%, through direct sulphur transfer by reaction with $PSCl_3$. The 1:1 adducts with thiourea diethylazodicarboxylate are also known[386] to convert Ph_3P to its sulphide (in the process being itself converted to carbodiimides).

ω-Mercaptoalkylphenylphosphines, e.g. **359** and **360**, on reaction with oxygen gave[387] alkylphenylphosphine sulphides **361**. Compounds **359** and **360** were prepared by the reaction of Ph(H)PNa with $Cl(CH_2)_nSH$ ($n = 2,3$) and cyclohexene sulphide. In the sulphides **359**, **360** and **361**, the hydrogen bound to sulphur is more acidic than that bound to phosphorus, as is evident by its preferential reaction with BuLi and Na and its reaction with ethylene and propylene oxide.

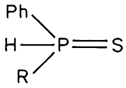


$n = 2, 3$

(359)

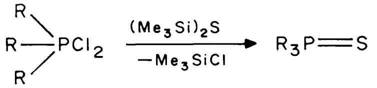


(360)

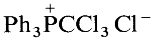


(361)

Phosphine sulphides are also obtained by reaction[388] of tertiary phosphine dihalides with $(Me_3Si)_2S$ (reaction 31). $Me_2P(S)Cl$ is also known to act as a sulphur transfer agent[389] in converting tributylphosphine to its sulphide. $(Bu_3Sn)_2S$ is known to be unreactive to Ph_3P in thf, MeCN or hydrocarbon solvents. However, it reacts at room temperature with CCl_4 to give the intermediate adduct **362**, which then reacts with $(Bu_3Sn)_2S$ to give Ph_3PS together with Bu_3SnCl and a phosphorus-containing resinous product derived from **363**. Sulphonium dicyanomethylides **364** (where R = R′ = benzyl or alkyl) react with Ph_3P to give the corresponding sulphides[389]. However, when R = R′ = aryl the transylidation reaction yields **365** according to equation 32.

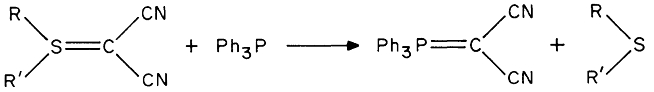


(31)



$Ph_3\overset{+}{P}CCl_3\,Cl^-$ $\qquad$ $Ph_3P{=}CCl_2$

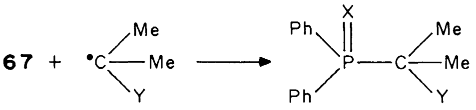
(362) **(363)**



(32)

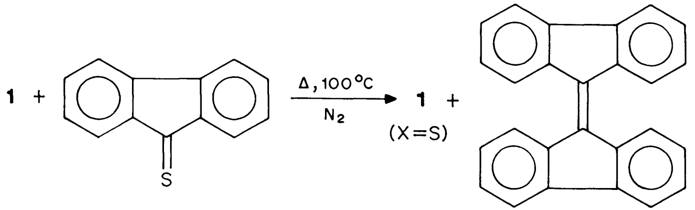
(364) **(365)**

Tetraphenyldiphosphine **67** (R = R′ = Ph; $X^1 = X^2$ = nil) is reported to react with carbon radicals to give **366** (X = nil; Y = CN, COOMe), which on sulphuration[390] yield the sulphides **366** (X = S). 9-Fluorenethione **367** is also known to act as a sulphur transfer agent, being itself converted into 9,9′-bifluorenyl in the process[391], e.g. on reaction with **1** (R = Bu; X = nil) (equation 33a). The thiadiazine **368** converts Ph_3P to Ph_3PS, being itself converted into pyrazole in the process[392], by ring contraction (equation 34).



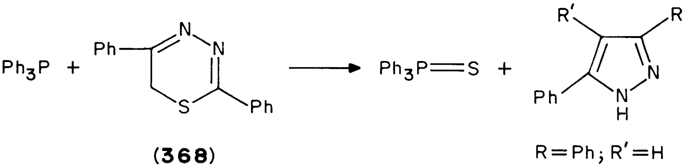
(33)

(366)



(33a)

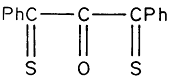
(367)



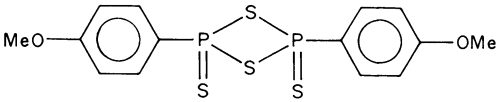
(368)

(34)

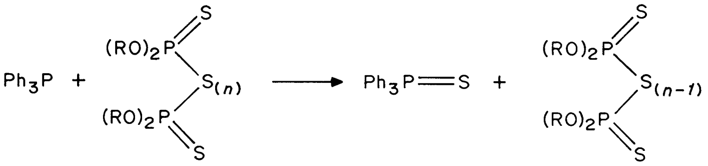
2-Oxo-1, 3-dithio-1,3-diphenylpropane (**369**) is also known to convert Ph_3P into Ph_3PS. However, some Ph_3PO is also formed in the reaction[393]. Diethyl dithiophosphorochloridite converts[394] Ph_3P into Ph_3PS in 61% yield. Lowesson's reagent (**370**) has also been used[395] for sulphurization of R_3P ($R = P$, Ph, Me_2OH), by refluxing them together in benzene. Phosphorus-containing polysulphides are also reported to convert[396] phosphines into phosphine sulphides as in equation 35.



(369)



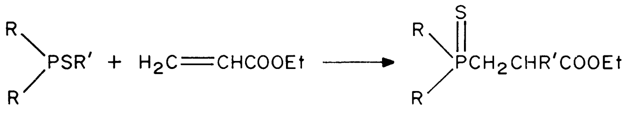
(370)



(35)

2. Through reactions of P^{III} compounds

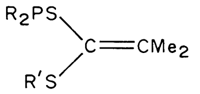
Phosphine sulphide **371** has been prepared by the reaction[397] of an alkylthiophosphonous acid with acrylic acid derivatives in the presence of sodium ethoxide in alcohol as a catalyst (equation 36). Dimethylphosphine halides, on reaction with methanethiols (and thier sodium salts), give Me_2PSMe. The latter, on reaction[177] with MeI, gives the phosphonium salt $Me_3P^+SMe\,I^-$, which on melting at 170 °C gives the sulphide **1** (R = Me; X = S).



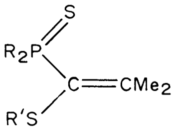
(36)

(371)

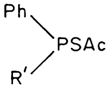
The Friedel–Craft's reaction of benzene, sulphur and PCl_3 is reported to give[398] Ph_3PS in good yields. The thiovinyl esters of P^{III} are known to give phosphine sulphides on rearrangement[399]. Thus, thermal rearrangement of **372** gives the phosphine sulphide **373** in 26–43% yields. Compounds **374** (R = Et; R′ = Me, Et) are prepared in 42–87% yields by the reaction of dialkyl chlorophosphines with $Me_2CHC(S)SR'$ in the presence of Et_3N in diethyl ether.



(372)

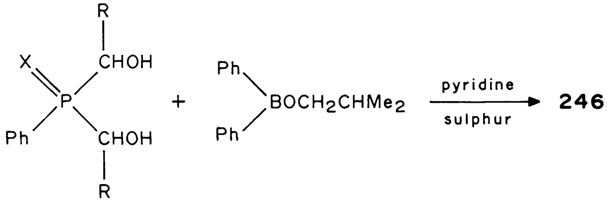


(373)



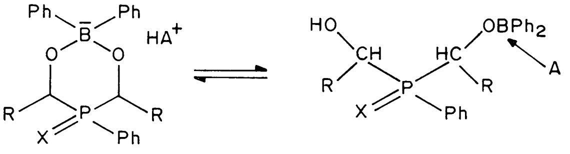
(374)

S-Acetyl thiophosphinites **374** are known[400] to rearrange to phosphine sulphides **12** (R′ = Et, Ph; R^2 = Ac; X = S). Compounds **374** were prepared by the reaction of phenylalkylchlorophosphines **312** (X = nil; R′ = Et, Ph) with AcSH in the presence of Et_3N. The reaction of bis(α-hydroxyalkyl)phenylphosphines **375** (X = nil) and isobutyldiphenyl borate **376** in the presence of a tertiary amine A, such as pyridine, and sulphur, is reported[401] to give dioxaboratophosphorinanes **246** (R = H, Me_2CH; X = S) in 25–45% yield. Thus, **246** exists in equilibrium with its open-chain form **377** (R = H, X = S; Y = NEt_3; R = Et, Me_2CH, X = S, Y = NEt_3) which is formed in 66% yield, by the treatment of phenylphosphine with CH_2O followed by reaction with **376** and pyridine, and then with sulphur (R = H, X = S, A = pyridine).



(37)

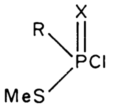
(375) **(376)**



(246) **(377)**

Sequential arylation of PCl_3 in the presence of $AlCl_3$ is also known[402]. Thus, PCl_3, $AlCl_3$ and benzene were heated at 80 °C for 6 h, followed by reaction with fluorobenzene and sulphur for 20 h to give **5** (R′ = Ph; R = *o*-, *m*-, *p*-FC_6H_4; X = S), *para* isomer 70%, *ortho* isomer 4.0% and also **5** (R = Ph, R′ = *p*-FC_6H_4) 2.2% together with **1** (R = *p*-FC_6H_4; X = S) in 5.4% yield. A similar reaction of $P(S)Cl_3$ with PhF and $AlCl_3$, followed by reaction with benzene, gave **5** (R′ = Ph; R = *p*-FC_6H_4; X = S) in 80% yield together with its *ortho*-isomer in 0.7% yield, and **1** (R = *p*-FC_6H_4; X = S) in 2.3% yield. $MeP(S)Cl_2$ likewise, when treated with $AlCl_3$ and PhF followed by treatment with benzene, gave sulphide **12** (R = Ph, R^1 = Me, R^2 = *o*-, *m*, *p*-C_6H_4), *para* isomer in 94.3% together with the *ortho* isomer in 3.8% yield.

1,4-Cycloaddition[403] of alkylthiophosphines **378** (R = Me, Ph; X = nil), by heating them with 1,3-dienes at 70–100 °C gave 3-phospholene sulphides **25** (R = Me, $R^1 = R^2$ = Me; R^1 = Me, R^2 = H; R = Ph, $R^1 = R^2$ = Me). The reaction proceeds via [1 + 4]cycloadducts, which in some cases were isolated. Compounds **378** (R = Me, Et, Ph) were prepared in 65–78% yield by methylthiolation of $RPCl_2$ with MeSH in the presence of trimethylamine.



(378)

B. Reactions Involving the Conversion of an Already Present P^V Nucleus

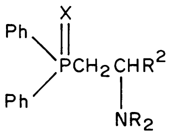
1. *Through reactions of phosphine sulphides*

Reduction of a variety of diaryl- and dialkyl-alk-1-ynylphosphine sulphides **5** (R = aryl, alkyl; R′ = alkynyl; X = S) by $LiAlH_4$ leads to the formation of *trans*-β-substituted vinyl sulphides[198] (see equation 15). The phosphol-3-enes **123** (R = Me; $R^1 = R^2$ = Ph; X = S) react[215] with R^3CN (R^3 = Ph, substituted Ph, 2-furyl,2-thienyl,4-pyridyl) to give 29–62% **170** (X = S), which on reaction with $HSiCl_3$ underwent ring contraction to **186** (X = S) (see also Section III.B.1). Diphenylphosphine sulphide on reaction[404] with BuLi gives the lithium derivative, which on reaction with MeI gives **5** (R′ = Me; X = S). Reaction of **19** (X = S; R = Ph) with magnesium yielded $Ph_2P(S)MgCl$, which on further reaction with **19** (R = Ph; X = S) yielded **67** (X = S) through the formation of a P–P bond.

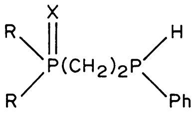
Reaction of $Ph_2P(S)M$ (M = Li, MgCl, Al) with *p*-benzoquinone[186] yielded **144** together with **145** (X = S). However, with M = FeCl in $Ph_2P(S)M$, the products were phosphinothioate **145** (X = S) (see also Section III.A.6). Quinolyl derivatives of phosphine sulphides **311** (X = S) can be prepared by a series of reactions[327], as detailed in Scheme 8, starting from dichlorophenylphosphine sulphide **310** (X = S) (see Section III.B.6).

The [3 + 2]cycloaddition of alkynyldiphenylphosphine sulphides with substituted diazoalkanes yield[237] thiophosphorylpyrazoles **219** (X = S) (see also Section II.B.1). Secondary phosphine sulphides **309** ($R' = R^2$; X = S) are known to react with triazolyl and imidazolyl ketones **238** to give thiophosphorylated alcohols **239** (X = S), having fungicidal activity[13] (see also Section III.B.1).

The addition of dialkylamines to vinylphosphine sulphides **5** (R = Ph; R′ = $CH{=}CHR^2$; X = S) leads[405] to the formation of **379** (R^2 = H, Me; NR_2 = Et_2N,1-pyrrolidinyl, piperidino; X = S). Compound **379** (X = S; R^2 = Me) was also prepared by reduction of the oxide **379** (X = O) with Cl_3SiH to phosphine **379** (X = nil), followed by its reaction with sulphur. Base-catalysed 1:1 addition of dimethylvinylphosphine sulphide **5** (R = Me) to phenylphosphine and to alkyl- and dialkyl-phosphines[406,407] gives crystalline sulphides **380** (X = S), which undergo desulphurization with $LiAlH_4$ in boiling dioxane to give the phosphines **380** (X = nil). Similar base-catalysed 1:1 addition of $PhPH_2$ to **5** (X = S; R = R′ = Ph) gives **380** (R = Ph). Sulphurization of phosphines has been used as a means of protecting the trivalent phosphorus in the synthesis of methylated poly(tertiary phosphines)[182.183,324]. 1-Phenyl-3,4-dimethylphosphole sulphide **25** (X = 5) reacted with *tert*-butyllithium at −170 °C under argon, to give an anion which reacted[408]

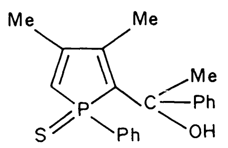


(379)

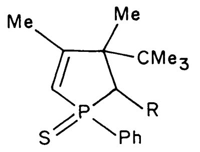


(380)

with aldehydes and ketones to give the corresponding derivatives, e.g. reaction with acetophenone gave **381** in 10% yield. Reaction of **25** (X = S) with excess of Me_3CLi gave a 3-*tert*-butylated derivative **382** [R = CMe(Ph)OH].

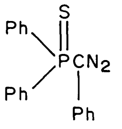


(381)

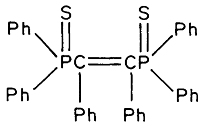


(382)

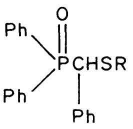
Tetraalkyldiphosphine disulphides **67** (R = R′ = Me, Et, Bu; X = S), on reaction with alkyl halides R^2Y give phosphine sulphides **5** (X = S; R = Me, Et, $PhCH_2$; Bu) in 73–90% yield, by cleavage[409] of the P—P bond. (Diphenylphosphinothioyl)phenyl diazomethane (**383**) on thermolysis in refluxing xylene gave the phosphine sulphide (carbene dimer) **384** in 88% yield[410], whereas refluxing in aqueous dioxane produced **384** together with **385** in 8% and 72% yield, respectively. Compound **384** was prepared in 37% yield by treating[411] benzyldiphenylphosphine sulphide **5** (R = Ph; R′ = CH_2Ph; X = S) with PhLi followed by its reaction with p-$MeC_6H_4SO_2N_3$.



(383)

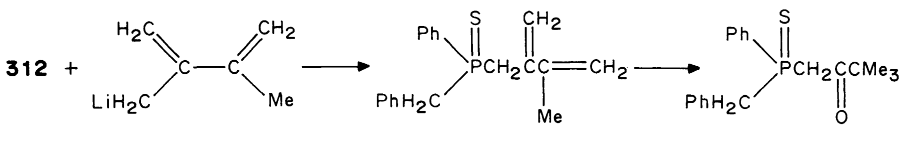


(384)

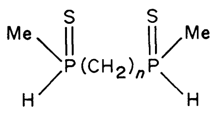


(385)

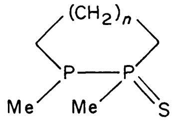
The facile transformation, via a pinacol rearrangement, of butadienylphosphine sulphide **387** into β-ketophosphine sulphide **388** (Scheme 9), has been reported[412]. Compound **387** is produced in 70% yield by the reaction of **312** (R = Ph, R′ = $PhCH_2$; X = S) with the lithium derivative **386**. Phosphine sulphides of the type **389** (n = 3,4), on reaction with Me_2NSiMe_3, are known to cyclize[413] to form the monosulphides **390** (n = 1,2) of 1,2-diphospholenes or 1,2-diphosphinanes. Akhmetova *et al.* reported[414] the synthesis of 7-(methoxycarbonyl)-3-phenyl-3-phosphabicyclo[3.3.1]nonan-9-one-3-



SCHEME 9. Conversion of butadienylphosphine sulphide.

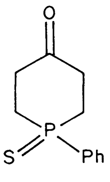


(389)

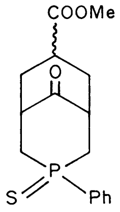


(390)

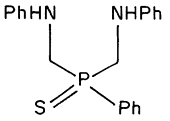
sulphide (**392**) in 30% yield by treating phosphorinane sulphide (**391**) with pyridine, followed by cyclization of the enamine with $(BrCH_2)_2CHCOOMe$. 1,3-Diborane-1,3,2,5-diazoboraphosphorinane sulphide (**394**) are prepared in 86% yield by cyclizing[415] **393** with B_2H_6.



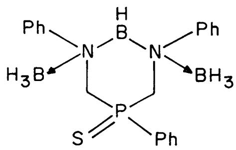
(**391**)



(**392**)

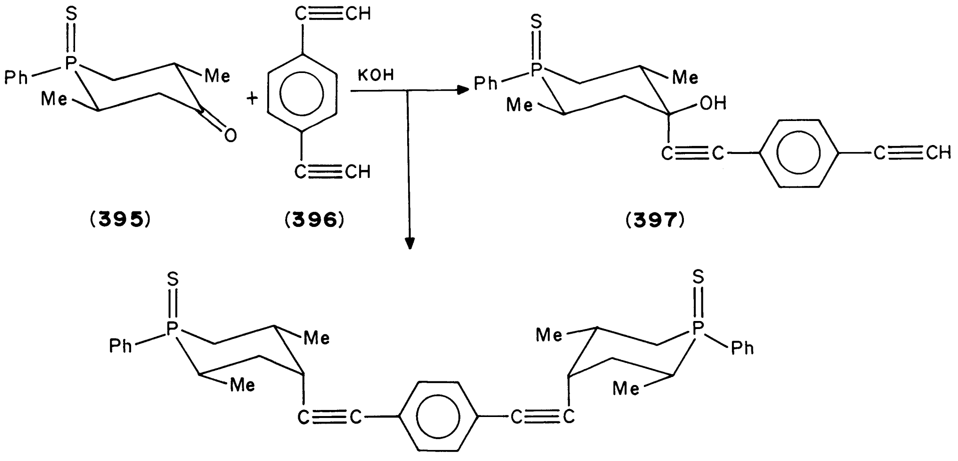


(**393**)



(**394**)

Stereoselective ethynylation of the *trans* isomer of phosphorinan-4-one (**395**) with **396** in the presence of KOH or $NaNH_2$ gave[416] the alcohol **397** and glycol **398** in the ratio 85:15 in liquid ammonia–$NaNH_2$ (Scheme 10).



(**395**) (**396**) (**397**)

(**398**)

SCHEME 10. Reaction of *trans*-thioxophosphorinan-4-one with *p*-diethynylbenzene.

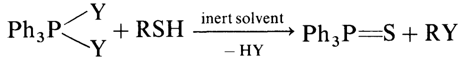
2. *Through reactions of* P^V *halides*

Reaction of dichlorophenylphosphine sulphide **310** (X = S) with 2 mol equiv. of vinylmagnesium bromide in thf at −70 °C gave divinylphenylphosphine sulphide **5**

($R = CH{=}CH_2$; $R' = Ph$; $X = S$), which on refluxing with a 20% excess of methylamine or aqueous alkylamine, afforded almost quantitative amounts of azaphosphorinane-4-sulphide **187** ($X = S$). Treatment of **187** ($X = O$; see Section III.B.1) with P_2S_5 in hot benzene also gave the sulphide **187**.

The reaction of 2-furyllithium **318** ($R' = Li$) with dialkyl chlorothiophosphates is reported[334] to give, through successive replacements of OR groups, the tris(2-furyl)sulphide **319** ($X = S$; see Section III.B.6). Phenylthiophosphoryl dichloride **310** ($X = S$), on Friedel–Craft's reaction with halobenzene, gives the sulphide **5** ($R' = Ph$), e.g. a mixture of the above chloride (2 mol), $AlCl_3$ (5 mol) and fluorobenzene (12 mol) was refluxed for 18 h under nitrogen to give the sulphide **5** ($R = p\text{-}FC_6H_4$, $R' = Ph$).

Tertiary phosphine sulphides and organic halides have been coproduced[417] by heating a thiol or dithiol, preferably in an inert solvent, with tertiary phosphine dihalide (reaction 38). Thus, Ph_3P (0.01 mol) in dry MeCN (60 ml) was stirred well at 0 °C whilst bromine (0.01 mol) was added over a period of 15–20 min. This was followed by the rapid addition of decane-1-thiol (0.01 mol) to the reaction mixture. The solvent was distilled off at 81 °C, accompanied by evolution of HBr. 1-Bromodecane was finally distilled at 138–139 °C/30 mmHg in 76% yield. The residue was then triturated with diethyl ether–pentane, followed by recrystallization from absolute alcohol to obtain Ph_3PS. Chlorophosphines **312** (X = nil) on reaction with the lithium derivative of methyldiphenylphosphine sulphide[418], prepared by reaction of Ph_3PS with methyllithium, gave phosphinomethylphosphine monosulphide **339** ($X^1 = S$; X^2 = nil; $R^1 = Me_2CH$, Ph; Ph, Me; Ph, Et; Me_2CH, $CHMe_2$).

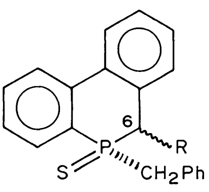


$$Ph_3P\begin{matrix}Y\\Y\end{matrix} + RSH \xrightarrow[-HY]{\text{inert solvent}} Ph_3P{=}S + RY \qquad (38)$$

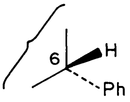
$Y = Cl, Br$ $\qquad$ R = decyl, hexyl, cyclohexyl

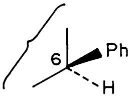
3. Through sulphurization of phosphine oxides

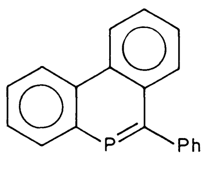
The *trans* isomers of tetraaryl- and -alkyl-vinylidenediphosphine dioxides **18** ($X = O$), on heating[54] for 2 h at 120 °C with sulphur, give the disulphide **18** ($X = S$) in 86% yield (see also Section III.A.1.b). The phosphaphenanthranone **110** is reported[164] to react with P_4S_{10} to give the isomeric phenanthrene thione **399** (R = α- or β-Ph; see Section III.A.4). Nickel-catalysed thermolysis of **399** at 275 °C gave 6-phenyl-5-phosphaphenanthrene **400**. Dialkylphosphine oxides $R_2P(O)H$ on reaction with P_4S_{10} at -30 to 20 °C in CH_2Cl_2 under nitrogen yielded[419] the corresponding sulphides **309** ($X = S$) in 55.5–62% yield. Phosphabicyclooctadiene oxide **402** ($X = O$) on sulphurization with P_4S_{10} yielded[420] the corresponding sulphide **402** ($X = S$). The oxide **402** was prepared, in turn, by Diels–Alder reaction of the phosphorin-1-oxide **401** with dimethylacetylene dicarboxylate.



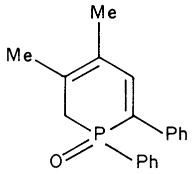
(399)

(399a)


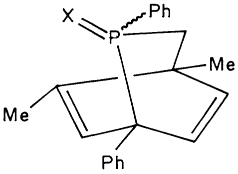
(399b)




(400)

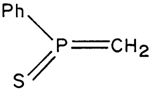


(401)

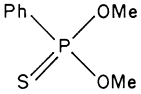


(402)

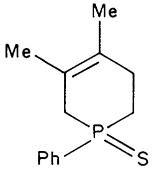
The sulphide **402** (X = S) on refluxing with toluene generated the *C*-unsubstituted methylenephosphine sulphide **403**, which was trapped by methanol or 2,3-dimethylbutadiene to give **404** or **405**.



(403)



(404)



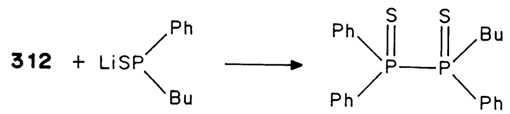
(405)

Reaction of sulphur with phospholes **25** (R = R′ = Me; X = O) led to the formation[421] of the sulphides **25** (X = S). Phospholes **25** (X = nil) were prepared by the cyclization of alkyl- or aryl-halophosphines in the presence of a tertiary amine with pK_a 5–11, e.g. treatment of a mixture of $PhPBr_2$ and $PhPCl_2$ with $H_2C{=}C(Me){=}CH_2$ in CH_2Cl_2 in the presence of α-picoline gave **25** (R = R′ = Me; X = nil) in 83.5% yield.

Optically active phosphine oxides of the type **12**, on reaction with boron trisulphide, give the corresponding sulphides[422] with high stereospecificity and net retention of configuration at phosphorus, e.g. (+)-(R)-cyclohexylmethylphenylphosphine oxide gave 76% of the corresponding sulphide with 95% optical purity.

4. *Through reaction of P_2S_5/P^V sulphur halides with organometallics or alkyl halides*

Grignard reaction of $PSCl_3$ with alkyl halides yielded[19a] phosphine sulphide **1** (see also Section III.A.2.b). Phosphine sulphides of the type **5** (X = S) are prepared by the reaction[85] of **12** ($R^1 = R^2$; X = S) with alkyl halides in the presence of magnesium (see Section III.B.6). Phosphorus thioxychloride reacts[423] with cyclohexylmagnesium chloride to give **309** (X = S), **67** (R = R′; X = S) and **1** (X = S; R = cyclohexyl). 1-Butyl-1,2,2-triphenyldiphosphine disulphide was prepared[424] by heating **312** ($R^1 = R^2$ = Ph; X = S) with **406** (reaction 39).



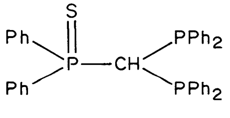
(406)

(39)

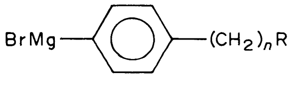
Dialkyl- and diaryl-phosphonothioic halides of the type **312** (X = S) and alkyl- and aryl-phosphinothioic dihalides **310** (X = S) are prepared by reaction[425] of alkyl halides with P_4S_3 at 250–339 °C. Thus, P_4S_3 (0.02 mol) and methyl chloride (0.118 mol) on heating at 235–240 °C for 12 h gave **312** ($R^1 = R^2 = R; X = S$) and **310** (R = Me, Bu, Ph, C_{1-20}-alkyl, C_{5-6}-cycloalkyl; halide = Cl, Br). Compounds **312** (X = S) are used for increasing the effectiveness of flotation of copper ores.

The reaction of thiophosphoryl chloride with PhLi gives the corresponding phosphine sulphides[426] of the type **1**. Thus, $P(S)Cl_3$ on reaction with PhLi gives Ph_3PS in 80% yield. The reaction proceeds via a metal–halogen exchange reaction, e.g. the reaction of $PSCl_3$ and BuLi gives, after hydrolysis, several products such as $Bu_2P(S)H$, Bu_3PS and $Bu_4P_2S_2$.

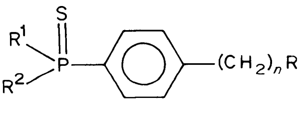
The (dialkylphosphino)diphenylphosphinomethane monosulphides **67** ($X^1 = S$, X^2 = nil; R = *tert*-butyl) were prepared[427] in 43% yield by treating $Ph_2P(S)CH_2Li$ with **312** ($R^1 = R^2$ = *tert*-butyl; X = nil). A similar reaction[428] of the lithium derivative of methyldiphenylphosphine sulphide with **312** ($R^1 = R^2$ = Ph; X = nil) gave **407** in 66% yield. Grignard reaction of **312** ($R^1 = R^2$ = Me, Et; X = S) with **408** (R = OMe, $OSiMe_3$) gave[429] the phosphine sulphide **409**. Fiaud[430] reported a stereoselective synthesis of allylicdiphenylphosphine sulphide (**410**) in high yields by the palladuim-catalysed substitution of allylic carboxylates with lithium diphenyl thiophosphides in thf containing $[Pd(PH_3)_4]$ at room temperature, with an overall retention of configuration (equation 40). Kyba and Liu[431] prepared the P_3 macrocylic phosphine-6-sulphide **415** by the reaction of bis(3-chloropropyl)-1-naphthylmethylphosphine sulphide (**412**) with bis(lithiophenylphosphino)benzene (**413**) to give **414**, followed by quantitative removal of 1-naphthylmethyl moiety with potassium naphthalenide (Scheme 11). 1-Naphthylmethylphosphine sulphide has been used as a protecting group for a P—H bond in a secondary phosphine and to convert 1-naphthylmethylphosphine (**411**) into **412**.



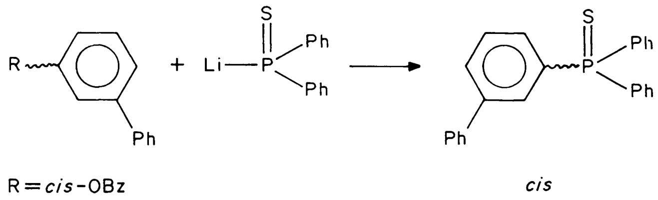
(407)



(408)

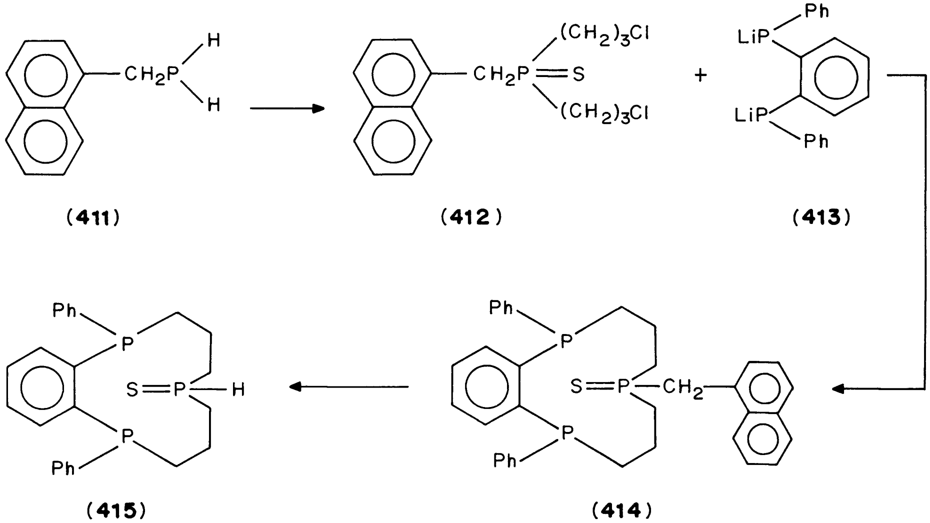


(409)



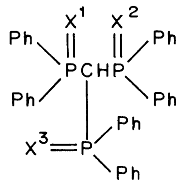
(410) (40)

Polydentate phosphorus-containing ligands of the type **34** and **416** can be prepared from their neutral precursors[432] by proton abstraction with LiOMe. Phosphine sulphides of the type **5** (R = halogen, Me, $MeOC_6H_4$; R′ = lower alkyl, aryl, X = S), useful in the preparation of fire-resistant polyoxyphenylenes, are prepared[433] from aryl- and alkyl-thiophosphoryl dihalides (**310**) and halobenzenes in the presence of Friedel–Craft's catalysts. Thus, refluxing $PhP(S)Cl_2$ (0.3 mol) with chlorobenzene (2 mol) and anhydrous $AlCl_3$ (1.6 mol) for 8 h gave bis(p-ClC_6H_4)phenylphosphine sulphide in about 80% yield. Similarly, stirring P(S) Cl_3 (0.1 mol) and $AlCl_3$ (0.5 mol) with **417** (0.7 mol) at 150 °C for 6 h gave a polymer in 36% yield. Compound **5** (R = p-ClC_6H_4; R′ = Ph; X = S) is also prepared by two variations[434] of a Friedel–Craft's reaction involving either treating



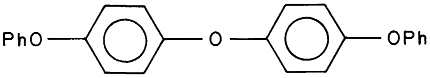
SCHEME 11. Synthesis of 11-P_3 macrocyclic phosphine sulphide.

benzene with PCl_3 and then the resulting unisolated intermediate with sulphur and halobenzene (halo = F, Cl, Br) (> 2 mol), or heating halobenzene with $P(S)Cl_3$ and then the unisolated intermediate with benzene. In both cases the reaction mixture is heated between 70 and 150 °C in the presence of an $Al(hal)_3$ catalyst. Thus, benzene (0.1 mol) and PCl_3(0.1 mol) were heated for 6 h at 80 °C under nitrogen in the presence of $AlCl_3$ (0.22 mol) and the resultant mixture was treated with sulphur (0.1 mol) and chlorobenzene (0.6 mol) and a refluxed for a further 6 h to give bis(*p*-chlorophenyl)phenylphosphine sulphide in 65% yield.



X^1, X^2, X^3 = O, S, Se

(416)



(417)

An efficient Friedel–Craft's-type preparation of Ph_3PS and its derivatives was reported by Olah *et al.*[435], involving $AlCl_3$-catalysed reactions of benzenes (or substituted benzenes) with P_4S_{10}. Tertiary halogen (X = F, Cl, Br)-substituted phenylphosphine-sulphides **5** are prepared by heating[436] a mixture of $PSCl_3$ with halobenzene, followed by addition of substituted benzene and continued heating. Thus, a mixture of $PSCl_3$(0.75 mol) and $AlCl_3$ (1.34 mol) in cyclohexane was refluxed for 8 h, followed by addition of toluene (3 mol) and refluxing for a further 5 h, when **5** (R = *p*-F-C_6H_4; R′ = *p*-MeC_6H_4; X = S) was produced in 85% yield. Tertiary phosphine sulphides of the type **1** (R = Me, Et, Bu, Ph; X = S) are also prepared[437] by the reaction of phosphorus with alkyl sulphides R_2S at 200–400 °C.

V. METHODS OF PREPARATION OF PHOSPHINE SELENIDES AND TELLURIDES

Selenophosphines and related compounds have been reviewed[22,23,438]. Some phosphine selenides have novel inclusion properties and act as highly selective hosts, e.g. 1,2-bis(diphenylphosphinoselenoyl)ethane **90** (R = Ph; X = Se) acts very selectively for *p*-xylene[439]. Thus, **90** (R = Ph; X = Se) formed stable inclusion compounds when crystallized from various pure solvents. However, when **90** (X = Se) was crystallized from certain solvent mixtures, there was remarkable guest selectivity. The preference shown for **90** (X = Se) is general for *para*-disubstituted mononuclear aromatics of similar size. The sulphide analogue of **90** also exhibited significant inclusion properties. Compound **90** (R = Ph; X = Se) (3 g) was dissolved in a mixture (25 ml) of equal volumes of *o*-, *m*-, *p*-xylene and ethylbenzene at 100 °C and the solution was cooled at 0.5–1 °C $\min^{-1}$ and inoculated with *p*-xylene crystals at 360 K to give the *p*-xylene adduct (2.9 g), which was thermally decomposed to give a product containing 95.5% *p*-xylene, 2.5% ethylbenzene, 1.2% *m*-xylene and 0.8% *o*-xylene. The crystal structure of the inclusion compound contains three host and one guest molecule in a unit cell. The adduct is of true clathrate type, with the highly ordered *p*-xylene guest being accommodated in an effectively closed case.

Brown *et al.*[440] measured the exchange of selenium between tertiary phosphine selenides and analogous tertiary phosphines and found it to be fairly fast on the NMR time scale at elevated temperature. In this it resembles the phosphine tellurides, where rapid tellurium transfer[441] has been observed in R_3PTe-R_3P. The corresponding sulphide derivatives redistribute themselves in analogous systems much more slowly.

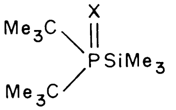
Phosphine tellurides have been used recently for the chemical transport[442] of tellurium under very mild conditions, i.e. they find application in the preparation of semiconductor materials.

A. Reactions Involving Conversion of P^{III} to P^{V}

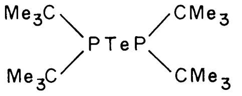
Diphenylphosphine selenide was prepared[443] by heating red selenium suspended in benzene with diphenylphosphine for 10 min at 70 °C. Dibutylphosphine selenide was obtained by passing H_2Se into a benzene solution of dibutyl(diethylamino)phosphine.

$Ph_4As^+Te^-CN$, on treatment with excess of Ph_3P in MeCN containing $LiClO_4$, is known to give $Ph_3PTe.PPh_3$ in which the P—Te—P configuration could be regarded[444] as one in which there is normal bond between tellurium and one of the phosphorus atoms, whereas the interaction between tellurium and the other phosphorus atom is weak. Tertiary phosphine selenides are also formed through selenium abstraction[445] in the reaction of diethyl diselenide with tertiary phosphines. Thus, photochemical deselenation of Et_2Se_2 by diphenylmethylphosphine gave **5** (R = Ph, R′ = Me; X = Se) in high yield together with Et_2Se.

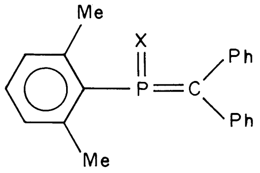
CSe_2 also is known[446] to react with Ph_3P in the presence of metal carbonyls to give Ph_3PSe. Aryl phosphines of the type **1** (R = Ph, *p*-ClC_6H_4 or *o*-, *m*-, *p*-MeC_6H_4) react with SeO_2 suspended in benzene–ethanol solution to give R_3PSe together with R_3PO in different proportions depending on the phosphine, the relative proportions of the reagents and the solvent[447]. Similar reaction of SeS_2 with Ph_3P gave a solid solution of Ph_3PS and Ph_3PSe on refluxing[448] for 2 h in excess of benzene. Insertion of tellurium[449] into **418** (X = nil) gave **418** (X = Te), which, however, disproportionated to give **419** and $(Me_3Si)_2Te$. Alkenebis(monophenylphosphine chalcogenides) **75** (R = Ph; R′ = H; X = Se; *n* = 2) were prepared by treating the corresponding phosphine **75** (X = nil) with selenium[368]. Reaction of **420** (X = nil) with selenium in benzene leads to the formation of stable *p*-2,6-dimethylphenyl-*C*-*C*-diphenylselenophosphine[450] **420** (X = Se), which is stable at room temperature but decomposes on heating with partial regeneration of the starting materials. No reaction, however, was observed between **420** (X = nil) and tellurium. The reactions of tri-*tert*-butyl phosphine with selenium and tellurium proceed quantitatively with formation[451] of the corresponding selenide and tellurides. The lithium derivatives of **7** ($R = R' = Ph$; $X^1 = X^2 = nil$) on treatment[452] with elemental selenium or tellurium give the mono-selenium or tellurium derivatives **421**. Reaction of acetylenic phosphines **336** (X = nil) with selenium leads to the formation[366] of the selenide **336** (X = Se, see also Section IV.A.1.a). Tetrakis(diphenylphosphino) allene **49** (X = nil), 2-phosphabicyclononanone **11** (X = nil), phosphastannianes **161** (X = nil), 3,4-dialkylphosphole **116** (X = nil), and pentaethylcyclopentaphosphine **8** (X = nil) (see Table 2 for further details) are all converted into their selenides (X = Se) by reaction with selenium. Likewise, dioxaphosphorinanes **352** (X = nil) also gave the selenide[378] (X = Se), as did 2-phosphabicyclodecanone **354** (see section IV.A.1.a), phosphabicyclodecanone[81] **43** (see Section II.A.1.e) and oxaborataphosphorinanes **246** (X = nil) (see Section IV.A.2), on reaction with selenium.



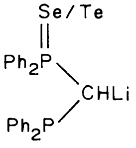
(**418**)



(**419**)

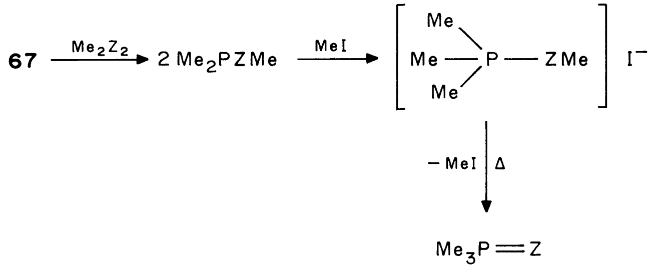


(**420**)



(**421**)

The exchange reaction of tetramethyl bisphosphines **67** ($R = R' = Me$; X = nil) with dimethyl dichalcogenides Me_2Z_2 (Z = S, Se, Te) leads to the formation[453] of the corresponding methyl chalcogenides Me_2PZMe. These on reaction with MeI give the phosphonium salt (see also ref. 177), which is converted to the corresponding chalcogenide on heating (reaction 41).



(41)

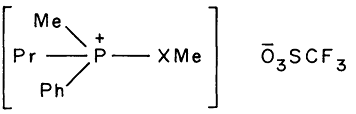
A simple and efficient method of preparing aromatic tertiary phosphine selenides is through the reaction of phosphines with potassium selenocyanate in acetonitrile (reaction 42)[454]. The reaction is specific for selenium and does not occur with the oxygen or sulphur analogues.

$$Ph_3P + KSeCN \longrightarrow Ph_3PSe + KCN \qquad (42)$$

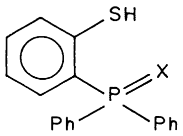
B. Reactions Involving Conversion of an Already Present P^V Nucleus

Phenylselenophosphoryl acid chloride **310** (R′ = Ph; X = Se) on Friedel–Craft's reaction with halobenzenes[312] gives the selenide **5** (X = Se; R′ = Ph) (see Section IV.B.2 for details). Phosphine selenides of the type 1 and **5** (X = Se) were prepared by the reaction[455] of organomagnesium compounds with selenophosphorus acid chlorides. Thus, the reaction of diethylselenophosphoryl chloride with R′MgBr gave 61.8–72.9% of **5** (R = Et, R′ = Et, Ph; X = Se) and the reaction of PhMgBr with $PhP(Se)Cl_2$ gave Ph_3PSe in 35.4% yield. Grim and Walton prepared[456] variously substituted **416** (X^1,X^2 = Se, S or O and X^3 = nil; X^1 = Se, S and X^2, X^3 = nil; X^1 = Se, X^2 = S and X^3 = nil) by reaction of $Ph_2P(Z)CH_2Li$ with $Ph_2P(X)Cl$(Z = Se, S, O or nil).

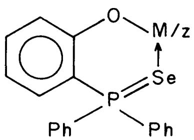
Stereospecific interconversion of chiral thiophosphines into selenophosphines has also been reported[457]. Thus, the conversion of chiral methylpropylphenylphosphine sulphide into the selenide and *vice versa* were accomplished by treatment of **422** (X = Se, S) with NaSeH or NaSH, respectively. Both reactions occur with retention of configuration at phosphorus and high stereospecificity. (2-Hydroxyphenyl)diphenylphosphine selenide **423** (X = Se) has been prepared[458] in 77% yield by heating the corresponding oxide **423** (X = O) with selenium. The selenide **423** (X = Se) forms complexes **424** with metals M (M = Ou, Ni, Co, Zn) in 72–85% yields.



(422)



(423)



(424)

VI. REFERENCES

1. (a) H. Sakai, *Kagaku Kogyo*, **27**, 984 (1976); *Chem. Abstr.*, **85**, 193374m (1976); (b) S. Verbanov and G. Borisov, *Acta Polym.*, **39**, 507 (1988).
2. (a) J. M. Biehler, P. LeRoy and S. Lecolier, *Fr. Pat.*, 2 238 709 (1975); *Chem. Abstr.*, **83**, 148432b (1975); (b) T. Matsumoto, A. Veda, T. Imamura and K. Tsujimoto, *Jpn. Pat.*, JP 63 313 795 (1988); *Chem. Abstr.*, **111**, 79200g (1989).
3. T. Saito, *Kagaku Kogyo*, **26**, 160 (1975); *Chem. Abstr.*, **83**, 52452g (1975).
4. Z. A. Sheka and E. I. Sinyavskaya, *Usp. Khim. Koord. Soedin.*, 113 (1975); *Chem. Abstr.*, **85**, 115909a (1976).
5. (a) *Jpn. Pat.*, 80 89 239 (1980); *Chem. Abstr.*, **94**, 30383k (1981); (b) *Jpn. Pat.*, 80 89 240 (1980); *Chem. Abstr.*, **94**, 30384m (1981).
6. W. Krause, J. Grosse and W. Flose, *Ger. Pat.*, 3 011 085 (1981); *Chem. Abstr.*, **95**, 203304m (1981).
7. E. A. O'Brien, T. O'Conner, M. R. J. Tuite and L. High, *Br., Pat.*, 2 182 039 (1987); *Chem. Abstr.*, **108**, 187199k (1988).
8. E. B. Rathbone, K. S. Mufti, R. A. Khan, P. S. J. Cheethan, A. J. Hacking and J. S. Dordick, *Br. Pat.*, 2 181 734 (1987); *Chem. Abstr.*, **109**, 108922k (1988).
9. L. Parts, M. L. Nelson and R. Z. Greenley, *US Pat.*, 3 294 708 (1966); *Chem. Abstr.*, **66**, 56001f (1967).
10. F. J. Welch, *US Pat.*, 3 519 607 (1970); *Chem. Abstr.*, **73**, 56775f (1970).
11. (a) R. Rabinowitz, *Ger. Pat.*, 1 241 995 (1967); *Chem. Abstr.*, **67**, 44417d (1967); (b) W. Ude, J. Knebel and G. Schroeder, *Ger. Pat.*, DE 3 521 124 (1986); *Chem. Abstr.*, **107**, 23912r (1987).
12. A. F. Pavlenko, Yu. V. Karabanov, V. P. Akkerman, U. P. Forsyuk, A. K. Reshetar and Ya. N. Ivashechenko, *Fiziol. Akt. B*, *Veshchestva*, **3**, 40 (1971); *Chem. Abstr.*, **76**, 42649t (1972).
13. (a) E. Lindner, K. A. Varughese, D, Huebner, O. Eberle and B. Schilling, *Z. Naturforsch., Teil B*, **41**, 708 (1986); (b) E. Lindner, B. Schilling and K. A. Varughese, *Ger. Pat.*, DE 3 344 663 (1985);

Chem. Abstr., **103**, 215547q (1985); (c) A. Weight, D. R. Callejas and H. Seeboth, *East Ger. Pat.*, 256 864 (1988); *Chem. Abstr.*, **110**, 57855b (1989).
14. L. Maier, *US Pat.*, 3 617 574 (1971); *Chem. Abstr.*, **76**, 49804y (1972).
15. Al. F. Kerst, *US Pat.*, 3 658 890 (1972); *Chem. Abstr.*, **77**, 48625z (1972).
16. (a) A. W. Frank, *US Patent*, 3 681 448 (1972); *Chem. Abstr.*, **77**, 140284k (1972); (b) T. K. Weiviorowski and D. J. Miller, *US Pat.*, 3 737 513 (1973); *Chem. Abstr.*, **79**, 56374y (1973).
17. A. P. Khardin, R. P. Bulankin and O. I. Tuzhikov, *USSR Pat.*, 423 815 (1974); *Chem. Abstr.*, **81**, 136747d (1974).
18. A. J. Robertson and J. B. Gallivan, *US Pat.*, 4 855 507 (1989); *Chem. Abstr.*, **112**, 77541r (1990).
19. (a) G. de Roughet and F. M. P. Etienne, *Ger. Pat.*, 2 254 479 (1973); *Chem. Abstr.*, **79**, 53551t (1973); (b) G. P. Schiemenz and H. Kaack, *Justus Liebigs Ann. Chem.*, **9**, 1494 (1973).
20. B. Lythgoe, T. A. Moran, M. E. A. Nambudiry, S. Ruston, J. Tideswel and P. W. Wright, *Tetrahedron Lett.*, **44**, 3863 (1975).
21. H. R. Hays and D. J. Peterson, in *Organic Phosphorus Compounds* (Eds G. M. Kosolapoff and L. Maier), Vol. 3, Wiley–Interscience, New York, 1972, pp. 341–500.
22. L. Maier, in *Organophosphorus Compounds* (Eds G. M. Kosolapoff and L. Maier), Vol. 4, Wiley–Interscience, New York, 1972, pp. 1–71.
23. J. A. Miller, in *Organophosphorus Chemistry*, Chemical Society, London: (a) Vol. 4, 1973, pp. 73–86; (b) Vol. 5, 1973, pp. 70–82; (c) Vol. 6, 1974, pp. 62–73; (d) Vol. 7, 1976, p. 66; (e) Vol. 8, 1977, pp. 71–83; (f) Vol. 9, 1976–77, pp. 80–100; (g) Vol. 10, 1979, p. 75; (h) Vol. 11, 1980, pp. 69–81; (i) Vol. 12, 1981, pp. 63–75; (j) Vol. 13, 1982, pp.62–76; (k) Vol. 14, 1983 pp. 77–94.
24. B. J. Walker, in *Organophosphorus Chemistry*, Chemical Society, London: (a) Vol. 16, 1986, pp. 79–99; (b) Vol. 17, 1986, pp. 81–102; (c) Vol. 18, 1987, pp. 83–103; (d) Vol. 19, 1988, pp. 70–86; (e) Vol. 20, 1989, pp. 72–86.
25. A. C. Massabni, *Ecletica Quim.*, **1**, 81 (1976).
26. L. Maier, in *Topics in Phosphorus Chemistry*, (Eds M. Grayson and E. J. Griffith), Vol. 2, Wiley–Interscience, New York, 1965, pp. 43–131.
27. K. D. Berlin and G. B. Butler, *Chem. Rev.*, **60**, 243 (1960).
28. K. Sasse, *Methoden der Organischem Chemie, Organische Phosphorverbindungen*, Vol. XII, Georg Thieme, Stuttgart, 1963, Part I, p. 127.
29. K. Weinberg, *US Pat.*, 3 751 482 (1973); *Chem. Abstr.*, **79**, 9237n (1973).
30. C. Ercolani, J. V. Quagliano and L. M. Vallarino, *Inorg. Chim. Acta*, **7**, 413 (1973).
31. N. Hagiwara, N. Takahashi and H. Kojima, *Jpn. Pat.*, 74 24 900 (1974); *Chem. Abstr.*, **82**, 86404n (1975).
32. R. Barral. C. Bocard and I. Seree de Roch, *Fr. Pat.*, 2 115 598 (1972); *Chem. Abstr.*, **78**, 58619k (1973).
33. R. K. Poddar and U. Agarwala, *Inorg. Nucl. Chem. Lett.*, **9**, 785 (1973).
34. M. Baudler, P. Koch, J. Hasenbach and J. Hahn, *Z. Anorg. Allg. Chem.*, **576**, 17 (1989).
35. S. M. Nelson, M. Perks and B. J. Walker, *J. Chem. Soc., Perkin Trans. 1*, 1205 (1976).
36. J. D., Curry, *US Pat.*, 3 760 000 (1973); *Chem. Abstr.*, **79**, 126609e (1973).
37. R. N. Il'yasov, G. M. Akhmetova, B. M. Butin and K. B. Erzanov, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, **2**, 57 (1986).
38. H. H. Karsch, *Chem. Ber.*, **115**, 823 (1982).
39. G. Frey, H. Lesiecki, E. Lindner and G. Vordermaier, *Chem. Ber.*, **112**, 763 (1979).
40. E. Lindner and H. Lesiecki, *Z. Naturforsch., Teil B*, **33**, 849 (1978).
41. E. Lindner and G. Frey, *Chem. Ber.*, **113**, 2769 (1980).
42. G. Vordermaier and E. Lindner, *Chem. Ber.*, **112**, 1456 (1979).
43. H. Lesiecki, E. Lindner and G. Vordermaier, *Chem. Ber.*, **112**, 793 (1979).
44. A. Skowronska, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **21**, 459 (1973).
45. L. D. Quin, E. D. Middlemas, N. S. Rao, R. W. Miller and A. T. Mcphail, *J. Am. Chem. Soc.*, **104**, 1893 (1982).
46. H. Staendeke and W. Klose, *Ger. Pat.*, 2 156 203 (1973); *Chem. Abstr.*, **79**, 53553v (1973).
47. W. Hewertson, *Ger. Pat.*, 1 960 731 (1970); *Chem. Abstr.*, **73**, 56570k (1970).
48. N. Weferling, *Ger. Pat.*, DE 3 626 969 (1988); *Chem. Abstr.*, **109**, 6738n, (1988).
49. B. I. Stepanov, L. I. Chekunine and A. I. Bokanov, *Zh. Obshch. Khim.*, **43**, 2648 (1973).
50. W. J. Vullo, *US Pat.*, 3 495 257 (1970); *Chem. Abstr.*, **72**, 90623u (1970).
51. R. B. King and P. R. Heckley, *Phosphorus*, **3**, 209 (1974).

52. Z. N. Mironova, E. N. Tzvetkov, A. V. Nikolaev, M. I. Kabachnik and Yu. A. Dyadin, *Zh. Obshch. Khim.*, **33**, 1217 (1974).
53. R. K. Valetdinov and Sh. I. Zaripov, *Zh. Obshch. Khim.*, **45**, 1943 (1975).
54. N. P. Nesterova, T. Ya. Medved, Yu. M. Policarpov and M. I. Kabachnik, *Izv. Akad. Nauk SSSR., Ser. Khim.*, 2295 (1974).
55. I. G. Malakhova, E. N. Tsvetkov and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 174 (1975).
56. V. V. Karmachev, T. V. Vasil'eva, B. I. Bryantsov and V. A. Kukhtin, *Zh. Obshch. Khim.*, **46**, 1264 (1976).
57. R. Leuchenbach, *Tetrahedron Lett.*, **24**, 2017 (1976).
58. B. A. Arbuzov, O. E. Erastov, G. N. Nikonov, R. P. Arshinova and R. A. Kadyrov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **3**, 721 (1980).
59. H. Schmidbauer and T. Pollok, *Helv. Chim. Acta*, **67**, 2175 (1984).
60. C. C. Santini and F. Mathey, *J. Organomet. Chem.*, **266**, 285 (1984).
61. T. Kaufmann, E. Antfang and J. Olbrich, *Tetrahedron Lett.*, **25**, 1963 (1984).
62. S. Franks, F. R. Hartley and D. J. A. Macaffrey, *J. Chem. Soc., Perkin Trans. 1*, 3029 (1979).
63. B. Lythgoe, T. A. Moran, M. E. N. Nambudiry and S. Ruston, *J. Chem. Soc., Perkin Trans. 1*, 2386 (1976).
64. N. N. Bychkov, A. J. Bokanov and B. I. Stepanov, *Zh. Obschch. Khim*, **49**, 1460 (1979).
65. S. O. Grim, S. A. Sangokoya, I. J. Colquhoun, W. McFarlane and R. K. Khanna, *Inorg. Chem.*, **25**, 2699 (1986).
66. R. Neidlein, W. G. Dauben, A. S. Funhoff and R. R. Ollman, Jr, *Chem. Ber.*, **121**, 2121 (1988).
67. *Neth. Pat.*, 79 03 216 (1980); *Chem. Abstr.*, **95**, 43654v (1981).
68. D. G. Gillespie, B. J. Walker, D. Stevens and C. A. McAuliffe, *J. Chem. Soc., Perkin Trans. 1*, 1697 (1983).
69. K. Ellrich and C. Herzig, *Ger. Pat.*, 34 43 221 (1986); *Chem. Abstr.*, **105**, 191396c (1986).
70. (a) V. V. Malovik, I. K. Mazepa, M. D. Pipovarov, V. Ya. Semenii, N. G. Feshchenko and A. V. Kirsanov, *Khim. Tekhnol. (Kiev)*, **2**, 13 (1974); *Chem. Abstr.*, **81**, 105643n (1974); (b) V. V. Malovik, M. D. Pipovarov and V. Ya. Smenii, *Khim. Tekhnol. (Kiev)*, **4**, 16 (1975); *Chem. Abstr.*, **84**, 59655e (1976).
71. G. V. Roeschenthaler, *Z. Anorg. Allg. Chem.*, **479**, 159 (1981).
72. K. Dziwok, J. Lachmann, G. Mueller, H. Schmidbaur and D. L. Wilkinson, *Chem. Ber.*, **123**, 423 (1990).
73. S. Chan and H. Goldwhite, *Phosphorus Sulfur*, **4**, 33 (1978).
74. A. N. Pudovik, G. V. Romanov and T. Ya. Stepanova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1**, 2649 (1979); *Chem. Abstr.*, **92**, 129022n (1980).
75. I. L. Knunyants, A. V. Davydov and Yu. A. Sizov, *Zh. Vses. Khim. Ova.*, **22**, 104 (1977); *Chem. Abstr.*, **87**, 39585r (1977).
76. A. G. Rowley and J. R. F. Steedman, *Chem. Ind. (London)*, **10**, 365 (1981).
77. W. J. Stec, A. Okruszek and J. Michalski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **21**, 444 (1973).
78. M. Gorio, B. C. Castellani, M. Cola and A. Perrote, *J. Inorg. Nucl. Chem.*, **36**, 1168 (1974).
79. A. N. Nesmeyanov, V. D. Vil'chevskaya, A. I. Krylova, S. Yu. Nekrasov and V. S. Tolkunova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **3**, 706 (1976).
80. B. M. Butin, G. M. Isaeva and K. B. Erzhanov, *Zh. Obshch. Khim.*, **56**, 2690 (1986).
81. Yu. G. Bosyakov, O. V. Shiganakova and D. G. Kim, *Zh. Obshch. Khim.*, **58**, 1530 (1988).
82. H. Schmidbaur and K. H. Racthlein, *Chem. Ber.*, **107**, 712 (1974).
83. A. Venezel, *Rum. Pat.*, 77 975 (1982); *Chem. Abstr.*, **99**, 140165b (1983).
84. T. S. Lobana, *Natl. Acad. Sci. Lett. (India)*, **8**, 271 (1985).
85. G. A. Olah, B. G. M. Gupta, A. Garcia-Luna and S. C. Narang, *J. Org. Chem.*, **48**, 1760 (1983).
86. A. N. Pudovik, I. V. Gur'yanova, V. P. Kakurina and N. P. Anoshina, *Zh. Obshch. Khim.*, **41**, 1227 (1971).
87. S. M. Bloom, S. A. Buckler, R. F. Lambert and E. V. Merry, *J. Chem. Soc. D*, 870 (1970).
88. D. W. Allen, F. G. Mann and J. C. Tebby, *J. Chem. Soc., Perkin Trans. 1*, 2793 (1972).
89. M. Fild and T. Stankiewicz, *Z. Anorg. Allg. Chem.*, **406**, 115 (1974).
90. Farbwerke Hoechst, *Fr. Pat.*, 2 082 398 (1972); *Chem. Abstr.*, **77**, 140288q (1972).
91. H. Schmidbauer and T. Pollok, *Angew. Chem.*, **98**, 365 (1986).
92. H. Schmidbauer, T. Pollok, G. Reber and G. Mueller, *Chem. Ber.*, **120**, 1403 (1987).

93. (a) D. Brandes and A. Blaschette, *J. Organomet. Chem.*, **99**, C-33 (1975); (b) L. Wozniak, J. Kowalski and J. Chojnowski, *Tetrahedron Lett.*, **26**, 4965 (1985).
94. K. Akiba, T. Yoneyama and N. Inamoto, *Bull. Chem. Soc. Jpn*, **49**, 2023 (1976).
95. G. Keglevick and L. D. Quin, *Phosphorus Sulfur*, **26**, 129 (1986).
96. F. T. H. Lee, *Eur. Pat.*, 98 251 (1984); *Chem. Abstr.*, **100**, 175065k (1984).
97. T. H. Chan and K. T. Nwe, *Phosphorus*, **3**, 225 (1974).
98. M. Demarcq and J. Sleziona, *Ger. Pat.*, 2 461 906 (1975); *Chem. Abstr.*, **84**, 44346f (1976).
99. Y. Xu, Z. Li, J. Xia, H. Guo and Y. Huang, *Synthesis*, **9**, 781 (1984).
100. R. L. Wife, J. J. M. Snel and O. A. B. Van, *Eur. Pat.*, 183 290 (1986); *Chem. Abstr.*, **105**, 976922 (1986).
101. W. Bergeret, J. C. Gautier, S. Raynal and S. Boileau, *Eur. Polym. J.*, **19**, 1113 (1983).
102. N. Suzuki and M. Yamsahita, *Shizuoka Daigaku Kogakubu Kenkyu Hokoku*, **32**, 95 (1981); *Chem. Abstr.*, **98**, 89508r (1983).
103. H. Kosaka, N. Mito, M. Sasaki and H. Okuda, *Jpn. Kokai, Tokkyo Koho, Jpn. Pat.*, 63 218 684[88 218 684](1988); *Chem. Abstr.*, **110**, 95539 (1989).
104. R. E. Hall, A. Kessler and A. R. McLain, *US Pat.*, 3 459 808 (1969); *Chem. Abstr.*, **71**, 81524q (1969).
105. M. Maumy, *Bull. Soc. Chim. Fr.*, **4**, 1600 (1972).
106. M. Baudler, J. Vesper and H. Sandmann, *Z. Naturforsch., Teil B*, **28**, 224 (1973).
107. B. I. Stepanov, L. I. Chakunina and A. I. Bokanov, *Zh. Obshch. Khim.*, **43**, 2648 (1973).
108. F. Mathey and J. P. Lampin, *Tetrahedron*, **31**, 2685 (1975).
109. M. Rotem and Y. Kashman, *Tetrahedron Lett.*, **1**, 63 (1978).
110. E. Vilkas, M. Vilkas, J. Sainton, B. Meunier and C. Pascard, *J. Chem. Soc., Perkin Trans. 1*, 2136 (1980).
111. V. A. Chauzov, Yu, N. Studnev, L. S. Rudnitskaya and A. V. Fokin, *USSR Pat.*, 1 188 177 (1985); *Chem. Abstr.*, **105**, 141390 (1986).
112. V. A. Chauzov, Yu, N. Studnev, L. S. Rudnitskaya and A. V. Fokin *USSR Pat.*, 1 209 696 (1986); *Chem. Abstr.*, **105**, 153319x (1986).
113. V. A. Chauzov, Yu, N. Studnev, L. S. Rudnitskaya and A. V. Fokin, *USSR Pat.*, 1 209 695 (1986); *Chem. Abstr.*, **105**, 134145w (1986).
114. M. V. Livantsov, A. A. Prishchenko and I. F. Lutsenko, *Zh. Obshch. Khim.*, **57**, 884 (1987).
115. E. L. Sukman *US Pat.*, 4 101 655 (1978); *Chem. Abstr.*, **90**, 17684k (1979).
116. O. Dalh. *J. Chem. Soc., Perkin Trans. 1*, 947 (1978).
117. B. N. Laskorin, V. V. Yakshin and M. I. Tymonyuk, *USSR Pat.*, 1 143 749 (1985); *Chem. Abstr.*, **103**, 54288p (1985).
118. H. Quast and M. Heuschmann, *Liebigs Ann. Chem.*, **5**, 977 (1981); *Chem. Abstr.*, **95**, 169280p (1981).
119. V. L. Foss, V. A. Solodenko, Yu, A. Veits and I. F. Lutsenko, *Zh. Obshch. Khim.*, **49**, 1724 (1979).
120. A. K. Bhattacharya and G. Thyagarajan, *Chem. Rev.*, **81**, 415 (1981).
121. A. I. Razumov, *Zh. Obshch. Khim.*, **29**, 1635 (1959).
122. B. Lippsmeier, K. Hestermann and M. Reuter, *Ger. Pat.*, 2 413 823 (1976); *Chem. Abstr.*, **84**, 180395y (1976).
123. E. N. Tsvetkov, T. E. Kron and M. I. Kabachnik, *USSR Pat.*, 495 324 (1975); *Chem. Abstr.*, **84**, 90304p (1976).
124. E. N. Tsvetkov, T. E. Kron and M. I. Kabachnik, *USSR Pat.*, 4 95 323 (1975); *Chem. Abstr.*, **84**, 90305p (1976).
125. (a) Hoechst, *Neth. Pat.*, 75 01 707 (1975); *Chem. Abstr.*, **84**, 122033t (1976); (b) B. Lippsmeier, K. Hestermann and G. Heymer, *Ger. Pat.*, 2 407 460 (1975); *Chem. Abstr.*, **84**, 17557u (1976).
126. R. Z. Aliev and V. K. Khairullin, *Zh. Obshch. Khim.*, **46**, 266 (1976).
127. V. M. Zimin, R. V. Zhuk and B. M. Gladshtein, *USSR Pat.*, 455 971 (1975); *Chem. Abstr.*, **82**, 171192m (1975).
128. K. Tamae, H. Yamamoto, H. Matsumoto, N. Miyake, T. Hayashi and M. Kumado, *Tetrahedron Lett.*, **6**, 1389 (1977); *Jpn. Kokai Tokkyo Koho*, Jpn. Pat., 7939059 (1979); *Chem. Abstr.*, **91**, 91764v (1979).
129. L. Maier, *Helv. Chim. Acta.*, **51**, 405 (1968).
130. L. Maier, R. Gredig, A. Hauser and R. Battagello, *Helv. Chim. Acta*, **52**, 858 (1969).
131. (a) E. W. Koos, J. P. Vander Kooi, E. E. Green and J. K. Stille, *J. Chem. Soc., Chem. Commun.*,

1085 (1972); (b) M. Yamashita, K. Tsunekawa, M. Sugiura, T. Oshikawa and S. Inokawa, *Synthesis*, **1**, 65 (1985).
132. Y. Ishizuka and I. Higashimakihara, *Jpn. Pat.*, 73 04 451 (1973); *Chem. Abstr.*, **79**, 5457v (1973).
133. D. Gloyna, U. Lachmann and H. G. Henning, *J. Prakt. Chem.*, **317**, 840 (1975).
134. L. Maier, *Phosphorus*, **1**, 245 (1972).
135. p. Lechtken, I. Buethe, M. Jacobi and W. Trimborn, *Ger. Pat.*, 2 909 884 (1980); *Chem. Abstr.*, **94**, 103 560c (1981).
136. P. Lechtken I. Buethe, and A. Hesse, *Ger. Pat.*, 2 830 927 (1980); *Chem. Abstr.*, **93**, 46823u (1980).
137. N. L. J. M. Broekhof, E. P. Van, G. A. Vander, *Recl. J. R. Neth. Chem. Soc.*, **103**, 312 (1984).
138. R. A. Khachtryan, R. K. Lulukyan, S. A. Ovsepyan and M. G. Indzhikyan, *Arm. Khim. Zh.*, **38**, 377 (1985); *Chem. Abstr.*, **105**, 172576v (1986).
139. A. V. Kharitonov, A. E. Antoshin, A. N. Pushin and E. N. Tsvetkov, *Zh. Obshch. Khim.*, **58**, 1021 (1988).
140. K. A. Petrov, V. A. Chauzov and V. P. Pokatun *USSR Pat.*, 106 700 (1984); *Chem. Abstr.*, **100**, 210155p (1984).
141. K. A. Petrov, V. A. Chauzov and V. P. Prokatun, *Zh. Obshch. Khim.*, **53**, 541 (1983).
142. S. Boileau, T. D. Nguyen and J. C. Gautier, *Eur. Pat.*, 31 761 (1981); *Chem. Abstr.*, **96**, 86742y (1982).
143. N. S. Kozlov, V. Z. Pak and E. A. Britan, *Zh. Obshch. Khim.*, **49**, 2392 (1979).
144. S. Nakasato, H. Hirata and K. Higuchi, *Yukagaku*, **27**, 513 (1978); *Chem. Abstr.*, **89**, 163680y (1978).
145. B. N. Laskorin, V. V. Yakshin and L. T. Sokalskaya, *Zh. Strukt. Khim.*, **19** 757 (1978); *Chem. Abstr.*, **90**, 55021w (1979).
146. C. Charrier and F. Mathey, *Tetrahedron Lett.*, **27**, 2407 (1978).
147. H. J. Kleiner and H. Staendecke, *Ger. Pat.*, 1 952 605 (1972); *Chem. Abstr.*, **77**, 5611z (1972).
148. B. M. Gladshtein, V. M. Eimin, V. G. Noskov, L. Z. Soborovskie, B. P. Timoshevski and L. N. Shitov, *Khim. Primen. Fosfororg. Soedin. Tr. Konf. 4th*, Nauka, Moscow, 1969, p. 279; *Chem. Abstr.*, **78**, 124681c (1973).
149. S. Kh. Nurtdinov and N. M. Ismagilova, *USSR Pat.*, 414 270 (1974); *Chem. Abstr.*, **80**, 146405b (1974).
150. S. Kh. Nurtdinov, R. Sh. Gubaidullina, V. S. Kukushkina, R. B. Sultanova, T. C. Zykova and V. S. Tsivunin, *Zh. Obshch. Khim.*, **44**, 1661 (1974).
151. I. Shahak and Y. Sasson, *Synthesis*, 358 (1974).
152. K. Weinberg and J. E. Mekeon, *US Pat.*, 3 780 112 (1973); *Chem. Abstr.*, **80**, 70966v (1974).
153. V. K. Khairullin and R. Z. Aliev, *Zh. Obshch. Khim.*, **44**, 1683 (1974).
154. J. P. Lampin and F. Mathey, *Fr. Pat.*, 2 242 398 (1975); *Chem. Abstr.*, **83**, 164369s (1975).
155. V. I. Vysotskii, E. V. Pavlycheva and M. N. Tilichenko, *USSR Pat.*, 445 670 (1974); *Chem. Abstr.*, **82**, 73169q (1975).
156. O. Awerbouch and Y. Kashman, *Tetrahedron*, **31**, 33 (1975).
157. D. J. H. Smith and S. Tripett, *J. Chem. Soc., Perkin Trans. 1*, 963 (1975).
158. M. Huche and P. Cresson, *Bull. Soc. Chim. Fr.*, 800 (1975).
159. S. Kh. Nurtdinov, I. M. Kashirskaya, N. M. Ismagilova, T. V. Zykova, R. A. Salakhutdinov and V. S. Tsivunin, *Zh. Obshch. Khim.*, **49**, 100 (1979).
160. V. K. Khairullin, G. V. Dimitrieva, I. A. Aleksandrova and A. E. Arbuzov, *USSR Pat.*, 332 738 (1973); *Chem. Abstr.*, **79**, 146655v (1973).
161. V. K. Khairullin, G. V. Dimitrieva, I. A. Aleksandrova and M. A. Vasyanina, *Izv. Akad. Nauk SSR, Ser. Khim.*, **12**, 2744 (1973).
162. L. D. Quin and J. E. MacDiarmid, *J. Org. Chem.*, **46**, 461 (1981).
163. M. El-Deek, G. D. MacDonell, S. D. Venkataramu and K. D. Berlin, *J. Org. Chem.*, **41**, 1403 (1976).
164. E. Nief, C. Charrier, F. Mathey and M. Simalty, *Tetrahedron Lett.*, **21**, 1441 (1980).
165. M. Baudler and G. Reuschenbach, *Z. Anorg. Allg. Chem.*, **464**, 9 (1980).
166. H. S. Freeman and L. D. Freedman, *ACS Symp. Ser.*, **171**, 291 (1981).
167. K. S. Fongers, H. Hogeveen and R. F. Kingma, *Tetrahedron Lett.*, **24**, 1423 (1983).
168. V. K. Kukhar, V. N. Zemlyanoi and A. M. Aleksandrov, *Zh. Obshch. Khim.*, **54**, 220 (1984).
169. S. Kh. Nurtdinov, R. A. Fakhrutdinova, T. A. Zykova, F. Sh. Shagvalaev, R. Z. Musin, Yu. Ya. Efremov and V. S. Tsivunin, *Zh. Obshch. Khim.*, **57**, 2277 (1987).

170. H. D. Block, *Ger. Pat.*, 2 606 682 (1977); *Chem. Abstr.*, **88**, 7051t (1978).
171. W. H. L. W. Tan and A. Foucand, *Tetrahedron Lett.*, **29**, 4581 (1988).
172. N. S. Issacs and G. N. El-Din, *Synthesis*, 967 (1989).
173. H. J. Kleiner, *Ger. Pat.*, 806 705 (1970); *Chem. Abstr.*, **73**, 45598z (1970).
174. H. J. Kleiner, *Ger. Pat.*, 1 806 707 (1970); *Chem. Abstr.*, **73**, 35508f (1970).
175. H. J. Kleiner, *Justus Liebigs Ann. Chem.*, 751 (1974).
176. Farbwerke Hoechst, *Fr. Pat.*, 2 015 823 (1970); *Chem. Abstr.*, **74**, 88129k (1971).
177. F. Seel and K. D. Velleman, *Chem. Ber.*, **105**, 406 (1972).
178. H. Oehme and R. Thamm, *J. Prakt. Chem.*, **315**, 526 (1973).
179. W. C. Kaska and L. Maier, *Helv. Chim. Acta*, **57**, 2250 (1974).
180. K. C. Hansen, G. B. Solleder and C. L. Holland, *J. Org. Chem.*, **39**, 267 (1974).
181. H. Oehme, K. Issleib and E. Leissring, *Phosphorus*, **3**, 159 (1973).
182. R. B. King and J. C. Cloyd, *Phosphorus*, **3**, 213 (1974).
183. D. L. Dubois, W. H. Myers and D. W. Meek, *J. Chem. Soc., Dalton Trans.*, 1011 (1975).
184. R. B. King and A. Efraty, *J. Chem. Soc., Perkin Trans. 1*, 1371 (1974).
185. T. E. Snider, D. J. Morris, K. C. Srivastava and K. D. Berlin, *Org. Synth.* **53**, 98 (1973).
186. K. Goda, H. Gomi, M. Yoshifugi and N. N. Inamoto, *Bull. Chem. Soc. Jpn.*, **47**, 2453 (1974).
187. F. Mathey, D. Thavard and B. Bartet, *Can. J. Chem.*, **53**, 855 (1975).
188. V. I. Vysotskii, E. V. Pavlycheva and M. V. Tilichenko, *Zh. Obshch. Khim.*, **45**, 1466 (1975).
189. I. N. Azerbaev, B. M. Butin and Yu. G. Bosvakov, *Zh. Obshch Khim.*, **45**, 1730 (1975).
190. L. Horner, H. Kunz and P. Walach, *Phosphorus*, **6**, 63 (1975).
191. J. R. Wiseman and H. O. Krabbenhoft, *J. Org. Chem.*, **41**, 589 (1976).
192. J. Emsley, T. B. Middleton and J. K. Williams, *J. Chem. Soc., Dalton Trans.*, 979 (1976).
193. B. A. Arbuzov, O. A. Erastov and G. N. Nikonov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (a) 735 (1980); (b) 1438 (1980).
194. V. I. Vysotskii and M. F. Rostovskaya, *Zh. Obshch. Khim.*, **53**, 2644 (1983).
195. A. Marinetti and F. Mathey, *J. Am. Chem. Soc.*, **107**, 4700 (1985).
196. H. Weichmann, B. Rensch, M. Dargatz and J. Meunier-Piret, *Bull. Soc. Chim. Belg.*, **98**, 1 (1989).
197. F. V. Bagrov, N. A. Razumova and A. A. Petrov, *Zh. Obshch. Khim.*, **42**, 792 (1972).
198. A. M. Aguiar, I. J. R. Smiley and N. S. Bhacca, *J. Org. Chem.*, **34**, 3349 (1969).
199. H. J. Kleiner, (a) *Ger. Pat.*, 1 902 444 (1970); *Chem. Abstr.*, **73**, 88023a (1970); (b) *Us Pat.*, 3 657 352 (1972); *Chem. Abstr.*, **77**, 88651m (1972).
200. V. A. Chauzov, Yu. N. Studnev, L. P. Kostina and A. V. Fokin, *USSR Pat.*, 1 525 163 (1989); *Chem. Abstr.*, **112**, 179477s (1990).
201. M. J. Gallagher and I. D. Jenkins, *J. Chem. Soc. C*, 210 (1971).
202. K. Zh. Kulumbetova, T. Ya. Medved and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2747 (1971).
203. (a) T. Minami, Y. Okada, R. Nomura, S. Hirota, Y. Nagahara and K. Fukuyama, *Chem. Lett.*, **4**, 613 (1986); (b) T. Minami and I. Hirao, *Jpn. Pat.*, 6 212 787 (1987); *Chem. Abstr.*, **106**, 176665a (1987).
204. F. Mathey and J. P. Lampin, *Tetrahedron Lett.*, 1949 (1972).
205. A. Naakgeboren, J. Meijer, P. Vermeer and L. Brandsma, *Recl. Trav. Chim. Pays-Bas.*, **94**, 92 (1975).
206. M. Yokoyama, *Jpn. Pat.*, 8 149 393 (1981); *Chem. Abstr.*, **95**, 133157q (1981).
207. L. Maier, *Phosphorus*, **1**, 245 (1972).
208. L. Maier, *Phosphorus*, **1**, 249 (1972).
209. (a) C. Beerman and H. J. Kleiner, *Ger. Pat.*, 2 060 217 (1972); *Chem. Abstr.*, **77**, 101894q (1972); (b) M. Reuter and H. J. Kleiner, *Ger. Pat.*, 2 219 173 (1973); *Chem. Abstr.*, **80**, 15066b (1974).
210. G. N. Tsvetkov, T. E. Geroleva and M. I. Kabachnik, *USSR Pat.*, 4 31 173 (1974); *Chem. Abstr.*, **81**, 63768z (1974).
211. J. Gloede, *J. Prakt. Chem.*, **314**, 281 (1972).
212. G. Borisov, *Vysokomol. Soedin., Ser. A*, **15**, 275 (1973); *Chem. Abstr.*, **79**, 5629c (1973).
213. A. N. Pudovik, R. A. Cherkasov, G. A. Kutyrev and V. V. Ovchinnikov, *USSR Pat.*, 403 683 (1973); *Chem. Abstr.*, **80**, 37280u (1974).
214. M. S. Chattha, S. S. Quo, J. A. Kuczkowski and A. M. Aguiar, *Phosphorus*, **3**, 65 (1973).
215. l. Eberhard, J. P. Lampin, F. Mathey and C. Badellon, *Tetrahedron.*, **29**, 2909 (1973).
216. D. J. Collins, L. E. Rowley and J. M. Swan, *Aust. J. Chem.*, **27**, 841 (1974).

217. Y. Seagull, I. Granoth and A. Kalir, *J. Chem. Soc., Chem. Commun.*, 501 (1974).
218. G. A. Kutyrev, R. A. Cherkasov and A. N. Pudovik, *Zh. Obshch. Khim.*, **44**, 1017 (1974).
219. J. P. Lampin and F. Mathey, *J. Organomet. Chem.*, **71**, 239 (1974).
220. (a) L. M. Yagupolskii, K. N. Bildonov, P. V. Serebrov, A. A. Goncharencho, V. Ya. Semenii, A. V. Kirsanov, M. I. Lyapunov, N. G. Feshchenko and V. N. Zavatskii, *USSR Pat.*, 384 349 (1974); *Chem. Abstr.*, **81**, 152414y (1974); (b) L. M. Yugupolski, V. N. Zavatskii, V. Y. Semenii, K. N. Bildonov, P. V. Serebrov, A. A. Goncharenko, A. V. Kirsanov, M. L. Lyapunov and N. G. Feschenko, *US Pat.*, 4 124 456 (1978); *Chem. Abstr.*, **90**, 87670y (1979).
221. M. I. Kabachnik, T. Ya, Medved, I. B. Goryunova, L. I. Tikhonova and E. I. Matrosov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2290 (1974).
222. H. Neumaier, M. Finke and R. Schueller, *Ger. Pat.*, 2 347 109 (1975); *Chem. Abstr.*, **83**, 28369q (1975).
223. A. H. Davidson and S. Warren, *J. Chem. Soc., Chem. Commun.*, 148 (1975).
224. A. B. Pepperman, G. J. Bourdreaux and T. H. Siddall, *J. Org. Chem.*, **40**, 2056 (1975).
225. S. G. Borleske and L. D. Quin, *Phosphorus*, **5**, 173 (1975).
226. J. M. Biehler, P. LeRoy and S. Lecolier, *Fr. Pat.*, 2 238 709 (1975); *Chem. Abstr.*, **83**, 148432b (1975).
227. R. Bodalski, K. M. Pietrusiewicz and J. Koszuk, *Tetrahedron*, **31**, 1907 (1975).
228. A. H. Davidson and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 639 (1976).
229. T. V. Yakovenko, R. K. Valetdinov and R. V. Vafina, *Zh. Obshch. Khim.*, **46**, 278 (1976).
230. V. K. Byistro, L. A. Krichevski and Z. M. Muldakhmetov, *Zh. Obshch. Khim.*, **46**, 783 (1976).
231. U. Lachmann, H. G. Henning and D. Gloyna, *J. Prakt. Chem.*, **318**, 489 (1979).
232. W. Winter, *Chem. Ber.*, **109**, 2405 (1976).
233. K. A. Petrov, V. A. Chauzov and T. S. Erokhina, *Khim. Elementoorg. Soedin.*, 200 (1976); *Chem. Abstr.*, **86**, 5543q (1976).
234. A. H. Davidson, I. Fleming, J. I. Grayson, A. Pearce, R. L. Snowden and S. Stewart, *J. Chem. Soc., Perkin Trans. 1*, 550 (1977).
235. V. I. Siele, *J. Heterocycl. Chem.*, **13**, 337 (1977).
236. H. D. Block, *Ger. Pat.*, 2 602 646 (1977); *Chem. Abstr.*, **87**, 168198r (1977).
237. H. Heydt and M. Regitz, *Justus Leibigs Ann. Chem.*, 1766 (1977).
238. A. N. Pudovik, N. G. Khusainova and Z. A. Nasybullina, *Zh. Obshch. Khim.*, **43**, 1683 (1973).
239. L. D. Quin and E. D. Middlemas, *Pure Appl. Chem.*, **52**, 1013 (1980).
240. M. Yamashita, K. Tsunekawa, M. Sugiura, T. Oshikawa and S. Inokawa, *Chem. Lett.*, 1673 (1983).
241. H. J. Meeuwissen, T. A. Vander Knapp and F. Bickelhaupt, *Tetrahedron*, **39**, 4225 (1983).
242. A. Sedqui, J. Vebrel and B. Laude, *Chem. Lett.*, 965 (1984).
243. D. G. Gilheany, D. A. Kennedy, J. F. Malone and B. J. Walker, *J. Chem. Soc., Chem. Commun.*, 1217 (1984).
244. E. N. Tsvetkov, T. E. Kron, E. S. Petrov and A. I. Shatenshtein, *Zh. Obshch. Khim.*, **54**, 2238 (1984).
245. M. Vogl and W. Riemenschneider, *Ger. Pat.*, DE 3 514 451 (1986); *Chem. Abstr.*, **106**, 188275s (1987).
246. V. V. Kormachev, Yu. M. Mitrasov and T. G. Kostantinova, *USSR Pat.*, 630257 (1978); *Chem., Abstr.*, **90**, 39036z (1979).
247. V. V. Kormachev and Yu. N. Mitrasov, *Fosfororg. Soedin. Polim.*, **4**, 23 (1978); *Chem. Abstr.*, **92**, 76609a (1980).
248. R. K. Valetdinov, A. N. Zuikova and R. D. Murtazina, *Otkrytiya Izobret Prom. Obraztsy Tovarnye Znaki*, **36**, 82 (1979); *Chem. Abstr.*, **92**, 42114v (1980).
249. V. V. Kormachev, T. V. Vasileva, V. A. Kukhtin, *Otkyrtiya Izobret. Prom. Obraztsy Tovarnye Znaki*, **55**, 92 (1978); *Chem. Abstr.*, **89**, 215555h (1978).
250. J. A. Miller and D. Stewart, *J. Chem. Soc., Perkin Trans. 1*, 1898 (1977).
251. Yu. A. Strepikheev, L. V. Kovalenko and Z. I. Yagnyukova, *Mosk. Khim. -Technol. Inst.*, Moscow, USSR *Deposited Doc.*, 1976, VINITI 3406-76; *Chem. Abstr.*, **89**, 129608w (1978).
252. V. K. Byistro, L. A. Krichevskii, Z. M. Muddakhmetov, *USSR Pat.*, 825 539 (1981); *Chem. Abstr.*, **95**, 133158r(1981).
253. S. H. Chevalier, J. C. Gautier and C. R. Soriaux, *Eur. Pat.*, 68 953 (1983); *Chem. Abstr.*, **98**, 160945p (1983).

254. V. A. Chauzov, Yu. N. Studnev, M. G. Iznoskova, L. S. Rudnitskaya and A. V. Fokin, *USSR Pat.*, 125 3978 (1986); *Chem. Abstr.*, **105**, 227015u (1986).
255. R. C. Santelli, *Synthesis*, **1**, 64 (1988).
256. G. Keglevich, I. Petnehazy, L. Toke, F. Janke, A. Szollosy, P. Miklos and G. Toth, *Magy. Kem. Foly.*, **95**, 79 (1989); *Chem. Abstr.*, **112**, 35998q (1990).
257. J. Elliott and S. Warren, *Tetrahedron Lett.*, **27**, 645 (1986).
258. G. N. Nikonov, A. A. Karasik and O. A. Erastova, *Izv. Akad Nauk SSSR, Ser. Khim.*, 1879 (1988); *Chem; Abstr.*, **110**, 75628j (1989).
259. G. Keglevich, I. Pentnehazy, P. Miklos, G. Toth and L. S. Toke, *Org. Chem.* (*Amsterdam*), **35**, 333 (1988); *Chem. Abstr.*, **111**, 134275m (1989).
260. J. I. Grayson, H. K. Norrish and S. Warren, *J. Chem. Soc.*, *Perkin Trans. 1*, 2556 (1976).
261. W. Herwig and H. J. Kleiner, *Ger. Pat.*, 2 523 145 (1976); *Chem. Abstr.*, **86**, 90983a (1977).
262. S.S. Kloze, *US Pat.*, 3 996 354 (1976); *Chem. Abstr.*, **86**, 10678w (1977).
263. H. Teichman, W. Thierfelder, E. Schaefer and A. Weight, *Tetrahedron Lett.*, **33**, 2889 (1977).
264. (a) Hoechst, *Neth. Pat.*, 76 05 380 (1977); *Chem. Abstr.*, **89**, 43780j (1978); (b) Hoechst *Jpn. Kokai*, 77 151 150 (1977); *Chem. Abstr.*, **89**, 215547g (1978).
265. H. Heydt and M. Regitz, *J. Chem. Res.*, **9**, 326 (1978).
266. M. Regitz, B. Weber and U. Eckstein, *Liebigs Ann. Chem.*, **7**, 1002 (1979).
267. H. Heydt, K. H. Buch and M. Regitz, *Liebigs Ann. Chem.*, **4**, 590 (1980).
268. M. Regitz, M. Boehshar, S. Arenz and H. Heydt, *Chem. Ber.*, **122**, 565 (1989).
269. J. Christopher and S. Warren, *J. Chem. Soc.*, *Perkin Trans. 1*, 3099 (1979).
270. P. W. Allace and S. Warren, *Tetrahedron Lett.*, **26**, 5713 (1985).
271. D. Gloyna, L. Alder, H. G. Henning, H. Goeppel, M. Siegmund and K. D. Schleinitz, *J. Prakt. Chem.*, **322**, 237 (1980).
272. H. J. Tilhard, H. Ahlers and T. Kauffmann, *Tetrahedron Lett.*, **21**, 2803 (1980).
273. S. D. Darling and S. J. Brandes, *J. Org. Chem.*, **47**, 1413 (1982).
274. W. H. Bergeret, J. C. C. G. Gautier, S. F. Raynal and S. Boileau, *Eur. Pat.*, 56 767 (1982); *Chem. Abstr.*, **97**, 198379z (1982).
275. E. R. N. Bornacini and R. Rossi, *J. Org. Chem.*, **55**, 2332 (1990).
276. L. S. Moskalevskaya, *Zh. Obshch. Khim.*, **53**, 545 (1983).
277. W. B. Cruse, O. Kennard and S. Warren, *J. Chem. Soc.*, *Perkin Trans. 1*, 243 (1984).
278. A. B. McElroy and S. Warren, *Tetrahedron Lett.*, **26**, 2119 (1985).
279. B. P. Friedrichsen and H. W. Whitlock, *J. Am. Chem. Soc.*, **111**, 9132 (1989).
280. N. G. Feshchenko, I. K. Mazepa, S. .I. Zhila and A. V. Kirsanov, *Zh. Obshch. Khim.*, **41**, 2375 (1971).
281. L. Maier, *Phosphorus*, **1**, 237 (1972).
282. E. Lindner and H. Beer, *Chem. Ber.*, **105**, 3261 (1972).
283. H. M. Priestley, *US Pat.*, 3 697 587 (1972); *Chem. Abstr.*, **78**, 29997b (1973).
284. R. Luckenbach, *Phosphorus*, **1**, 223, 229 (1972).
285. M. Simalty and M. H. Mebazaa, *Tetrahedron*, **28**, 3343 (1972).
286. M. Simalty and M. H. Mebazaa, *Fr. Pat.*, 2 134 148 (1973); *Chem. Abstr.*, **79**, 42683m (1973).
287. M. Zh. Ovakimyan, R. A. Khachatryan, A. M. Simonyan and M. G. Indzhikyan, *Arm. Khim. Zh.*, **26**, 1030 (1973); *Chem. Abstr.*, **81**, 13608b (1974).
288. R. A. Khachatryan, A. A. Simonyan, M. Zh. Ovakimyan and M. G. Indzhikyan, Arm. Khim. Zh., **27**, 65 (1974); *Chem. Abstr.*, 49760j (1974).
289. A. W. Frank and G. L. Drake, *US Pat.*, 367 971 (1973); *Chem. Abstr.*, **81**, 105698j (1974).
290. E. S. Kozlov and A. I. Sedlov, *Zh. Obshch. Khim.*, **44**, 1029 (1974).
291. K. L. Marsi and F. B. Burns, *Phosphorus.*, **4**, 211 (1974).
292. B. Lippsmeier, K. Hestermann and H. Neumaier, *Ger. Pat.*, 2 415 801 (1975); *Chem. Abstr.*, **84**, 59740d (1976).
293. (a) H. Staendeke, *Ger. Pat.*, 2 527 796 (1976); *Chem. Abstr.*, **86**, 121524h (1977); (b) H. Staendeke, K. Hestermann and B. Lippsmeier, *Ger. Pat.*, 2 511 933 (1976); *Chem. Abstr.*, **86**, 90017p (1977).
294. A. M. Torgomyan, M. Zh. Ovakimyan and M. G. Indzhikyan, *Arm. Khim. Zh.*, **31**, 669 (1978); *Chem. Abstr.*, **90**, 104068c (1979).
295. I. N. Zhumurov, I. M. Kosinskaya and A. M. Pinchuk, *Zh. Obshch. Khim.*, **51**, 1538 (1981).
296. G. Saheh, T. Minami, Y. Ohshiro and T. Agawa, *Chem. Ber.*, **112**, 355 (1979).
297. A. G. Abatjoglou and L. A. Kapicak, *Eur. Pat.*, 72 560 (1983); *Chem. Abstr.*, **98**, 198452p (1983).

298. T. Minami and T. Hirao, *Jpn. Kokai Tokkyo Koho, Jpn. Pat.*, 60 156 696 (1985); *Chem. Abstr.*, **104**, 109952d (1986).
299. L. D. Quin and S. C. Spence, *Tetrahedron Lett.*, **23**, 2529 (1982).
300. N. A. Bondarenko, M. V. Raitarskaya, M. V. Rudomino and E. N. Tsvetkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2397 (1987).
301. M. Wada, H. Ohta, N. Hashizume, M. Kanzaki, K. Hirata and T. Erabi, *Chem. Express*, **3**, 471 (1988).
302. M. Wada, K. Iwabuchi and H. Tsumaki, *Jpn. Pat.*, 63 275 595 (88 275 595) (1988); *Chem. Abstr.*, **110**, 231887a (1989).
303. V. Yu. Kovtum, V. A. Gilyaro and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2217 (1971).
304. J. I. G. Cadogan, R. J. Scott, R. D. Gee and I. Gosney, *J. Chem. Soc., Perkin Trans. 1*, 1694 (1974).
305. A. Skowronska and E. Krawezyk, *Synthesis*, **6**, 609 (1983).
306. R. Luckenbach, *Synthesis.*, 307 (1973).
307. R. Luckenbach and K. Kern. *Chem. Ber.*, **108**, 3533 (1975).
308. M. Mikolajczyk and J. Luczak, *Synthesis.*, 114 (1975).
309. M. Mikolajczyk and J. Luczak, *J. Org. Chem.*, **43**, 2132 (1978).
310. E. Weiss, *Ger. Pat.*, DE 3 426 721 (1986); *Chem. Abstr.*, **105**, 115205z (1986).
311. E. Weiss, *Ger. Pat.*, DE 3 532 360 (1987); *Chem. Abstr.*, **107**, 7389v (1987).
312. H. J. Kleiner, and E. Weiss, *Ger. Pat.*, DE 3 532 359 (1987); *Chem. Abstr.*, **017**, 23498k (1987).
313. J. Knaebel and W. Ude, *Ger. Pat.*, DE 3 636 001 (1988); *Chem. Abstr.*, **109**, 37994k (1988).
314. W. J. Stec, A. Okruszek and J. Michalski, *J. Org. Chem.*, **41**, 233 (1976).
315. C. H. Chen and K. E. Brighty, *Tetrahedron Lett.*, **21**, 4421 (1980).
316. H. J. Knaebel and W. Ude, *Ger. Pat.*, DE 3 544 065 (1987); *Chem. Abstr.*, **106**, 96891t (1987).
317. R. S. Davidson, M. D. Walker and R. K. Bhardwaj, *Tetrahedron Lett.*, **28**, 2981 (1987).
318. R. S. Davidson and M. D. Walker, *Tetrahedron Lett.*, **29**, 1827 (1988).
319. R. K. Bharadwaj and R. S. Davidson, *Tetrahedon.*, **43**, 4473 (1987).
320. J. E. Baxter, R. S. Davidson, M. D. Walker and H. J. H. Hageman, *J. Chem. Res.* (*S*), 164 (1988).
321. S. J. Buckland and R. S. Davidson, *J. Chem. Res.* (*S*), 192 (1986).
322. R. B. Wetzel and G. .L. Kenyon, *J. Am. Chem. Soc.*, **94**, 1174 (1972).
323. R. B. Wetzel and G. L. Kenyon, *J. Org. Chem.*, **39**, 1531 (1974).
324. R. B. King, J. C. Cloyd and P. N. Kapoor, *J. Chem. Soc., Perkin Trans. 1*, 226 (1973).
325. A. D. Brown, Jr, And G. M. Kosolapoff, *J. Chem. Soc. C*, 839 (1968).
326. B. V. Timokhin, E. F. Grechkin and J. Bychkova, *USSR Pat.*, 330 175 (1972); *Chem. Abstr.*, **77**, 48630x (1972).
327. V. V. Kormachev, T. V. Vasil'eva, B. I. Ionin and V. A. Kukhtin, *Zh. Obshch. Khim.*, **45**, 307 (1975).
328. K. A. Petrov, V. A. Chauzov and N. Yu. Mal'kevich, *Zh. Obshch. Khim.*, **47**, 2516 (1977).
329. Ya. A. Levin, R. I. Pyrkin and M. M. Gilyazov, *Zh. Obshch. Khim.*, **42**, 1166 (1972).
330. B. V. Timokhin, V. L. Dmitriev, E. F. Grechkin and A. V. Kalabina, Zh. Obshch. Khim., **46**, 490 (1976).
331. V. L. Dmitriev, B. V. Timokhin, A. V. Kalabina and V. V. Samorodov, *Zh. Obshch. Khim.*, **48**, 52 (1978).
332. V. K. Byistro, L. A. Krichevskii and Z. M. Muldakhmetov, *Tezisy Dokl. Vses. Konf. Khim. Atsetilena, 5th*, 242 (1975); *Chem. Abstr.*, **89**, 6373h (1978).
333. S. V. Fridland, I. A. Shkurai and L. I. Lapteva, *Zh. Obshch. Khim.*, **52**, 850 (1982).
334. S. Andreae and H. Seeboth, *Z. Chem.*, **19**, 98 (1979).
335. L. F. Filimonova, L. V. Kaabak and A. P. Tomilov, *Zh. Obshch. Khim.*, **39**, 2174 (1969).
336. N. G. Feshchenko and T. I. Aleksaeva, *Methody. Poluch. Khim. Reakt. Prep.*, **19**, 111 (1969); *Chem. Abstr.*, **75**, 20515y (1971).
337. A. V. Kirsanov, I. K. Mazepa, V. Ya. Semenii, N. P. Chernukho, Yu. E. Briskin and N. G. Feshchenko, *USSR Pat.*, 276 949 (1970); *Chem. Abstr.*, **74**, 142056z (1971).
338. L. V. Kaabak, S. L. Varshavskii, M. I. Kabachnik, N. I. Kalitina, N. Y. Myagkaya and A. P. Tomilov, *USSR Pat.*, 230 241 (1968); *Chem. Abstr.*, **71**, 3474j (1969).
339. L. V. Kabbak, S. l. Varshavskii, N. I. Kalitina, L. A. Koshechkina and M. I. Kabachnik, *USSR Pat.*, 359 254 (1972); *Chem. Abstr.*, **78**, 137009q (1973).
340. L. V. Kabaak, S. L. Varshavskii, N. Y. Myagkaya, L. A. Koshechkina, N. I. Kalitina and M. I. Kabachnik, *USSR Pat.*, 362 024 (1972); *Chem. Abstr.*, **78**, 111509c (1973).

341. E. R. Bornancini, R. A. Alonso and R. A. Rossi, *J. Organomet. Chem.*, **270**, 177 (1984).
342. Yu, V. Kandul, V. Ya Semenii, M. D. Pivovarov, V. V. Malovik, I. K. Mazepa and N. G. Feshchenko, *USSR Pat.*, 529 614 (1978); *Chem. Abstr.*, **89**, 129710y (1978).
343. Institute of Organic Chemistry, Academy of Sciences, Ukraine, USSR, *Jpn. Kokai*, 77 142 017 (1977); *Chem. Abstr.*, **89**, 197712a (1978).
344. V. Ya. Semenii, G. G. Khort, V. V. Malovik, A. V. Bulanovich, V. A. Boudar, T. P. Evtushenko and N. G. Su. Feshchenko, *Otkrytiya, Izobret. Prom. Obraztsy, Tovarnye Znaki.*, **13**, 98 (1981); Institute of Organic Chemistry, Academy of Sciences, Ukraine, *USSR Pat.*, 819 114 (1981); *Chem. Abstr.*, **95**, 43353w (1981).
345. E. H. Uhing and A. D. F. Toy, *US Pat.*, 4 051 463 (1977); *Chem. Abstr.*, **88**, 7056y (1978).
346. M. Regitz, W. Illger and G. Mass, *Chem. Ber.*, **111**, 705 (1978).
347. E. D. Middlemas and L. D. Quin., *J. Am. Chem. Soc.*, **102**, 4838 (1980).
348. G. F. Meijs, *Tetrahedron Lett.*, **26**, 105 (1985).
349. G. Borisov, Kh. Sivriev and S. Vurbanov, *Polikondesns. Protesessy, Tr. Mezhdunar. Simp. 5th*, 73 (1975); *Chem. Abstr.*, **85**, 124387f (1976).
350. E. S. Kozlov and V. I. Tovstenko, *Zh. Obshch. Khim.*, **50**, 1499 (1980).
351. J. Navech, R. Kraemer and J. P. Majoral, *Tetrahedon Lett.*, **21**, 1449 (1980).
352. R. Appel and V. Barth, *Tetrahedron Lett.*, **21**, 1923 (1980).
353. G. Maerkl, G. Yu. Jin and Ch. Schoerner, *Tetrahedron Lett.*, **21**, 1409 (1980).
354. G. Maerkl and G. Yu. Jin, *Tetrahedron Lett.*, **21**, 3467 (1980).
355. C. H. Chen, K. E. Katherine and F. M. Michaels, *J. Org. Chem.*, **46**, 361 (1981).
356. G. Maerkl, G. Adolin, F. Kees and G. Zander, *Tetrahedron Lett.*, 3445 (1977).
357. J. Navech, J. P. Majoral, A. Merien and R. Kraemer, *Phosphorus Sulfur.*, **18**, 27 (1983).
358. M. Baudler, L. De Riese-Meyer and C. Wiaterek, *Z. Naturforsch, Teil B*, **44**, 375 (1989).
359. M. Baudler, Y. Aktalay and V. Arndt, *Angew. Chem.*, **95**, 1005 (1983).
360. M. Baudler, M. Schnalke, C. Wiaterek, S. Opiela and J. Hahn, *Z. Anorg. Allg. Chem.*, **578**, 7 (1989).
361. R. N. Il'yasov, B. M. Butin and K. B. Erzhanov, *Zh. Obshch. Khim.*, **56**, 1425 (1986).
362. A. P. Khardin, O. I. Tuzhikov, O. N. Gulyaeva and T. V. Khokhlova, *USSR Pat.*, 574 449 (1977); *Chem. Abstr.*, **88**, 7054w (1978).
363. M. Baudler and P. Koch, *Z. Naturforsch., Teil B*, **44**, 1167 (1989).
364. H. Tokunaga, K. Akiba and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **45**, 506 (1972).
365. R. Appel and R. Mikler, *Chem. Ber.*, **107**, 2658 (1974).
366. G. Himbert and M. Regitz, *Chem. Ber.*, **107**, 2513 (1974).
367. S. O. Grim and J. D. Mitchell, *Inorg. Chem.*, **16**, 1762, 1770 (1977).
368. G. Grossman, B. Walther and U. Gastrach-Mey, *Phosphorus Sulfur*, **11**, 259 (1981).
369. H. H. Karsch. *Chem. Ber.*, **115**, 818 (1982).
370. J. Omelanczuk, W. Perlikowska and M. Mikolajczyk, *J. Chem. Soc. Chem. Commun.*, 24 (1980).
371. A. P. Khardin, O. I. Tuzhikov and V. Yu. Lomakin, *Zh. Obshch. Khim.*, **53**, 1429 (1983).
372. A. Henne, A. Hesse, G. Heil and G. Schornick, *Eur. Pat Appl.*, 47 902 (1982); *Chem. Abstr.*, **97**, 128616a (1982).
373. R. Weisheit, R. Stendel, B. Messbauer, C. Langer and B. Walther, *Z. Anorg. Allg. Chem.*, **504**, 147 (1983).
374. T. A. Mastryukova, I. M. Aladzheva, O. V. Bykhovskaya, I. V. Leont'eva, P. V. Petrovski and M. I. Kabachnik, *Zh. Obshch. Khim.*, **54**, 36 (1984).
375. M. Caira, R. H. Neilson, W. H. Watson, P. Wisian-Neilson and Z. M. Xie, *J. Chem. Soc., Chem. Commun.*, 698 (1984).
376. Z. M. Xie, P. Wiesian-Neilson and R. H. Neilson, *Organometallics*, **4**, 339 (1985).
377. J. M. Alcaraj and F. Mathey, *Tetrahedron Lett.*, **25**, 4659 (1984).
378. B. A. Arbuzov, O. A. Erastov, A. S. Ionkin and S. N. Ignat'eva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 640 (1986); 418 (1987).
379. B. A. Arbuzov, O. A. Erastov and A. S. Ionkin, *Izv. Akad. Nauk SSSR, Ser Khim.*, 2506 (1986).
380. P. A. Manniner, *Finn. Pat.*, 71 564 (1986); *Chem. Abstr.*, **108**, 132045b (1988).
381. Yu. G. Bosyakov, A. P. Logunov, G. P. Revenko and G. O. Atezhanova, *Zh. Obshch. Khim.*, **59**, 338 (1989).
382. J. L. Bookham and W. McFarlane, *Polyhedron*, **7**, 129 (1988).
383. J. Barluenga, F. Palacios, F. J. Gonzalez and S. Fustero, *J. Chem. Soc., Chem. Commun.*, 1596 (1988).

384. S. Chan and H. Goldwhite, *Phosphorus Sulfur.*, **4**, 33 (1978).
385. V. V. Malovik, V. A. Bonder, L. A. Kozachko, N. P. Chernukho and V. Ya. Semenii, *USSR Pat.*, 763 352 (1980); *Chem. Abstr.*, **94**, 30919q (1981).
386. O. Mitsunobu, K. Kato and M. Tomari, *Tetrahedron*, **26**, 5731 (1970).
387. K. Issleib and K. D. Franze, *J. Prakt. Chem.*, **315**, 471 (1973).
388. L. N. Markovskii, T. N. Dubinina, E. S. Levchenko, V. P. Kukhar and A. V. Kirsanov, *Zh. Obshch. Khim.*, **8**, 1822 (1972).
389. K. Wallenfels, K. Friedrich and J. Rieser, *Justus Leibigs Ann. Chem.*, 656 (1976).
390. R. Okazaki, Y. Hirabayashi, K. Tamura and N. Inamoto, *J. Chem. Soc., Perkin Trans. 1*, 1034 (1976).
391. Y. Ogata, M. Yamashita and M. Mizutani, *Bull. Chem. Soc. Jpn.*, **49**, 1721 (1976).
392. W. D. Pfeiffer and E. Bulka, *Synthesis*, 485 (1977).
393. B. A. Arbuzov, N. A. Polezaeva and M. N. Agafonov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2101 (1976).
394. V. A. Al'fonsov, G. U. Zamaletdinov, K. M. Enikeev, A. V. Il'yasov, E. S. Batyeva and A. N. Pudovik, *Zh. Obshch. Khim.*, **56**, 1697 (1986).
395. N. G. Zabirov, R. A. Cherkasov, I. S. Khalikov and A. N. Pudovik, *Zh. Obshch. Khim.*, **56**, 2673 (1986).
396. N. A. Tolmacheva, B. A. Khaskin and N. N. Mel'nikov, *Zh. Obshch. Khim.*, **48**, 1078 (1978).
397. A. N. Pudovik and T. M. Sudakova, *USSR Pat.*, 276 952 (1970); *Chem. Abstr.*, **74**, 142057a (1971).
398. G. A. Olah and D. Hehemann, *J. Org. Chem.*, **42**, 2190 (1977).
399. M. N. Danchenko, I. Yu. Budilova and A. D. Sinitsa, *Zh. Obshch. Khim.*, **55**, 939 (1985).
400. V. A. Al'fonsov, D. A. Pudovik, E. S. Batyeva and A. N. Pudovik, *Zh. Obshch. Khim.*, **55**, 2203 (1985).
401. B. A. Arbuzov, G. N. Nikonov and O. A. Erastov, *Izv. Akad. Nauk, SSSR, Ser. Khim.*, 2359, 2362 (1985).
402. E. Erwin and H. J. Kleiner, *Phosphorus Sulfur.*, **34**, 39 (1987).
403. J. Apitz, J. Grobe and L. V. Due, *Z. Naturforsch., Teil*, **43**, 257 (1988).
404. T. Emoto, H. Gomi M. Yoshifuji, R. Okazaki and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **47**, 2449 (1974).
405. D. J. Collins, S. A. Mollard, N. Rose and J. M. Swan, *Aust. J. Chem.*, **27**, 2365 (1974).
406. (a) R. B. King, J. C. Cloyd, Jr, and P. K. Hendrik, *J. Am. Chem. Soc.*, **95**, 5083 (1973); (b) R. B. King and J. C. Cloyd, Jr, *J. Am. Chem. Soc.*, **97**, 46, 53 (1975).
407. R. B. King, J. C. Cloyd, Jr. and R. H. Riemann, *J. Org. Chem.*, **41**, 972 (1976).
408. F. Mathey, *Tetrahedron*, **30**, 3127 (1974).
409. E. N. Tsvetkov, T. P. Chepaikina and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 426 (1979).
410. M. Yoshifuji, J. Tagawa and N. Inamoto, *Tetrahedron Lett.*, 2415 (1979).
411. B. Divisia, *Tetrahedron*, **35**, 181 (1979).
412. K. M. Pietrusiewicz, K. Monkiewicz and R. Bodalski, *Pol. J. Chem.*, **57**, 637 (1983).
413. R. Schmutzler, O. Stelzer and N. Weferling, *Chem. Ber.*, **121**, 391 (1988).
414. G. M. Akhmetova, G. M. Isaeva and B. M. Butin, *Zh. Obshch. Khim.*, **58**, 1831 (1988).
415. A. A. Karasik, S. N. Ignat'eva, O. A. Erastov and B. A. Arbuzov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2190 (1988).
416. A. P. Logunov, E. G. Yalovenko, S. D. Dzhailanov and Yu. G. Bosyakov, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, 80 (1989); *Chem. Abstr.*, **112**, 36005a (1990).
417. M. J. Dagani, *US Pat.*, 3 624 159 (1971); 3 763 241 (1973); *Chem. Abstr.*, **76**, 46304z (1972); **79**, 137275u (1973).
418. S. O. Grim and J. D. Mitchell, *Synth. React. Inorg. Met. Org. Chem.*, **4**, 221 (1974).
419. H. J. Kleiner, *Ger. Pat.*, 2 335 462 (1975); *Chem. Abstr.*, **82**, 171196r (1975).
420. E. Deschamps and F. Mathey, *J. Chem. Soc., Chem. Commun.*, 1214 (1984).
421. A. Breque, G. Muller, H. Bonnard, F. Mathey and P. Savignac, *Eur. Pat. Appl.*, 41 447 (1981); *Chem. Abstr.*, **96**, 143076x (1982).
422. B. E. Maryanoff, R. Tang and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 273 (1973).
423. B. V. Timokhin, N. A. Sukhorukova, E. F. Grechkin and V. I. Glukhikh, *Zh., Obshch. Khim.*, **45**, 2561 (1975).

424. B. V. Timokhin, N. A. Sukhorukova, E. F. Grechkin and V. I. Glukhich, *USSR Pat.*, 534466 (1976); *Chem. Abstr.*, **86**, 121516g (1977).
425. A. D. F. Toy and E. H. Uhing, *US Pat.*, 4076746 (1978); *Chem. Abstr.*, **89**, 43771g (1978).
426. B. V. Timokhin and N. A. Sukhorukova, *Zh. Obshch. Khim.*, **49**, 1235 (1979).
427. S. O. Grim, P. H. Grim, I. T. Colquhoun and W. McFarlane, *Inorg. Chem.*, **19**, 3195 (1980).
428. S. O. Grim, L. C. Satek and J. D. Mitchell, *Z. Naturforsch., Teil B*, **35**, 832 (1980).
429. Y. Kawakami, R. A. Murthy and Y. Yamashita, *Synth. Commun.*, **13**, 427 (1983).
430. J. C. Fiaud, *J. Chem. Soc., Chem. Commun.*, 1055 (1983).
431. E. P. Kyba and S. T. Liu, *Inorg. Chem.*, **24**, 1613 (1985).
432. S. O. Grim, S. A. Sangokoya, I. J. Colquhoun, W. McFarlane and R. K. Khanna, *Inorg. Chem.*, **25**, 2699 (1989).
433. W. Ude, S. Besecke, A. Riemann and G. Schroeder, *Ger. Pat.*, 3425282 (1986); *Chem. Abstr.*, **105**, 79895y (1986).
434. H. J. Kleiner and E. Weiss, *Ger. Pat.*, DE 3426722 (1986); *Chem. Abstr.*, **105**, 115206a (1986).
435. G. A. Olah, A. Berrier and L. Ohannesian, *Nouv. J. Chem.*, **10**, 253 (1986).
436. E. Weiss and H. J. Kleiner, *Ger. Patent*, DE 3601247 (1987); *Chem. Abstr.*, **107**, 134489c (1987).
437. E. H. Uhing and A. D. F. Toy, *US Pat.*, 4052463 (1977); *Chem. Abstr.*, **88**, 7056y (1978).
438. (a) J. Michalski, *Ann. N. Y. Acad. Sci.*, **192**, 90 (1972); *Chem. Abstr.*, *77*, 19697u (1972); (b) J. Michalski and A. Markowska, in *Organic Selenium Compounds: Their Chemistry and Biology* (Eds. D. L. Klayman and W. H. H. Gunther), Wiley–Interscience, New York, 1973 pp. 326–377.
439. (a) D. H. Brown, R. J. Cross and D. D. MacNicol, *Chem. Ind.* (*London*), 766 (1977); (b) D. H. Brown, R. J. Cross and D. D. MacNicol, *Ger. Pat.*, 2815615 ?(1978); *Chem. Abstr.*, **90**, 203656z (1979); (c) D. H. Brown, R. J. Cross, P. R. Mallison and D. D. MacNicol. *J. Chem. Soc., Perkin Trans. 2*, 993 (1980).
440. (a) D. H. Brown, R. J. Cross and R. Keat, *J. Chem. Soc., Chem. Commun.*, 708 (1977); (b) D. H. Brown, R. J. Cross and R. Keat, *J. Chem. Soc., Dalton Trans.*, 871 (1980).
441. W. W. Du Mont and H. J. Kroth, *J. Organomet. Chem.*, **113**, C-35 (1976).
442. M. I. Steigerwald and C. R. Sprinkle, *Organometallics*, **7**, 245 (1988).
443. L. Maier, *US Pat.*, 3534104 (1970); Chem. Abstr., **74**, 53984h (1971).
444. T. Austad, T. Rod, K. Ase, J. Songstad and A. H. Norbury, *Acta. Chem. Scand.*, **27**, 1939 (1973).
445. R. J. Cross and D. Mullington, *J. Chem. Soc., Chem. Commun.*, 455 (1975).
446. I. S. Butler, D. Cozak and S. R. Stobart, *Inorg. Chem.*, **16**, 1779 (1977).
447. S. I. A. El Sheikh, M. S. Patel, B. C. Smith and C. B. Waller, *J. Chem. Soc., Dalton Trans.*, 641 (1977).
448. V. Kirshnan, A. Dutta and S. V. L. Narayanan, *Inorg. Nucl. Chem. Lett.*, **13**, 517 (1977).
449. W. W. Du Mont, *Angew. Chem.*, **92**, 562 (1980).
450. T. A. Knapp, M. Vos and F. Bickelhaupt, *J. Organomet. Chem.*, **244**, 363 (1983).
451. W. W. Du Mont, *Z. Naturforsch, Teil B*, **40**, 1453 (1985).
452. M. Lusser and P. Peringer, *Inorg. Chim. Acta*, **127**, 151 (1987).
453. A. J. Ashe, III, and E. G. Ludwig, Jr, *J. Organomet. Chem.*, **308**, 289 (1986).
454. P. Nicpon and D. W. Meek, *Inorg. Chem.*, **5**, 1297 (1966).
455. N. A. Buina, F. G. Sibgatullina and I. A. Nuretdinov, *Zh. Obshch. Khim.*, **49**, 2386 (1979).
456. S. O. Grim and E. D. Walton, *Phosphorus Sulfur*, **9**, 123 (1980).
457. J. Omelanczuk and M. Mikolajczyk, *Phosphorus Sulfur*, **15**, 321 (1983).
458. A. A. Shvets, L. D. Popov, V. A. Kogan, V. V. Litvinov and L. N. Etmetchenko, *Zh. Obshch. Khim.*, **58**, 104 (1988).

CHAPTER **7**

Chemical properties and reactions of phosphine chalcogenides

R. S. EDMUNDSON

Retired from Department of Chemistry, University of Bradford, Bradford, West Yorkshire BD7 IDP, UK

The chemistry of organophosphorus compounds, Volume 2, Phosphine oxides, sulphides, selenides and tellurides
Edited by Frank R. Hartley. © 1992 John Wiley & Sons, Ltd. ISBN: 0-471-93056-3

I. INTRODUCTION

Tertiary phosphines, R_3P, and their chalcogenide derivatives, (**1**) (X = O, S, Se or Te), have been known since the early days of organophosphorus chemistry. The latter group is characterized by the possession of three, formally single, phosphorus—carbon bonds, in addition to the bond between the phosphorus and chalcogen atom, and whose character may vary considerably depending on both the group(s) R and the element X. The series of so-called tertiary compounds is thus clearly distinguishable from similar derivatives of secondary and primary phosphines which possess one and two phosphorus—hydrogen bonds, respectively.

$$\underset{\mathbf{(1)}}{R_3P{=}X} \qquad \underset{\mathbf{(2.1)}}{R_2P({=}X)H} \qquad \underset{\mathbf{(2.2)}}{R_2P{-}XH} \qquad \underset{\mathbf{(3.1)}}{RP({=}X)H_2} \qquad \underset{\mathbf{(3.2)}}{RP({-}XH)H}$$

An important feature of the chemistries of the secondary and primary phosphine chalcogenides, where these compounds actually exist, is their participation in the dyad prototropic equilibria $\mathbf{2.1} \rightleftharpoons \mathbf{2.2}$ and $\mathbf{3.1} \rightleftharpoons \mathbf{3.2}$. The secondary and primary phosphine chalcogens are thus each able to form two series of derivatives based on tri- or tetra-coordinate geometry. Those derivatives having tricoordinate structures are not the direct concern of the present chapter, which, in addition to describing the reactions of the tertiary phosphine chalcogenides, also reviews briefly reactions of the secondary and primary phosphine derivatives, particularly those which directly involve the phosphorus—hydrogen bond itself.

The tertiary phosphine oxides were, for a long time, considered to be amongst the most stable organophosphorus compounds with regard to both thermal stability and the action of common chemical reagents. Thus, triphenylphosphine oxide is thermally stable up to about 450 °C, although the higher chalcogenides are less so. The oxides are now known, however, to be more reactive than was at one time thought. The chemical reactivity of a tertiary phosphine chalcogenide is a function of the particular chalcogen present, in addition to the nature of the organic ligands attached to phosphorus. Indeed, part of the usefulness of many such compounds depends on the ease of cleavage of a phosphorus—carbon bond.

The nature of the P=X bond is not a subject of detailed discussion in this chapter, although a very brief general consideration is perhaps desirable. Although widely represented as a phosphorus-to-chalcogen double bond, the true nature of the bond depends on the individual element X, and also on the nature of the electronic interactions between phosphorus and the ligands R, e.g. whether these are halogen atoms or organic groups. It has been suggested, for instance, that the phosphoryl bond in a simple trialkylphosphine oxide has almost triple bond character.

Whatever the true nature of the P=X bond in any particular phosphine chalcogenide, such compounds are well known to form complexes through the atom X with an extremely wide range of compounds, including oxides, halides and other derivatives of both metals and non-metals. Phosphine oxides, in particular, form strong hydrogen bonds with carboxylic acids, phenols, alcohols and even more weakly bonding species such as $CHCl_3$, to yield complexes of various stoichiometries, mostly detectable spectroscopically, but sometimes isolable; triphenylphosphine oxide forms isolable hydrates. With strong mineral acids, the structure of the complex may lie between that of a simple hydrogen-bonded species and a fully protonated ion (Scheme 1). Hydrogen bonding, normally intermolecular, as in the cases just mentioned, and for appropriately separated groups as in the oxide $Ph_2P(O)(CH_2)_nOH$ when $n = 4$, is intramolecular for $n = 1\text{–}3$[1].

$$R_3P{=}O + HX \rightleftharpoons R_3P{=}O\cdots H\cdots X \rightleftharpoons R_3P^+OHX^-$$

SCHEME 1

The basicity of a tertiary phosphine oxide is due to the nucleophilic character of the phosphoryl group and its desire to protonate; as a class, such oxides are weaker bases than the corresponding tertiary amine oxides, but are stronger bases than similar carbonyl compounds.

Organic derivatives of the phosphinoyl* group, $H_2P(O)$—, exert an electron-attracting effect by induction or mesomerism, in appropriate environments, to an extent dependent on the attached organic groups. This electronic influence leads to enhanced acidity of compounds having hydrogen atoms on carbon bonded directly to phosphorus, and a greater potential for tautomerism. Thus, 1-(diphenylphosphinoyl)propan-2-one,†

---

*This terminology is becoming more widely accepted (IUPAC) than the term phosphinyl, although the latter is used by *Chemical Abstracts*; for further discussion of terminology, see Chapter 1 of Volume 1.

†This compound might also be termed (2-oxopropyl)diphenylphosphine oxide. Both types of nomenclature will be used interchangeably in this chapter.

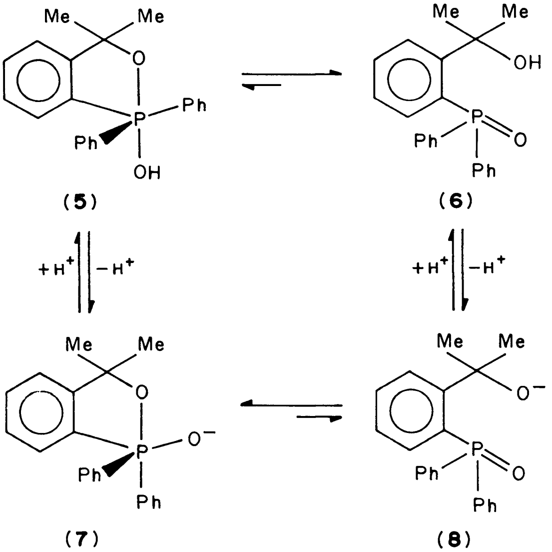
$Ph_2P(O)CH_2COMe$, contains about 2% of an enol (i.e. oxygen acid) form, an enol content very much greater than that in acetone itself or even in benzyl methyl ketone[2].

Evidence for prototropy involving the phosphoryl group in tertiary phosphine oxides seems to have come to light only recently. Diphenylphosphinoylbis(phenylsulphonyl)-methane normally exists in the CH form (**4.1**) and is a relatively strong acid with pK_a 3.27 in 95% aqueous EtOH. The rapid acidification of a solution of its sodium salt leads to samples enriched in the form **4.2**, as evidenced by the presence of two signals in its ^{31}P NMR spectrum, and the formation of an *O*-Me derivative on reaction with MeI, Me_2SO_4 or CH_2N_2. The ylide form reverts to the CH acid form when such samples are recrystallized[3,4].

$$\underset{\textbf{(4.1)}}{Ph_2P(O)CH(SO_2Ph)_2} \rightleftharpoons \underset{\textbf{(4.2)}}{Ph_2P(OH){=}C(SO_2Ph)_2}$$

There is also some evidence for the limited occurrence of 'ring-chain' tautomerism involving the phosphoryl group as exemplified in Scheme 2. Although the equilibrium between structures **5** and **6** lies well over to **6**, the equilibrium between **7** and **8** is strongly biased towards the pentacoordinate form **7**[5].

The chemical reactions of phosphine oxides[6,7] and sulphides, selenides and tellurides[8,9] have been reviewed; the reader should consult those sources for most literature references published before about 1965. The emphasis in this chapter is on those reactions discovered or developed during the last two to three decades, and the scope covers reported developments up to the end of 1990, with *Chemical Abstracts* surveyed to the end of Volume 113.



SCHEME 2

The chemistry of phosphine chalcogenides is discussed here in terms of the properties of the P=X bond and the reactions of the organic ligands attached to phosphorus. Included is a special section dealing with phosphine oxide carbanions and the special role they play in organic synthesis (the Horner reaction). Other sections deal with the stability of the intervening phosphorus—carbon bond and the chemistry of secondary and primary phosphine chalcogenides, treated separately because of the special properties endowed on these compounds by the phosphorus—hydrogen bond.

II. REACTIONS OF THE CHALCOGENIDE GROUP

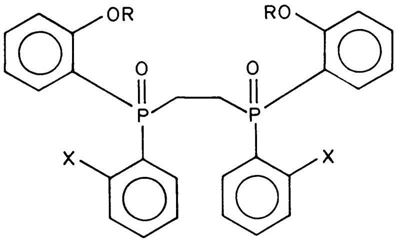
This section is intended as an outline of those reactions by which the chalcogenide group, P=X (X = O, S, Se or Te) can be removed so as to leave the corresponding phosphine, and also the various reactions by means of which one such group may be converted into another or to yet other groupings. Both types of sequence are of importance in synthetic organophosphorus chemistry.

A. Reduction of Quinquevalent Tetracoordinate Compounds to Tervalent Tricoordinate Compounds

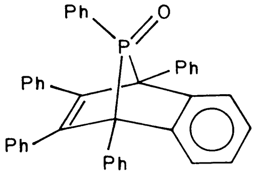
The removal of the P=X bond from phosphine chalcogenides can be achieved through the use of a wide variety of types of reagents acting under very varied conditions. Not all of the reactions described would necessarily be considered as being of value for synthetic purposes, since it has often been found that slight variations in experimental conditions may lead to an unexpected outcome with respect to either the nature or the stereochemistry of the reaction product(s).

1. Phosphines from phosphine oxides

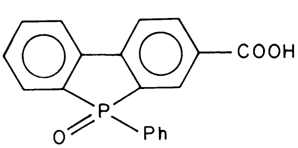
The potential for the use of simple metal hydrides in reductions of phosphine oxides to phosphines has not been fully explored. Successful reductions of simple trialkyl- and triaryl-phosphine oxides to the respective phosphines have been performed with the hydrides of calcium or aluminium. CaH_2 reduces Ph_3PO to Ph_3P, the yield of the latter decreasing with increase in reaction temperature, but some cleavage to benzene and Ph_2PH, which may be accompanied by the liberation of diphenylphosphinic acid, is also observed[10]. AlH_3 is a better reagent for the reduction of the oxides **9** (X = H or



(9)



(10)



(11)

OR; R = H, Me, Et or Bu^t)[11]. $Ph_3P(O)$ has also been reduced by trialkylboranes, dimeric dialkylboranes and borane–trialkylamine complexes, and even by a triphenylphosphine–borane complex at 120–150 °C[12], but the reduction may also be achieved by the use of SmI_2 in thf–hmpa at lower temperatures[13]. Oxides with at least one P-aryl grouping are reduced in moderate yield by a stoichiometric amount of $[Cp_2TiCl_2]$–Mg in thf, and the yields for the series $Ph_nP(O)Me_{3-n}$ increase as n increases; other tertiary phosphine oxides, e.g. Bu_3PO, may not be reduced by this reagent[14].

Much more attention has been focused on the use of $LiAlH_4$ and other complex hydrides. $Ca(AlH_4)_2$ is useful for the reduction of trialkylphosphine oxides but not for the triaryl analogues. On the other hand, $LiAlH_4$ reduces Ph_3PO satisfactorily in diethyl ether, but reactions in solvents with higher boiling points are again accompanied by fission to Ph_2PH; nevertheless, several successful reductions with $LiAlH_4$, with yields in the range 60–80%, have been reported[15,16]. Neither $LiAlH_4$ nor $LiAlH(OBu^t)_3$ was of value in attempted reduction of phosphine oxides at the low temperatures necessarily required to prevent valence isomerization of phosphonin 1-oxides[17], and attempted reduction of a bridged phosphine oxide (**10**) also failed because of the elimination of the phosphorus bridge and the formation of 1,2,3,4-tetraphenylnaphthalene[18].

Although the use of $LiAlH_4$, with its known ability to reduce a wide range of functional groups, might thus seem to have distinct disadvantages for synthetic purposes, one of its main drawbacks is, without doubt, the possibility of reduction accompanied by racemization. Some optically active phosphine oxides, e.g. (*S*)-(−)-Bu^tMePhPO, have been reduced with little loss of optical purity[19], whereas for other compounds, e.g. 5-phenyl-5*H*-dibenzophosphole-3-carboxylic acid 5-oxide (**11**), reduction to the phosphine is accompanied by reduction of the COOH group and by complete racemization.

In 1969, Mislow and coworkers[20] reported that phosphine oxides may undergo stereomutation in the presence of $LiAlH_4$ even before the actual reduction process has commenced. In thf at room temperature, (+)-MePhPrPO is almost completely racemized before 10% reduction has occurred; similar observations were made with the *cis* and *trans* forms of 1-phenyl-2,2,3,4,4-pentamethylphosphetane 1-oxide, stereomutation being completed within 10 min. Complexes of the type $Li[Al(OHPR_3)_4]$ may play a role in such stereochemical changes[20].

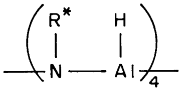
The addition of $CeCl_3$ to mixtures of triarylphosphine oxides and $LiAlH_4$ in thf results in much increased yields of the phosphines, although again this may be accompanied by complete racemization, a feature found for (*S*)-(2-An)MePhPO[21]. Reduction of phosphine oxides with $NaBH_4$ occurs only in the presence of $CeCl_3$; initially this reaction yields the phosphine–BH_3 complex (60–90%) from which the borane may be removed, with retention of configuration relative to the starting oxide, by treatment with Et_2NH[22].

Reduction of phosphine oxides with simultaneous asymmetric induction has been observed following the use of the chiral aminoalanes **12** and **13** (where R* represents a chiral organic group). Reduction of racemic MePhPrPO with the alane **13** derived from methyl-(*S*)-2-phenylethylamine afforded a 30% yield of the phosphine possessing about 20% induced optical activity. Potential difficulties in the widespread use of the procedure are well illustrated by the reduction of 3-methyl-1-phenyl-3-phospholene 1-oxide (**14**),[†] when both the extent and the sign of the induced optical activity are dependent on the presence of Et_3N, and also the reaction temperature within fairly narrow limits[23].

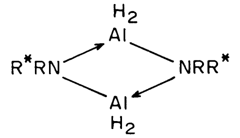
Far more extensively used than any of the hydride or other metal reagents hitherto mentioned have been a variety of silicon compounds. A mixture of methylchlorosilanes reduces Ph_3PO in very high yield but the scope of this reduction procedure has not

---

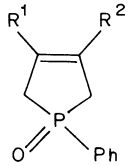
[†] Such compounds may also be referred to (and currently are in *Chemical Abstracts*) as 2,5-dihydro-1*H*-phospholes.



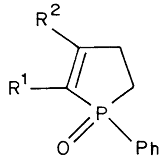
(12)



(13)



(14) $R^1 = Me; R^2 = H$
(15) $R^1 = R^2 = Me$
(16) $R^1 = R^2 = H$



(17) $R^1 = H; R^2 = Me$
(18) $R^1 = R^2 = H$
(19) $R^1 = Ph; R^2 = H$

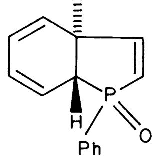
been explored[24]. Polysiloxanes, $(OSiHMe)_n$, may be employed in the presence or absence of a solvent, but higher temperatures are required for the reduction of triarylphosphine oxides; yields of about 60–90% have been achieved using diethylene glycol dimethyl ether as solvent, and the reagent has been used successfully with the cyclic oxides **15** and **17**[10].

Much attention has been focused on the use of trichlorosilane and the phenylsilanes, Ph_nSiH_{1-n}. Advantages in the use of the phenylsilanes as reducing agents include their ready availability, either commercially or through the reduction of the corresponding chlorides with $LiAlH_4$, and the high reaction yields coupled, under appropriate circumstances, with very high stereospecificity with retention of configuration. Phenylsilane has been used for the reduction of allylic phosphine oxides (**20**) and the phosphine oxide moiety $R_2P(O)\,(CH_2)_n$— bound to a solid support[25], and also phosphine oxides having the general structures $Ar_2P(O)Me$[26] and $RMeP(O)Ph$[27]. Indeed, phenylsilane has been described as the reagent of choice for the reduction of phosphine oxides[28].

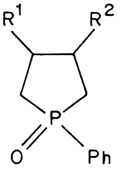
$Ph_2P(O)CR^1R^2CH{=}CH_2$ **(20)**

$Ph_2P(O)(CH_2)_nCN$ **(21)**

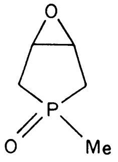
Diphenylsilane reduces the α-(diphenylphosphinoyl)alkyl cyanides **21** ($n = 1,3$ or 4)[29], and both mono- and di-phenylsilane reagents have been employed in the reduction of *P*-oxides of phospholenes, e.g. **15**, **18** and **19**[10], **16** and **22**[30], phospholanes, e.g. **23** and **24**[31,32], epoxides of types **25**–**27**[33] and simple phosphorinanes and phosphepanes **28**–**30**[28,34].



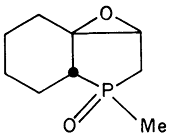
(22)



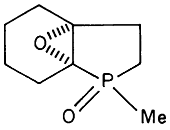
(23) $R^1 = H, R^2 = Me$
(24) $R^1 = R^2 = Br$



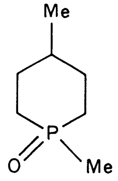
(25)



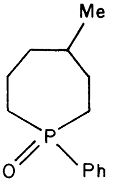
(26)



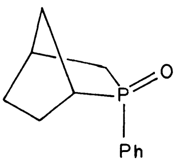
(27)



(28)



(29)



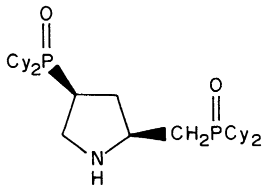
(30)

Phenylsilane deoxygenates (R)-($-$)-($PhCH_2$)MePrPO to the (S)-(+)-phosphine of comparable optical purity, and a similar result is observed for (S)-($-$)-($PhCH_2$)MePhPO, i.e. reaction with retention of configuration[35]; by contrast, the same reagent reduces $(R)_P$-(menthyl)MePhPO to a 9:1 mixture of the $(S)_P$ and $(R)_P$ phosphines[36]. Epoxy, cyano, bromo and vinyl groups are evidently tolerated by the phenylsilane reagents.

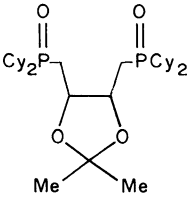
Trichlorosilane (silicochloroform), $SiHCl_3$, has been the most widely examined of all the silicon hydrides for the deoxygenation of phosphine oxides. It is a powerful reagent, capable of reducing many types of phosphine oxides; at the same time, however, it is one which has to be used with some caution, particularly with regard to the assignment of configurational changes at phosphorus, and it is recommended that such assignments in the product phosphines be checked by re-oxidation with H_2O_2 (retention of configuration) or by spectroscopic means, e.g. ^{13}C NMR spectroscopy.

In a pioneering study, Horner and Balzer[37] showed that trichlorosilane reduced phosphine oxides with retention of configuration; however, reduction in the presence of Et_3N or, even better, Bu_3N, resulted in inversion of configuration at phosphorus, whereas the use of pyridine or N,N-diethylaniline brought about no such change. In practice, the reagent is employed with or without added base in a solvent ($CHCl_3$, benzene or a higher boiling aromatic), generally under reflux conditions. Phosphine oxides so reduced include trialkyl[38], dialkylaryl[39,40], alkyldiaryl[41,42] and triaryl[38,43] derivatives, in which several functional groups, including CN, COOH, COOR, NO_2,

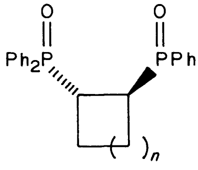
(n= 2 or 3)[52] and **37**[53]



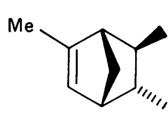
(31)



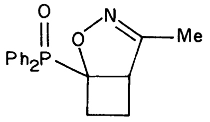
(32)



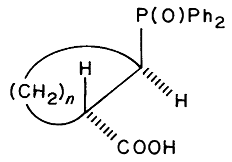
(33)



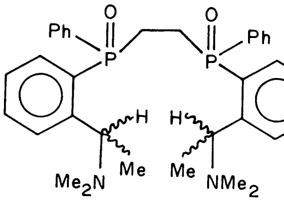
(34)



(35)



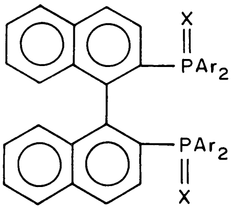
(36)



(37)

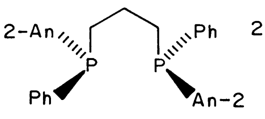
NR_2, $NR_3{}^+$ or OMe, particularly when attached to aromatic rings, are unaffected by the reagent. Other phosphine oxides of some special interest and which have been successfully reduced include 2-(dicyclohexylphosphinoyl)-4-[(dicyclohexylphosphinoyl)-methyl]pyrrolidine (**31**)[44], 4,5-bis[(dicyclohexylphosphinoyl)methyl]-2,2-dimethyl-1,3-dioxolane (**32**)[45] and the diphenylphosphinoyl compounds **9**[11,46,47], **33** ($n = 0$[48] or 1[49]), the enantiomers of methylnorphos dioxide (**34**)[50], **35**[51], racemic **36**.

Other applications include the syntheses of optically active forms of the binaps ligands **38** (X = lone pair; Ar = Ph, 4-tol, or 4-Bu^{t}C$_6$H$_4$) from the resolved forms of the binaps dioxides **38** (X = O)[54], and of the ligands **39** and **40** (using *N*,*N*-diethylcyclohexylamine as base in MeCN)[55], during which inversion at phosphorus was assumed to have taken place. In the presence of Et_3N, the reagent reduced (*R*)-(menthyl)methylPhPO to a 4:1 mixture of $(R)_P$ and $(S)_P$ phosphines, i.e. with largely, but by no means exclusively, inversion[36].

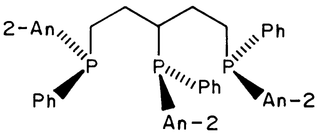


(38)

An = anisyl

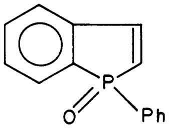


(39)

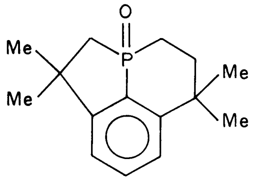


(40)

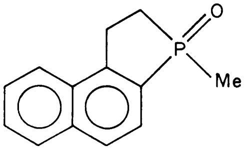
The many types of cyclic phosphines oxides possessing the phosphorus atom in a non-bridging position, which have been reduced to the corresponding phosphines by trichlorosilane, in the presence or otherwise of added amine, include phospholes and their benzo derivatives, e.g. **41**[56]; phospholenes and their benzo derivatives, e.g. **42**[57], **43**[58], **44**[59], **45** and **46**[60], **47**[61], **48** and **49**[62]; **17**[37]; 5,10-dihydrodibenzo [*b*,*e*]phosphorins,



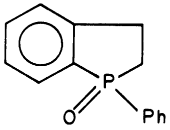
(41)



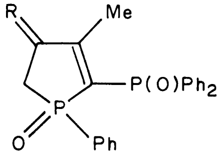
(42)



(43)

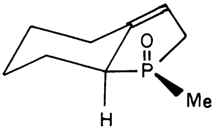


(44)

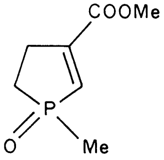


(45) $R = CH_2$

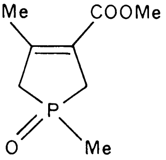
(46) $R = O$



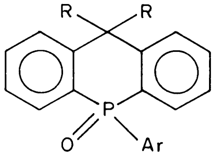
(47)



(48)

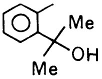


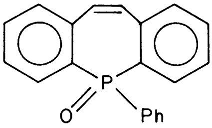
(49)



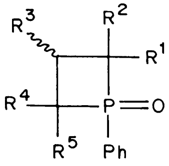
(50) $R_2 = {=}O$; Ar = Ph

(51) R = Me, Ar =

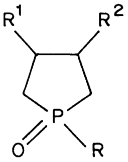




(52)

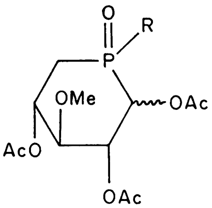


(53)

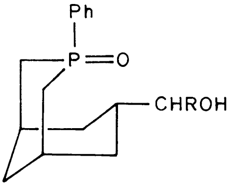


(54) $R = Me$; $R^1 = H$; $R^2 = Me$

(55) $R = CH_2Ph$; $R^1 = R^2 = Br$

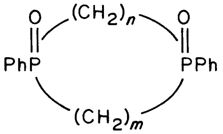


(56)

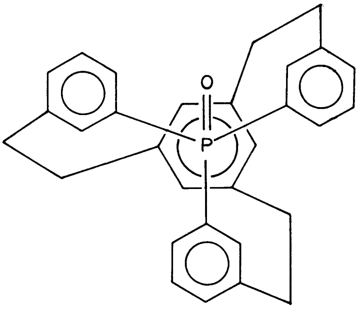


(57)

e.g. **50**[63] and **51**[64]; 5-phenyl-5*H*-dibenzo[*b*, *f*]phosphepin 5-oxide **52**[65]; the phosphetanes **53** (R^1–R^5 = H or Me)[66]; phospholanes, e.g. **54**[67] and **55**[68]; phosphorinanes **56** (R = Et or Ph)[69]; **57** (R = H or Ph)[70,71]; the large-ring compounds **58**[72]; and the phosphacyclophane **59**[73]. Within these systems, OAc, OMe, Br, CH_2OH, CR_2OH and COOMe groups appear to tolerate the reagent.

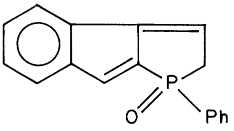


(**58**) *n* = 8 or 10 ; *m* = 8, 10 or 12

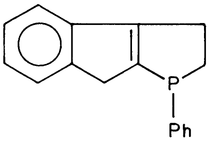


(**59**)

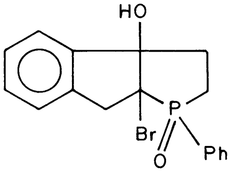
A few examples exist for which unfortunate side-reactions become prominent. Thus, attempted reduction of the oxide **60** yields the phosphine **61**, also obtained when **62** is similarly reduced. In the presence of pyridine, **60** is simply deoxygenated[74].



(**60**)

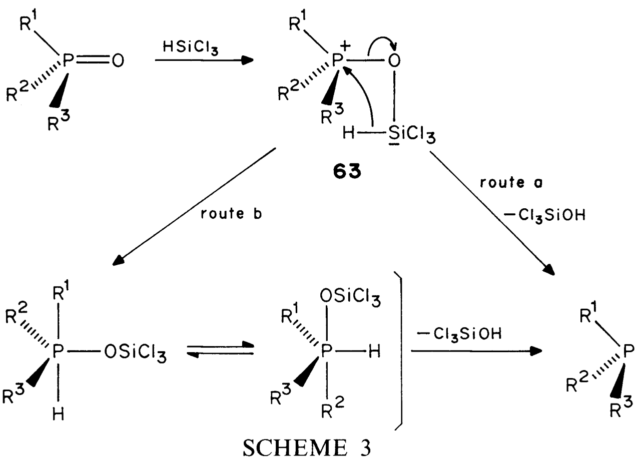


(**61**)



(**62**)

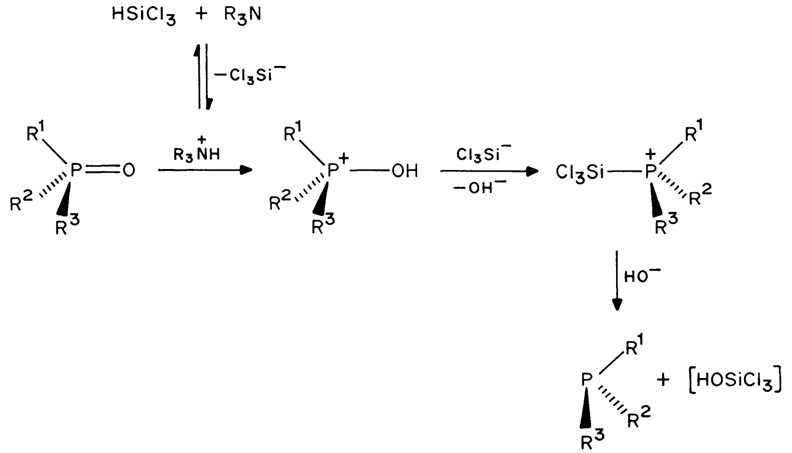
Horner and Balzer[37] rationalized their original observations on the trichlorosilane reduction of phosphine oxides, with net retention, with an explanation (Scheme 3)



SCHEME 3

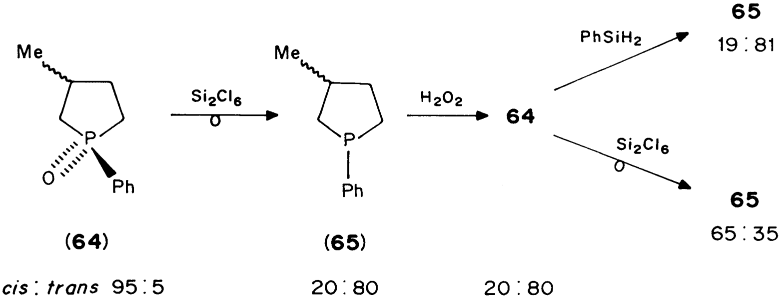
involving complexation and a hydride shift followed (route a) by direct loss of silicon; later authors raised the possibility of the intermediacy of pentacoordinate species (route b), possibly resulting from a rearrangement of structure **63**[75].

To rationalize the net inversion observed when the oxides are reduced in the presence of Et_3N, Horner and Balzer stressed the importance of complexation between the reagent and the added tertiary base (and certainly such complexation is well known to occur), but this consideration has been shown to be unimportant[75]. More striking is the possible relevance of base strength. When a base with $pK_B <$ ca 5 (Et_3N, pK_B 3.26) is used, largely inversion of configuration is observed. Largely retention of configuration is to be noted using those bases with pK_B of $\geqslant$ ca 7 (pyridine, pK_B 8.81; Et_2NPh, pK_B 7.44). Moreover, the type of base is also of some importance; the use of primary or secondary amines can lead to results entirely different from those observed with tertiary amines. A further complicating feature is the dependence of the final stereochemical outcome on the nature of the reaction solvent; $HSiCl_3$ with Et_2NPh in benzene or dibutyl ether reduces $(PhCH_2)MePhPO$ largely with retention of configuration, but in acetonitrile the reaction proceeds with predominant inversion. A mechanism proposed later[75] for the inversion process is oulined in Scheme 4, but here again there remains the question as to the possible participation of pentacoordinate intermediates in the later stages.



SCHEME 4

The potential usefulness of disilane derivatives with Si—halogen bonds as reducing agents was suggested by two features of silicon chemistry: the known reducing power of such compounds, and the fact that the freshly prepared adduct from $HSiCl_3$ and Et_3N liberated hydrogen when placed in aqueous base. Thus, the oxides MePhP(O)R (R = allyl, $PhCH_2$ or 4-An), each of 100% optical purity, were reduced to the corresponding phosphines of 67, 95, and 94% optical purities, respectively, and with inverted configurations, when treated with Si_2Cl_6, similar results being obtained with the use of Si_3Cl_8[75]. Configurational inversions were also noted in the reductions of (R)-Bu^{t}MePhPO[76], and both $(R)_P$ and $(S)_P$-(menthyl)MePhPO[36]. Extensive inversion also occurred in the reduction of a 95:5 *cis*: *trans* mixture of 3-methyl-1-phenylphospholane 1-oxides (**64**) (Scheme 5)[32].

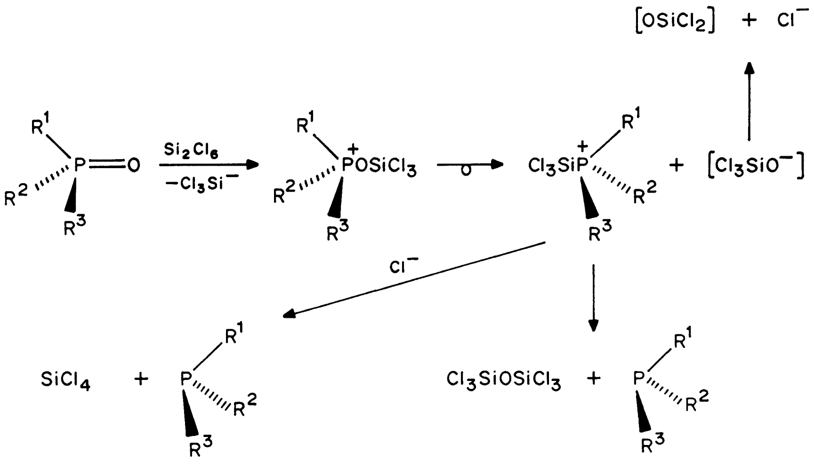


SCHEME 5

The lack of stereospecificity in reductions by Si_2Cl_6 has been attributed to the formation of $SiCl_4$ and the stereomutation that this compound is known to cause[77,78]. When the phosphine **65** was treated with $SiCl_4$, the *cis:trans* composition ratio 20:80 became 45:55[32]. At room temperature, $SiCl_4$ causes complete stereomutation of $(PhCH_2)MePhPO$ in MeCN during 20 min, and the degree of stereomutation increases if the contact time between substrate/product and Si_2Cl_6 reagent (and thus also $SiCl_4$) is greater than about 5 min.

A proposed mechanism (Scheme 6) for reductions with S_2Cl_6 accommodates the formation of $SiCl_4$, and the sequence probably proceeds via the intermediate $R^1R^2R^3P(OSiCl_3)SiCl_3$, which is unlikely to undergo isomerization since the more electronegative groups are already in the apical positions of a trigonal bipyramid.

Phosphetane 1-oxides are reduced by silicon reagents under conditions significantly milder than those normally required for unbranched acyclic phoshine oxides, although the outcome of such reductions may be less predictable. There appears to be no stereospecificity dependence on the presence, or otherwise, of a tertiary base (Et_3N, pyridine) for reductions with $SiHCl_3$ which, for this group of substrates, has been used with[66,79,80] or without base[79,81]; in the presence of Et_3N, $SiHCl_3$ reduces hexamethyl-

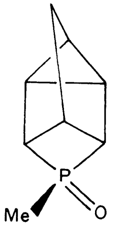


SCHEME 6

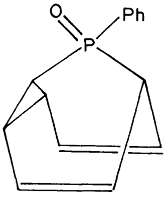
phosphetane 1-oxide with retention of configuration, and although the same reagent in the presence of pyridine also reduces 2,2,3-trimethyl-1-phenylphosphetane 1-oxide stereospecifically, the reduction of the latter phosphetane oxide by $SiHCl_3$ in the presence of Et_3N depends on the ratio of substrate to reagents for the stereochemical outcome. Other reagents which have been used with phosphetane substrates include 'silicone fluid'[81], $PhSiH_3$[82] and Si_2Cl_6[78]. 4-Methyl-4-phosphatetracyclo[3.3.0.0^{2,8},0^{3,6}]octane 4-oxide (**66**) is reduced, with 100% yield, to the *endo* phosphine (inversion) with $SiHCl_3$ alone[83] but to a mixture of *endo* and *exo* products in the ratio 2:1 when pyridine is present[79].

As the severe angular constraint present in the phosphetane ring is relaxed, as it is in the monocyclic phospholane and larger saturated ring systems, reduction of the oxides to the parent phosphines by silicon reagents proceeds more predictably with retention of configuration.

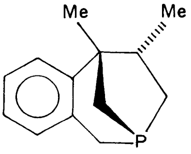
A structural feature which has been shown to have a pronounced effect on the final reaction outcome is the constraint imposed by phosphorus at a bridgehead position. When the phosphorus bridge produces no particular strain, reductions of *P*-oxides proceeds normally, as has been found for compounds **67** with $SiCl_6$[18], *endo*-3-phenyl-3-phosphabicyclo[3.2.1]octane 3-oxide (**30**) with $PhSiH_3$ and compound **68** with $SiHCl_3$ alone[34,84], the phosphines being obtained essentially with retained stereochemistry and no loss of phosphorus bridge.



(66)



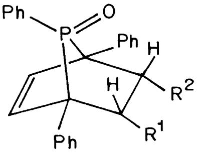
(67)



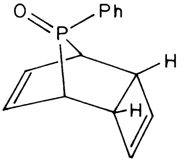
(68)

Many compounds in the 7-phosphanorbornene system, of which **10** is one, behave unusually towards silicon reducing agents. Thus, with Si_2Cl_6, [79] **10** loses the phosphorus bridge to yield 1,2,3,4-tetraphenylnaphthalene, as it does when treated with $LiAlH_4$[18]. Initially, the *syn*-1,4,7-triphenyl-7-phosphabicyclo[2.2.1]hept-5-enes **69** and **70** with $SiHCl_3$–pyridine yield the corresponding *syn*-phosphines, but for each the main isolable product is $(PhP)_4$. With $SiHCl_3$ alone, 9-phenyl-9-phosphatricyclo[4.2.1.0^{2,5}]nona-3,7-diene 9-oxide (**71**) is reduced but the product rapidly loses bridgehead phosphorus as $PhPH_2$ to give cyclooctatetraene; addition of pyridine to the initial reduction mixture allows the isolation of the expected *anti*-phosphine in ca 80% yield.

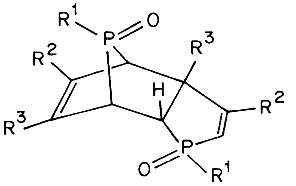
The most unusual results relate to the 3a,4,7,7a-tetrahydro-4,7-phosphinidine-1*H*-phosphindoles **72**–**76**, recognizable as phosphole 1-oxide dimers. When treated with $SiHCl_3$ in boiling benzene, these compounds lose the bridging phosphorus as R^1PH_2 and the 1-R^1-*cis*-3a,7a-dihydrophosphindoline (**78**, $R^1 = Me$ or Ph) co-products are isolable[59,79]. The presence of pyridine, although not always required, as, for example, for **74** and **75**, certainly allows normal reductions to proceed with high yields and with retention of molecular geometry. Reductions of the same compounds with $PhSiH_3$ consistently afforded the bisphosphines with inverted geometry at the bridgehead phosphorus atom as the main products (ca 70%), together with the isomer with retained *syn* geometry as the minor products (8–27%).



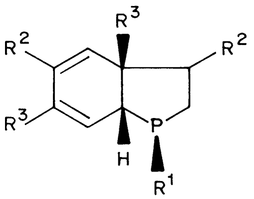
(69) $R^1 = CN$; $R^2 = H$
(70) $R^1 = R^2 = COOMe$



(71)

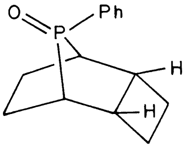


(72) $R^1 = Me; R^2 = R^3 = H$
(73) $R^1 = Ph; R^2 = R^3 = H$
(74) $R^1 = R^2 = Me; R^3 = H$
(75) $R^1 = Ph; R^2 = Me; R^3 = H$
(76) $R^1 = R^2 = R^3 = Me$
(77) $R^1 = Ph; R^2 = R^3 = Me$

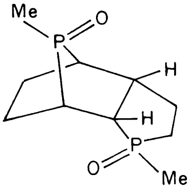


(78)

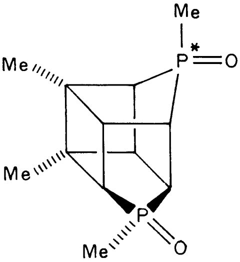
The fragmentations with loss of bridgehead phosphorus are examples of retro-cycloaddition reactions (in this case retro-McCormick reactions) and they do not occur for fully saturated analogues. The 7-phosphanorbornane **79** and 1-*syn*-8,8-dimethyl-2,3,3a,4,5,6,7,7a-octahydro-4,7-phosphinidine-1*H*-phosphole (**80**) are reduced by $SiHCl_3$ with configurational retention in 93% and 30% yields, respectively. The cage compound **81** is reduced by $SiHCl_3$ alone with inversion of P* stereochemistry, but, in the presence of pyridine, or when $PhSiH_3$ is employed, the stereochemistry is retained at both phosphorus centres.



(79)

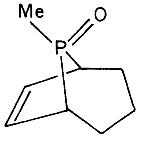


(80)

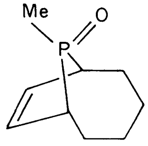


(81)

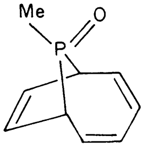
Angular constraint can be relieved by enlarging the component rings of such molecules. Both 8-phosphabicyclo[3.2.1]octene **82** and its homologue **83**, as mixtures of *syn* and *anti* isomers, afford mixtures of the phosphines of comparable stereochemical content when deoxygenated with $SiHCl_3$ irrespective of the presence, or otherwise, of pyridine; interestingly, the 9-phosphabicyclo[4.2.1]nonatriene **84** with $SiHCl_3$ alone gives only phosphine with retained geometry.



(82)

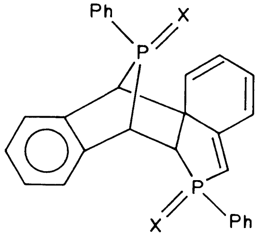


(83)

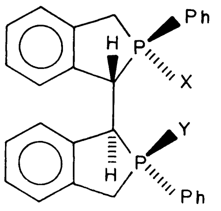


(84)

Compound **85** behaves even more unusually when treated with $SiHCl_3$. In the presence of Et_3N at ambient temperature, cleavage occurs at one of two possible positions to give the bisphosphindoline monoxide (**86.1**). Loss of PhPO from a bridging position evidently does not occur, nor does reduction to the bisphosphine **86.2** unless the reaction temperature is raised to 60 °C; both products may be oxidized to the bisoxide[84].



(85)



(86.1) X = lp†, Y $=$ O
(86.2) X = Y = lp^{a}

There are thus many opportunities to make erroneous predictions about the stereochemical outcome of reductions of phosphine oxides with silicon-containing reagents; nevertheless they are powerful reagents. The existence of isomerization and retro-cycloaddition processes calls for the participation of pentacoordinate intermediates.

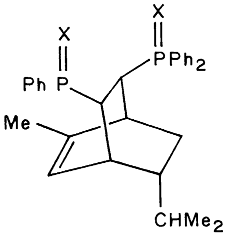
2. Phosphines from phosphine sulphides, selenides and tellurides

Several types of tertiary phosphine sulphides have been desulphurized successfully by a wide variety of reagents under conditions which have ranged from mild to severe. Iron powder, NaH at 250–300 °C or Na with naphthalene[85] were amongst the earliest reagents used. Sodium under boiling toluene has been the reagent of choice for alkyldiarylphosphine sulphides; specifically, this reagent has used in the synthesis of (*S*, *S*)-phellanphos (**87**) (X = lp) and norphos (**88**) (X = lp) by the removal of the thiophosphoryl sulphur from the corresponding sulphides, in turn obtained from phellandrene and nopadiene, respectively[86]. Unlike oxygen from a phosphine oxide, sulphur is removable from a phosphine sulphide under Birch conditions [Li–NH_3 (l)]. By contrast to the high reactivity shown towards Ph_3PS, sodium with naphthalene fails to desulphurize $Me_2P(S)CH_2CH_2P(S)Me_2$, a compound also unreactive to $LiAlH_4$ in thf[87]. Nevertheless, $LiAlH_4$ in dioxane has proved popular as a desulphurizing agent. Luchenbach[88], using

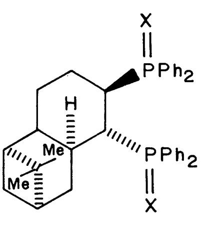
---

† lp = Lone pair of electrons.

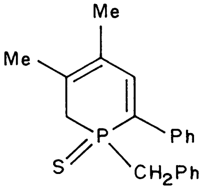
(*R*)-(+)-MePhPrPS showed that, in either thf or dibutyl ether at 65 °C, $LiAlH_4$ removed the sulphur with complete retention of configuration at phosphorus. The 1,2-dihydrophosphorin 1-sulphide **89** was desulphurized by nickel powder at high temperature, but also suffers debenzylation to 2-phenyl-4,5-dimethylphosphorin[89].



(87)



(88)



(89)

In studies on poly(tertiary phosphine) ligands, King and coworkers resorted to their synthesis through the corresponding sulphides, since this obviated the need to work with more volatile and obnoxious phosphines; the synthesis of the target compounds was completed by the removal of sulphur with $LiAlH_4$ in boiling dioxane. In this way the phosphine sulphides $Me_nP(S)\,(CH{=}CH_2)_{n-3}$ proved more attractive staring materials than the corresponding phosphines. An example of their use is illustrated in Scheme 7[90,91].

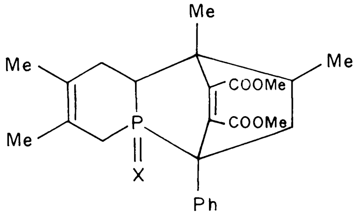
$$Me_2P(S)CH{=}CH_2 \xrightarrow{Ph_2PH} Ph_2PCH_2CH_2P(S)Me_2 \xrightarrow{LiAlH_4} Ph_2CH_2CH_2PMe_2$$

SCHEME 7

Amongst the more recent developments in desulphurization processes is the use of metal complexes. Mathey found that the slight reduction to the phosphine when 3,4-dimethyl-1-phenyl-3-phospholene 1-sulphide was treated with nickelocene at 110 °C for 20 h increased if the reaction was carried out in diglyme[92,93]. Most of the product phosphine was evidently incorporated into a complex, but could be liberated from that with NaCN in MeOH, or by *N*-methylimidazole[94] or $(MeO)_3P$[95]. The treatment of a tertiary phosphine sulphide with $[Fe(CO)_5]$ at 130–150 °C yields the complex $[R_3PFe(CO)_4]$ which, with $CuCl_2$ in MeOH, gives $[(R_3P)_2Fe(CO)_2Cl_2]$; when heated, or when treated with *N*-methylimidazole, such complexes release the phosphine in a process compatible with the presence of alcohol and carbonyl functions. This procedure appears to have the advantage over the nickelocene process in being less sensitive to steric hindrance around phosphorus[96].

Other reagents which have been explored for the purpose of removing the higher chalcogens are compounds of tervalent phosphorus, including trialkyl phosphites and hexamethylphosphorous triamide for triarylphosphine sulphides[97,98] and tris(2-cyanoethyl)phosphine[99] and tributylphosphine for phosphole 1-sulphides[100]. The bicyclic phosphorin sulphide **90.1** suffers fragmentation when treated with Bu_3P in benzene at 150 °C, but it is unclear whether the fragmentation occurs before, or after, elimination of sulphur[101].

Phosphine selenides and, even more particularly, tellurides, are notoriously unstable and lose the chalcogen spontaneously[102].



(**90.1**) X = S

(**90.2**) X = O

Of greater interest are those occasions on which the P = X bond finds itself near to a tervalent phosphorus atom in the same molecule. Does chalcogen transfer occur spontaneously? When **91.1** is heated at 160 °C in ethylene glycol dimethyl ether the sulphur is transferred to the more basic, tervalent, phosphorus atom to give **91.2** to the extent of about 85%; during the course of the reaction the disulphide **91.3** and the diphosphine **91.4** were identified as intermediates[103]. The extent of the transfer depends on the basicity of the phosphine moiety and, for example, does not occur cleanly for the di-*tert*-butylphosphine **92**[104]. In addition, mixtures of disulphides **93.1** and diphosphine **93.2** equilibrate to the monosulphide **93.3** when $n = 2$ but not when $n = 1$. The transfer of selenium or tellurium to the phosphine phosphorus is fast on the NMR time scale; mixing **93.4** ($n = 1$) and the corresponding diphosphine results in the immediate formation of the monoselenide **93.5** ($n = 1$), in a process faster than that for the analogous sulphides[105]. In the case of tellurium, Te-bridged species may be formed as indicated in Scheme 8[106].

$Ph_2P(X)CH_2P(Y)Me_2$
(**91.1**) X = S; Y = lp
(**91.2**) X = lp; Y = S
(**91.3**) X = Y = S
(**91.4**) X = Y = lp

$Ph_2P(S)CH_2PBu^t_2$
(**92**)

$Ph_2P(X)(CH_2)_nP(Y)Ph_2$
(**93.1**) X = Y = S
(**93.2**) X = Y = lp
(**93.3**) X = S; Y = lp
(**93.4**) X = Y = Se;
(**93.5**) X = Se; Y = lp

$$\mathrm{Bu^t_3P(Te) + Bu^t_3P} \xrightleftharpoons{\text{rapid}} \mathrm{Bu^t_2PTePBu^t_2}$$

$$\begin{tikzcd} \mathrm{Bu^t_3P(Te) + Bu^t_2PEMe_3} \arrow[r] & \mathrm{Bu^t_2PTeEMe_3} \arrow[d, shift left] \\ \mathrm{E = Si,\ Ge\ or\ Sn} & \mathrm{(Me_3E)_2Te + Bu^t_2PTePBu^t_2} \arrow[u, shift left] \end{tikzcd}$$

SCHEME 8

Additional to its use for the deoxygenation of tertiary phosphine oxides, Si_2Cl_6 has also been employed for the removal of sulphur from phosphine sulphides[104]. The use of chiral phosphine sulphides has demonstrated the stereospecificity of the reaction with retention of configuration at phosphorus[107].

A well characterized indirect method for the removal of sulphur or selenium from a tertiary phosphine sulphide or selenide consists in the formation of a quaternary salt (Section II.C) with subsequent removal of the chalcogen as a disulphide or deselenide. Thus, electrolysis of the salt $Ph_3P^+SMe\ MeSO_4^-$ yields 69% Ph_3P. The cleavage of the salts is also accomplished when they are treated with sodium ethylthiolate, as exemplified in equation 1[108]. That cleavage of the quaternary salts occurs with retention of configuration is shown by the formation of (*R*)-(+)-Bu^tEtPhP from the (*S*)-(+)-sulphide via the (*S*)-(−)-methylthiophosphonium triflate[108].

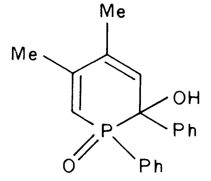
$$Ph_3P^+SMe\,CF_3SO_3^- + EtSNa \longrightarrow Ph_3P + Me_2S_2 + Et_2S_2 + MeSSEt \qquad (1)$$

In the case of particularly reactive compounds, e.g. tris(2,6-dimethoxyphenyl)-phosphine sulphides, a solution of an alkyl- or aryl-thiol (rather than its sodium salt) in MeOH is sufficient to complete the reaction[109]. Other quaternary salts of the same type have been cleaved by KCN in the presence of 18-crown-6 in CH_2Cl_2[110].

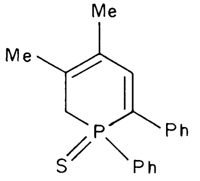
B. Interconversions of Quinquevalent Tetracoordinate Compounds

1. *Phosphine sulphides, selenides or tellurides from phosphine oxides*

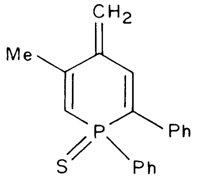
Early reports indicated that tertiary phosphine sulphides could be prepared from the corresponding phosphine oxides by simply heating them with elemental sulphur at a moderate to high temperature, but such reports appear not to have been substantiated. Triarylphosphine oxides yield the corresponding sulphides when heated with P_4S_{10}[98,111] and enantiomers of MePhPrPO yield the racemic sulphide with the same reagent[112], although optically active sulphides do not racemize under the same conditions. The fused-ring tetrahydrophosphorin 1-oxide **90.2** has been converted into the sulphide[101], while the dihydrophosphorin 1-oxide **94** suffered dehydration and rearrangement during the sulphurization reaction with the same reagent to give **95** and **96**[113].



(94)



(95)



(96)

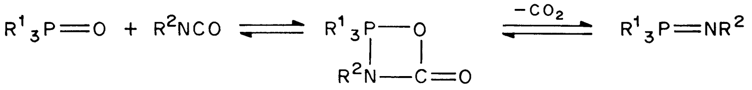
It is perhaps surprising that 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulphide (Lawesson's reagent), generally thought to be sulphurization reagent superior to P_4S_{10}, appears to have been used very seldom, a rare example of its use being in the conversion of the *endo*-dimeric phosphole dioxide **77** into the corresponding disulphide[114].

An unusual sulphurization reagent is B_2S_3 which, within the narrow range of substrate compounds examined, affords moderate conversions of phosphine oxides into the sulphides; stereospecificity was 65% with predominant retention of configuration for acyclic oxides, with some slight loss of optical purity, but with the loss in the latter for isomeric phosphetane oxides[115].

The reported formation of 5-phenyl-5*H*-dibenzophosphole 1-selenide, and of Ph_3PSe, by treatment of the corresponding oxides with Se–KH_2PO_4 at 270–370 °C, is possibly no more than sequential deoxygenation and selenation[116].

2. *Phosphine imides from phosphine oxides*

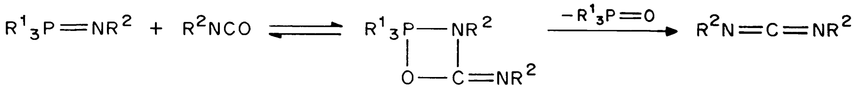
The first observations on the catalytic role of tertiary phosphine oxides on the formation of carbodiimides from isocyanates appear to have been made by Monagle and coworkers[117], who, from a study of the kinetics of the liberation of CO_2, recognized that the interaction occurred in two distinct stages. The first stage leads, via a four-membered ring pentacoordinate intermediate or transition state (**97**), to a phosphine imide as in Scheme 9. The sequence is reversible; phosphine imides are known to react with carbonyl compounds, including CO_2, when, in the latter case, isocyanates are formed.



(**97**)

SCHEME 9

The second stage, as in the Scheme 10, consists in the interaction of the imide and a second mole of isocyanate in a rapid process also proceeding through a similar type of intermediate or transition state. The overall reaction is that represented in equation 2.



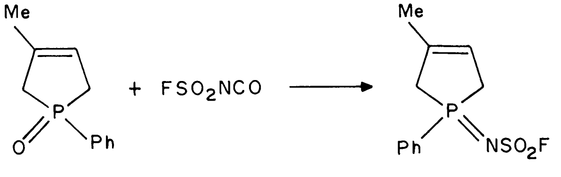
(**98**)

SCHEME 10

$$2R^2NCO \longrightarrow R^2N{=}C{=}NR^2 + CO_2 \qquad (2)$$

The first stage (Scheme 9) is rate determining, the reactions of phosphine imides with R^2NCO being 10^5–10^7 times faster than those of, for example, the oxides $Ph_nP(O)Et_{3-n}$. 1-Phenylphospholane 1-oxide is 10^3 times more reactive than $PhP(O)Et_2$ as a catalyst, whereas the ratio of catalytic power of the imide is only ca 10[118]. The most effective catalyst is 3-methyl-1-phenyl-3-phospholene 1-oxide.

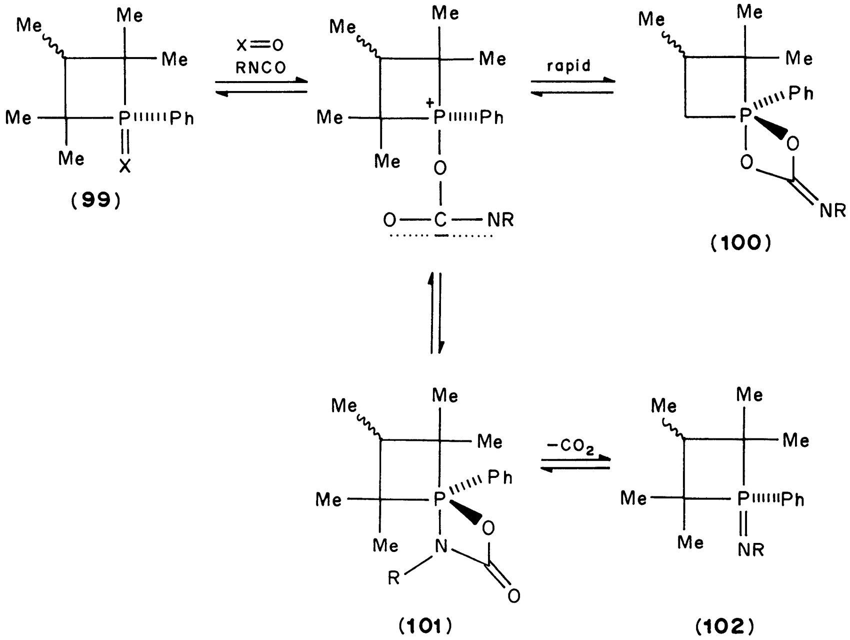
The formation of an imide from an isocyanate and a phosphine oxide (reaction 3) has since been demonstrated by other workers, but in this case the reaction proceeds no further[119].



(3)

The results of a study on the liberation of ^{18}O (as CO_2) from an oxide enriched at the phosphoryl group were also consistent with the overall picture represented in Schemes 9 and 10[120] but, because of difficulties in the interpretation of the kinetic results, Aksnes and Frøyer[118] proposed the participation of betaine intermediates which cyclize to give **97** and **98**.

Hall and Smith[121] investigated the stereochemical course of the reactions between cyclic phosphine oxides, as exemplified by the geometric isomers of phosphetane 1-oxides, and the isocyanates RSO_2NCO (R = Cl or 4-tol). Both *cis*- and *trans*-2,2,3,4,4-pentamethyl-1-phenylphosphetane 1-oxide gave imides with retention of configuration at phosphorus (Scheme 11).



SCHEME 11

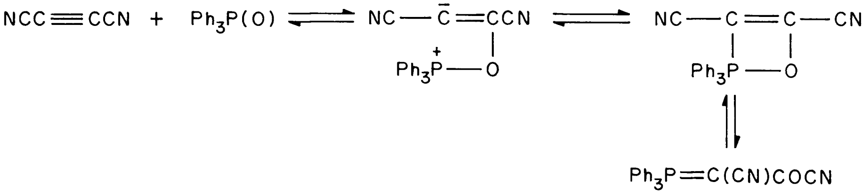
The proposed mechanism takes into account the types of betaine suggested by Aksnes and Frøyer[118], and which lead to pentacoordinate species of undetermined structure, although **101** is thought to be more probable than **100**. The reaction for the corresponding sulphide (**99**, X = S) was slower and 2 mol of TsNCO were required for each mole of sulphide, leading to **102** together with TsNCS via **99** (X = O). The formation of diphenylcarbodiimide from PhNCO and Ph_3PS at 165 °C had already been noted in 1964 by Maier[8].

In a second study, the reactions of acyclic phosphine oxides were shown to be slower than those of the phosphetane oxides; optically active oxides, e.g. enantiomers of $(PhCH_2)MePhPO$, are racemized faster (half-life ca 40 min) than the rate of formation of the imides (half-life ca 36 h). Three possible mechanisms were considered for the formation of a monocyclic phosphorane intermediate after initial betaine formation but, unfortunately, computer simulation of the kinetics failed to distinguish conclusively between them[122].

The feature distinguishing between the results of these two studies is clearly the constraint placed on stereomutational processes within any intermediate(s) by the presence of the phosphetane ring; this must occupy an equatorial–axial position in any pentacoordinate intermediate, and its formation would be followed by a collapse to give **102** with retention of configuration.

3. *Phosphine methylenes (ylides) from phosphine oxides*

Scheme 12 summarizes the remarkable interaction between triphenylphosphine oxide and acetylenes containing electronegative groups in a retro-Wittig reaction. The reactions between Ph_3PO and the acetylenes $RC{\equiv}CR'$, where $R = R' = CF_3$ or COOMe, and $R = CN$, $R' = H$, occur in the temperature range 120–200 °C[123].

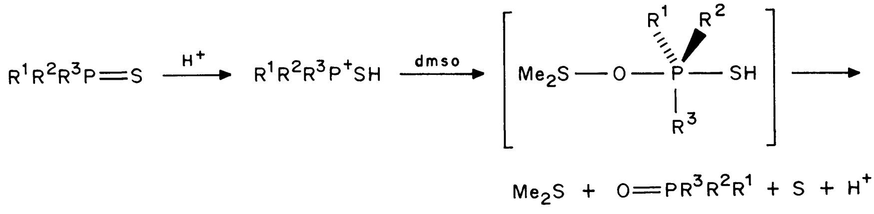


SCHEME 12

4. *Phosphine oxides from phosphine sulphides, selenides or tellurides*

Tertiary phosphine sulphides are relatively stable compounds which undergo atmospheric oxidation only on prolonged exposure, and they are therefore unlike the corresponding selenides and tellurides, which are much more readily oxidized and which also liberate the chalcogen on exposure to light and particularly on contact with surfaces[102].

Many of the more powerful oxidizing agents not only convert the P=X grouping (X = S, Se, or Te) into P=O, but also bring about additional, perhaps unwanted, reactions. Thus the action of nitric acid on Ph_3PS yields tris(3-nitrophenyl)phosphine oxide, also obtainable by the direct nitration of Ph_3PO; other dialkylarylphosphine sulphides behave analogously[124]. The treatment of (*R*)-(+)-MePhPrPS with HNO_3 at room temperature yields the (*S*)-(−)-oxide in a highly stereospecific reaction with inversion; when N_2O_4 is used, there is marked racemization in addition to retention of configuration[125]. $KMnO_4$ or acid dichromate readily convert P=S into P=O, but simultaneously bring about the oxidation of, for example, alkyl groups attached to aromatic rings. MePhPrPS is oxidized by $KMnO_4$–pyridine with predominant inversion of configuration at phosphorus. The same phosphine sulphide is oxidized by H_2O_2, and unlike the case of the corresponding selenide, the stereospecificity is here unaffected by experimental conditions such as change of solvent and reaction temperature[126].

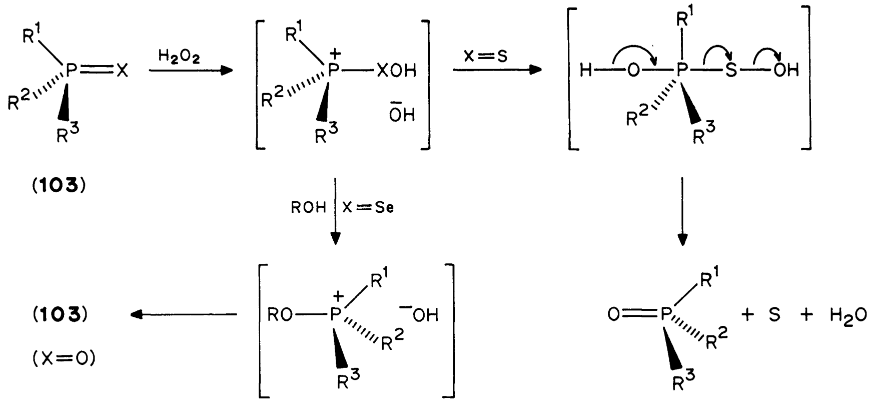


SCHEME 13

Following earlier proposals by Mikołajczyk in 1966, Luchenbach also suggested the use of dmso under acidic conditions, and showed that with tertiary phosphine sulphides and, incidentally, tertiary arsine sulphides also, the oxidation proceeded with predominant inversion of configuration (Scheme 13)[127,128]. This stereochemical outcome was also recognized by Mikołajczyk in a revision of the earlier conclusions, the reactions being catalysed by acid or iodine (5%)[129]. The reaction, equally applicable to tertiary phosphine selenides[129,130], is also catalysed by metalloporphyrins aided by added imidazole[131]. Tertiary phosphine selenides are oxidized in high yield by selenoxides (equation 4)[132] with retention of configuration accompanied by some racemization[133].

$$R^1Se(O)R^2 + R^3{}_3PSe \longrightarrow R^3{}_3PO + R^1SeR^2 + Se \qquad (4)$$

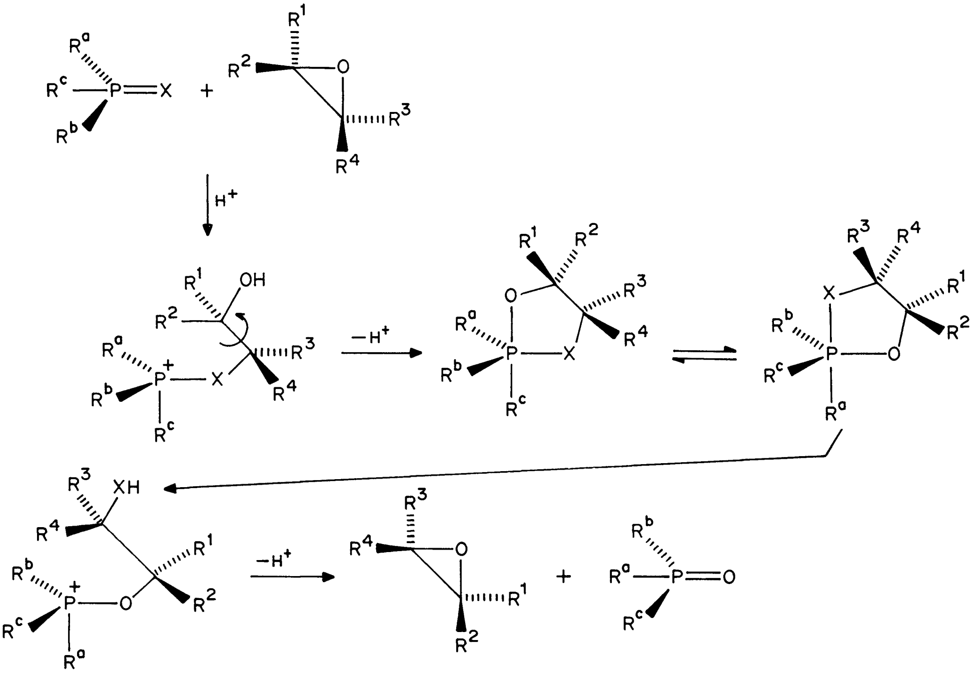
By contrast to the reactions involving tertiary phosphine sulphides, the stereochemical course of the oxidation of the phosphine selenides with H_2O_2 depends on the solvent system. Net retention of configuration is observed for solutions in MeOH or EtOH, but the introduction of thf to methanolic solutions, or the use of entirely different solvents, e.g. acetone, pyridine, nitromethane or even Bu^tOH, leads to inversion of configuration. The effect of reaction temperature then depends, in the case of selenides only, on the particular solvent; stereospecificity for reactions in $MeNO_2$ is independent of temperature, but for ethanolic solutions a rise in reaction temperature improves the stereospecificity. This is possibly the result of a lowering of the stability of a pentacoordinated intermediate so reducing the time available for stereomutation; the net retention of configuration observed for reactions in primary alcohols has been explained by assuming direct participation of the solvent (Scheme 14)[126].



SCHEME 14

Other peroxidic substances useful for the oxidation of tertiary phosphine sulphides and selenides include dioxiranes[134] and bis(trimethylsilyl) peroxide[135]; reactions with the latter reagent are catalysed by $AlCl_3$ and occur at room temperature, when they are relatively quick for the selenides but slow for sulphides. Photogenerated peroxides oxidize both sulphides and selenides in the presence of Rose Bengal in yields which depend appreciably on the solvent[136,137]. Ozone, successful in the oxidation of Ph_3PS and Ph_3PSe, reacts with MePhRPS (R = Pr or $PhCH_2$) with essentially complete retention of configuration[138,139].

The synthesis of thiiranes and their selenium analogues from oxiranes also represents the conversion of R_3PX (X = S or Se) into the corresponding oxides; reactions, with high yields, are conducted in the presence of trifluoroacetic acid. By using a variety of oxiranes and Bu_3PSe, evidence has been collected to suggest the intermediacy of pentacoordinate compounds (Scheme 15). Selenium is retained in combined form for reactions involving epoxycyclohexane, and for those with 2-hexyloxirane selenium is liberated only on warming the reaction mixtures[101,140].



SCHEME 15

The oxidative removal of sulphur or selenium from the phosphine chalcogenide is also achievable using $(CF_3CO)_2O$ in CH_2Cl_2, in a reaction accelerated by the presence of pyridine. Optically active sulphides suffer complete racemization, selenides with net inversion and a high degree of racemization; however, optically active oxides are also racemized. Pentacoordinate species of the type $R_3P(OCOCF_3)(SCOCF_3)$ are thought to be involved[141,142].

The treatment of triarylphosphine sulphides with $SOCl_2$ at room temperature can give large yields of the phosphine oxide accompanied, in the case of Ph_3PO itself, by ca 25% of Ph_3PCl_2; under different conditions (Section II.D), the latter may be the main product, but even so its formation allows an indirect means of reaching the oxide which may be obtained through several reactions of the dichloride[143]. An additional, but again indirect, procedure for chalcogen interchange consists in the decomposition of quaternary salts $R^1{}_3P^+SR^2\ X^-$ (Section II.C) with alkali, a reaction explored originally as early as 1907 by Hantzsch[6–9].

C. Quaternary Phosphonium Compounds from Phosphine Chalcogenides

Early work by Mann and Watson[144] demonstrated that the treatment of pyridinylphosphine sulphides, $Ph_n(2\text{-pyr})_{3-n}PS$, with MeI under sealed-tube conditions (no reaction occurring in boiling benzene) resulted in complete fragmentation of the phosphine sulphide; the products included 2,2′-bipyridinyl bismethiodide together with trimethylsulphonium iodide, when $n = 2$; the former bis(methiodide) was also obtained from $(2\text{-pyr})_3PO$. When $n = O$, the products were 2,2′-bipyridinyl monomethiodide and trimethyl(2-pyridinyl)phosphonium iodide[144].

In general, alkoxy- and related phosphonium salts of the type **104** are obtainable by either of the two reactions indicated briefly in Scheme 16. Because of the lower nucleophilic power of the P=O group, phosphine oxides would be expected to be the least reactive of the chalcogenides in reaction (a). Normally, reactions of the oxides with simple alkyl halides do not occur, or the resultant salts are unstable, but some others, e.g. $R_3P^+(OSiMe_3)\,I^-$, from R_3PO (R = Et, Ph, or Me_3SiCH_2) and Me_3SiI, are isolable. Route (b) also generally fails to give isolable products, but such salts with $X = O$ are assumed to have been formed early during the course of Arbuzov reactions. The use of trialkyloxonium salts (Meerwein's salts) $R_3O^+Y^-$, where R is Me or Et and Y^- is PF_6^-, $SbCl_6^-$ or BF_4^-, is advantageous for trialkylphosphine oxides[145,146], triarylphosphine oxides[147] or cyclic phosphine oxides[148]. Elsewhere, dimethyl sulphate or sulphonic acid esters, e.g. CF_3SO_2OR (R = Me or Me_3Si), have been employed.

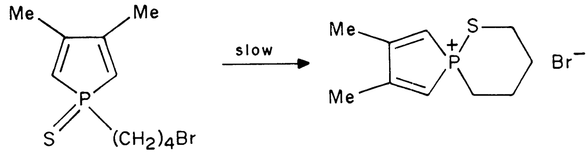
A relatively recent observation is of interest since it shows that the nature of the product from a triarylphosphine oxide and an oxonium salt depends on the manner of mixing; in addition to the 'normal' ethoxytriphenylphosphonium salt, oxybisphosphonium salts, $Ph_3P^+OP^+Ph_3\,2Y^-$, $Y^- = BF_4^-$ or $CF_3SO_3^-$, have been prepared[149].

$$R^1{}_3PX + R^2Y \xrightarrow{(a)} R^1{}_3P^+XR^2\,Y^- \xleftarrow{(b)} R^1{}_2PXR^2 + R^1Y$$

(104)

SCHEME 16

Not surprisingly, the formation of similar quaternary phosphonium salts from phosphine sulphides or higher phosphine chalcogenides is easier. Although Ph_3PS does not react with alkyl halides under normal conditions, it does so with trialkyloxonium salts[109,150]. In the case of more highly 'activated' phosphine sulphides, e.g. tris(2,6-dimethoxyphenyl)phosphine sulphide, direct reaction is feasible with alkyl bromides or iodides in benzene at room temperature to give isolable salts which are thermally stable[109]. The phosphole sulphide **105** undergoes slow intramolecular quaternization[151]. Unusually, Ph_3PS reacts with $NO^+\,BF_4^-$ to give the poorly stable salt $Ph_3P^+SSP^+Ph_3\,(BF_4^-)_2$[152]. Tertiary phosphine tellurides also react directly with MeI to give isolable methiodides of reasonable thermal stability[153].



(105)

The crystalline salts isolated from reactions between phosphine oxides and phosphoryl or thiophosphoryl halides are thought to have the structure $R_3P^+OP(Y)X_2\ X^-$ ($Y = O$ or S, $X = Cl$ or Br)[154].

Alkaline hydrolysis of alkoxy- or alkythio-phosphonium salts may, or may not, provide phosphine oxides with retained configuration at phosphorus; the phosphonium salts themselves retain the configuration of the chalcogenide from which they are prepared[107,108]. (*S*)-(+)-Me(2-Np)PhPO and (*S*)-(−)-MePhPrPS yield (ethyl)phosphonium salts which, on alkaline hydrolysis, give oxides in which the configuration at phosphorus has been retained; on the other hand, similar treatment of the (ethyl) quaternary salt from (*R*)-(+)-Bu^tMePhPO affords the oxide with inverted configuration[76].

D. Quinquevalent Pentacoordinate Compounds (Phosphoranes) from Phosphine Chalcogenides

Like the corresponding oxides, tertiary phosphine sulphides may be converted into the dichlorophosphoranes R_3PCl_2 by the action of hot $SOCl_2$[143]; other reagents which have been used for the oxides include oxalyl chloride[155], phosgene[156], methyl chloroformate[155] and PCl_5[157].

The analogous difluorophosphoranes have been obtained from the phosphine oxides with SF_4 or EF_3 (E = As or Sb) and by the use of the latter reagents with trialkylphosphine sulphides[158]. The reaction shown in equation 5 is also known[159]. Difluorophosphoranes are also obtainable from the sulphides by the action of sulphuryl chloride fluoride (Scheme 17)[160].

$$3(C_6F_5)_3P(S) + 2MF_3 \longrightarrow 3(C_6F_5)_3PF_2 + M_2S_3 \qquad (5)$$

The reactions between tertiary phosphine oxides and certain sources of iodine are complicated by the known propensity of phosphorus to form ionic polyhalides. The reactions between PI_5 and tricyclohexyl- and triphenyl-phosphine oxides have been investigated in some detail[161]. Tricyclohexylphosphine oxide yields Cy_3PI_2 together with POI_3 on the pathway to $Cy_3P^+I\ I_3^-$, and futher reaction between the latter and POI_3 furnishes more of the diiodophosphorane. Polyiodides up to and including the heptaiodide have been identified in the product mixtures the compositions of which depend on the ratios of reactants (equations 6 and 7).

$$R_3P(S) + SO_2FCl \longrightarrow R_3P^+SCl\ SO_2F^- \xrightarrow{-SO_2} R_3P^+F\ SCl^-$$

$$\xrightarrow{SO_2FCl} R_3PF_2 + SCl_2 + S + SO_2$$

SCHEME 17

$$2Ph_3P(O) + PI_5 \longrightarrow 2Ph_2PI_2 + 1/n(PO_2I)_n \qquad (6)$$

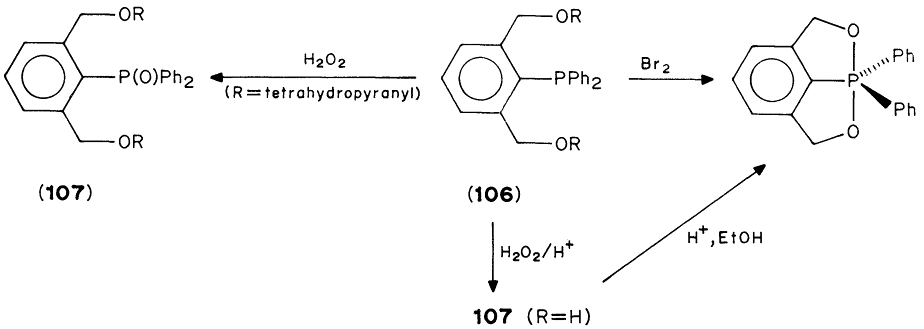
$$2Ph_3P(O) + 3PI_5 \longrightarrow 2(Ph_3P^+I)I_3^- + 2PI_3 + 1/n(PO_2I)_n \qquad (7)$$

A simple dioxyphosphorane has been identified spectroscopically as a product from the interaction of tris(trifluoromethyl)phosphine oxide and hexamethyldisiloxane (Scheme 18). Chemical identification followed from its ready transformation into trimethylsilyl bis(trifluoromethyl)phosphinate[162].

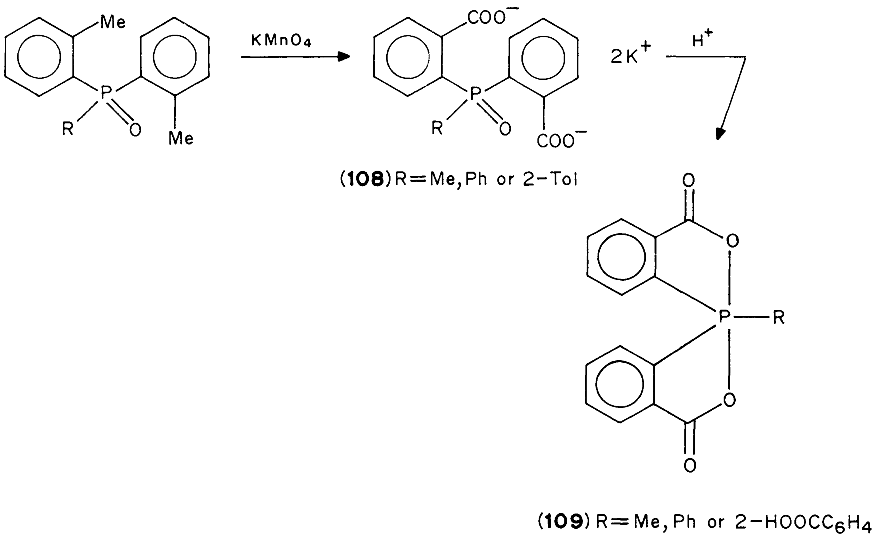
$$(CF_3)_3P(O) + (Me_3Si)_2O \longrightarrow (CF_3)_3P(OSiMe_3)_2 \longrightarrow (CF_3)_2P(O)OSIMe_3$$

SCHEME 18

The formation of other oxyphosphoranes depends on the proximity of the phosphoryl bond to other oxygen-containing functions, generally carboxyl or hydroxyl. Such appropriate closeness can arise when suitable phosphines are oxidized, as in Scheme 19 where, for the phosphine **106**, *O*-protection in the aromatic substituents prevents the formation of a phosphorane, and in Scheme 20, where acidification of the salts **108** leads, by spontaneous dehydration of the liberated dicarboxylic acid, to the oxyphosphorane **109**[163–165].



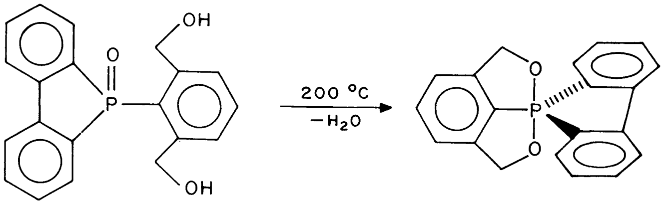
SCHEME 19



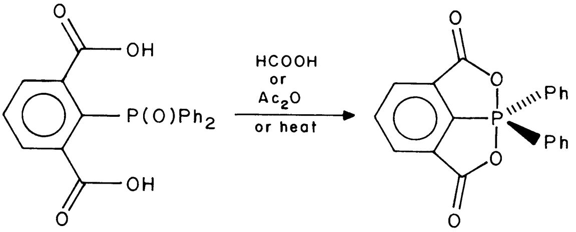
SCHEME 20

The conversion of a phosphine oxide into an oxyphosphorane by dehydration may be spontaneous, or it may be brought about in the ways shown in reactions 8[163] and 9[164].

The reaction between methyl 2-(diphenylphosphinoyl)benzoate and MeMgI (Scheme 2) yields the tertiary alcohol **6** which, when treated with NaH, yields the alkoxide **8**, which exists largely in the pentacoordinate form, **7**. On the other hand, the alcohol **6** is the main tautomer in the equilibration with the cyclic form **5**[5].

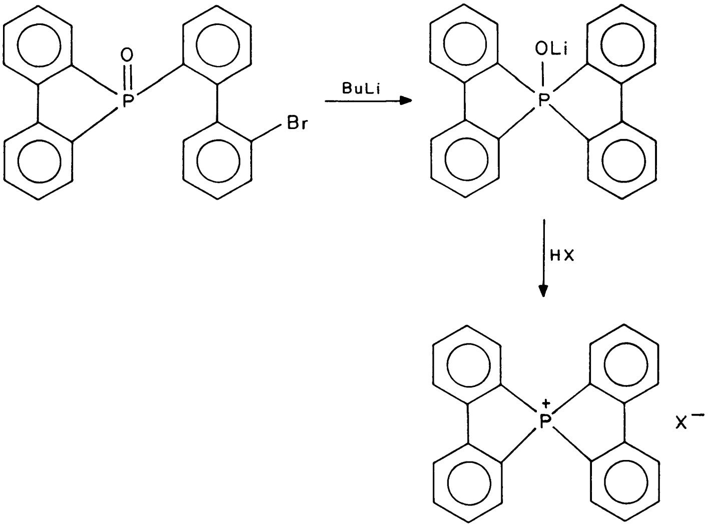


(8)



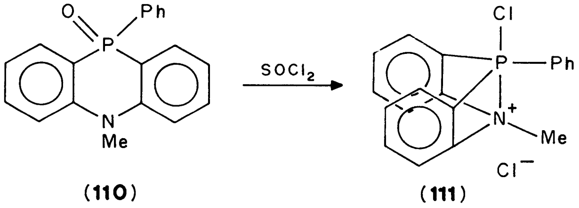
(9)

Acidification of the lithium salt obtained (Scheme 21) from the treatment of 5-(2′-bromobiphenyl)yl-5*H*-dibenzophosphole 5-oxide with BuLi fails to liberate a free hydroxyphosphorane, yielding instead a symmetrical phosphonium salt[166].



SCHEME 21

In an example of the formation of a pentacoordinate compound from a phosphine oxide, the oxide **110** when acted upon by $SOCl_2$ yields a mixed P^V-quaternary ammonium salt possessing a 'butterfly' structure (**111**)[167]. Finally, the reader is reminded that pentacoordinate species based on the 1,3,2-oxaselenaphospholane system have been detected spectroscopically during the reactions between tertiary phosphine selenides and epoxides (Section II.B).

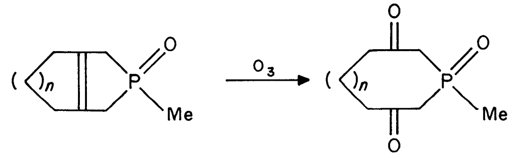


III. REACTIONS OF THE ORGANIC LIGANDS

A. Oxidation

Amongst the oxidation processes associated with the organic ligands of tertiary phosphine chalcogenides, four are recognized as being of significance. They are (1) oxidative cleavage of carbon—carbon multiple bonds, (2) oxidation of groups attached to aromatic nuclei, (3) epoxidation and (4) oxygen insertion.

The oxidative cleavage of carbon—carbon multiple bonds is well illustrated by the use of $KMnO_4$–$NaIO_3$ to oxidize allyldiphenylphosphine oxide to diphenylphosphinoylacetic acid, and the use of ozone followed by H_2O_2 to cleave diallylphenylphosphine oxide to $PhP(O)(CH_2COOH)_2$[168]. A similar oxidation of diphenyl(phenylethynyl)-phosphine oxide yields benzoic acid and diphenylphosphinoylformic acid, the latter then being rapidly cleaved to diphenylphosphinic acid[168]. A useful extension in the process is the cleavage of carbon—carbon double bonds bridging large rings systems as represented in equation 10; in this way, derivatives of even larger phosphacycloalkanes can be obtained[169].

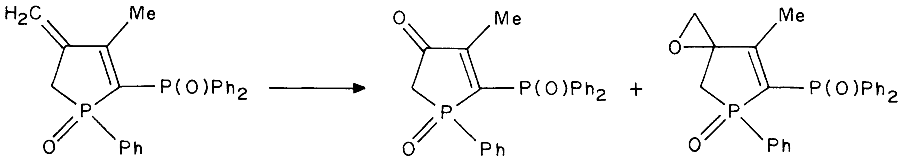


(10)

The oxidation of alkyl, and related, substituents on aromatic rings may be carried out successfully using $KMnO_4$–pyridine; when the resultant carboxyl groups are situated *ortho* to the phosphoryl group, mutual interaction might occur to afford products of a pentacoordinated nature (Scheme 20). When the substituents are situated *para* to a phosphoryl group, cyclization does not occur. Oxidation of alkyl substituents has also been carried out with derivatives of, for example, the 5*H*-dibenzophosphole and dibenzo[*b*,*e*]phosphorin systems.

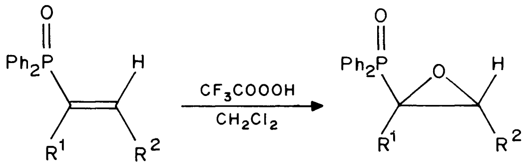
Normally, when similar phosphine sulphides are so treated, the resultant products are essentially phosphine oxides, but one example, viz. 4-diphenylphosphinothioylbenzyl alcohol, has been recorded for which oxidation by CrO_3–pyridine afforded the aromatic aldehyde with no attack on the thiophosphoryl group[170].

Epoxidation accompanies oxidative cleavage when the 2-(diphenylphosphinoyl)-phospholene 1-oxide **112** is treated with aibn[60]. Some early observations on the epoxidation process itself are of interest. Initial success in the first reported epoxidation of a 3-phospholene, using peroxyacetic acid or monoperoxyphthalic acid, was not matched with examples of 2-phospholenes[171,172], although these findings have since been challenged[33]. A possibly related phenomenon is the finding that diphenylvinyl-



(112)

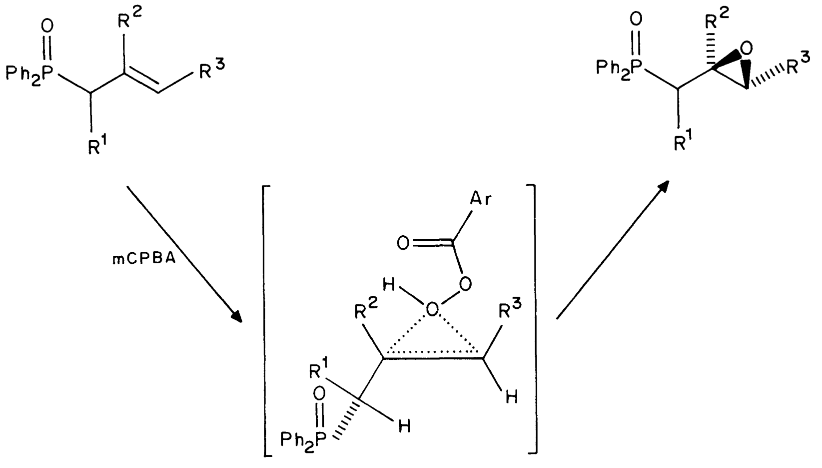
phosphine oxide is resistant to peroxy acids[126] whereas oxides substituted on the vinyl group are readily epoxidized (equation 11)[173].



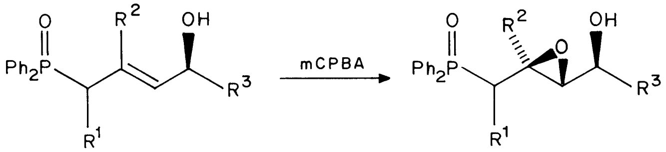
(11)

$R^1 = Me, Et, Pr$ or Ph; $R^2 = H, Me$, or Et; $R^1R^2 = (CH_2)_n$; $n = 4$ or 5

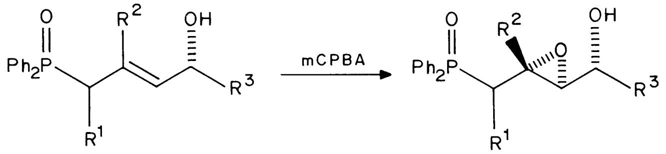
The epoxidation of allylic phosphine oxides by mCPBA is thought to proceed in a manner summarized in Scheme 22[174,176]. The stereochemistry of the process is thought to be controlled by the chiral centre at the carbon α to phosphorus, and rationalized by the transition state; the yields are very high, with stereospecificities of from 4:1 to 10:1. For δ-OH homoallylic oxides, the stereochemical control originates in the hydroxyl group with the stereoisomeric ratios being greater for one diastereoisomer (10–13:1) as opposed to the other (1.3–2.7:1); equations 12 and 13 indicate the main products of the reactions. The stereochemistry of the epoxides has been confirmed by X-ray diffraction studies[175].



SCHEME 22

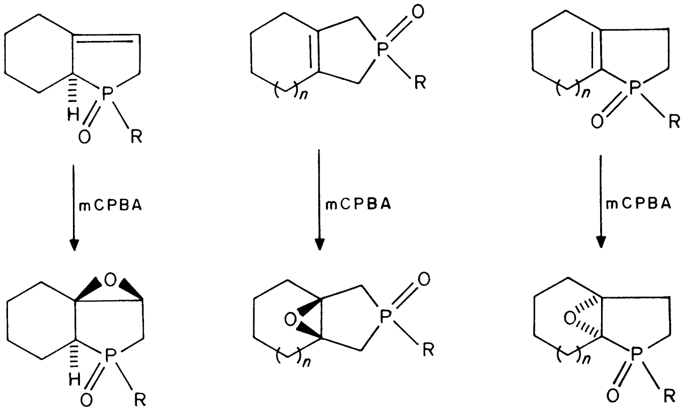


(12)

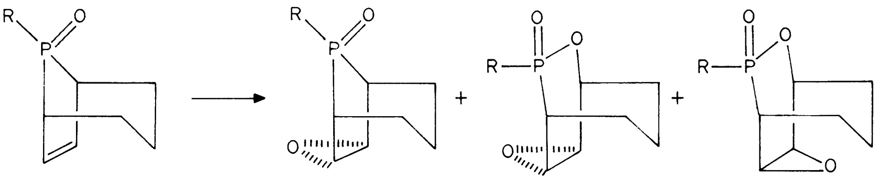


(13)

The stereochemistry of epoxidation has also been investigated using a series of 2- and 3-phospholenes[33]. 3-Methyl-3-phospholene 1-oxide itself, and 3-phospholenes fused to cyclopentano or cyclohexano rings on the b or c bonds, are epoxidized with mCPBA stereospecifically. When the cycloalkano group is fused to the b bond of a 2-phospholene, the epoxidation reaction also occurs readily but the orientation of the epoxide ring relative to the phosphoryl group is opposite to that experienced for the 3-phospholanes (Scheme 23).



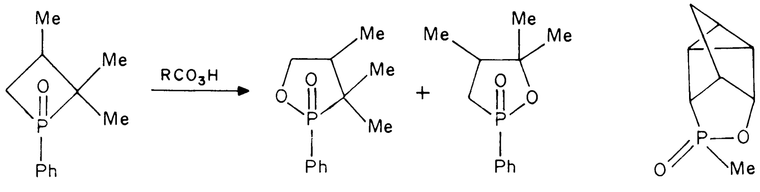
SCHEME 23



(113) (114) (115) (116)

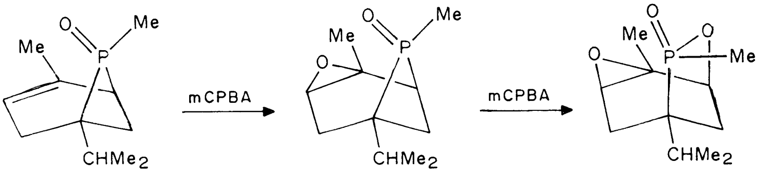
Epoxidation of the 8-phosphabicyclo[3.2.1]oct-6-enes (**113**) (R = Me or Ph) with mCPBA is slow and yields the β-epoxides **114** accompanied by other products identified as oxygen insertion compounds (cyclic phosphinic esters) **115** and the α-epoxy compound **116** when R = Ph. Epoxidation of the phosphorus epimer of **113** (R = Me) is faster, taking place effectively at room temperature with an identical relationship between epoxide group and geometry of ring fusion[117,178].

Phosphorus-containing ring systems in which the internal CCC angles are particularly constrained, e.g. the phosphetanes, undergo a Baeyer–Villiger-like insertion of oxygen between phosphorus and the carbon atom carrying fewer substituents (Equation 14a); here, **117** is the main product. The reaction occurs in the four-membered ring rather than in the less constrained five- or six-membered ring; thus **118** is obtained from **66**, and **119** reacts sequentially as indicated in equation 14b[179].



(117) **(118)**

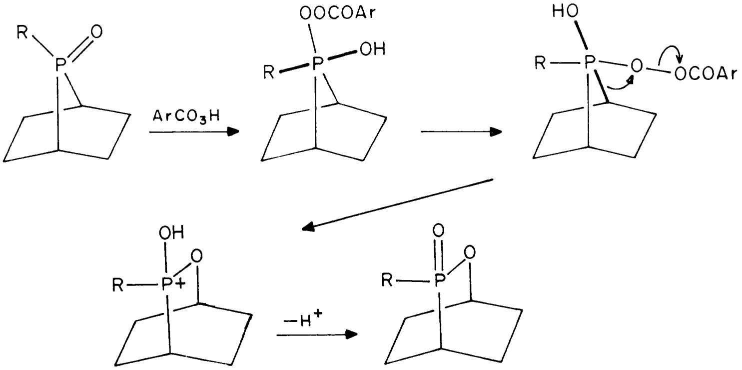
(14a)



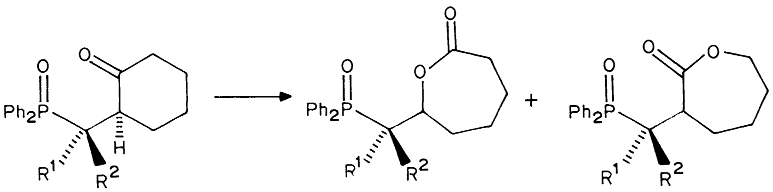
(119)

(14b)

The oxygen insertion has been formulated mechanistically in Scheme 24[179]. Scheme 25 outlines an application of the reaction which yields products having synthetic usefulness (Section V); cycloalkanones yield lactones and again the stereochemical control appears to depend on the stereochemistry at the α-carbon[180].

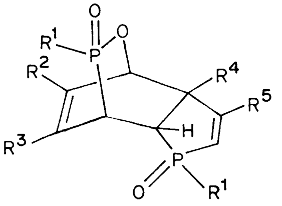


SCHEME 24



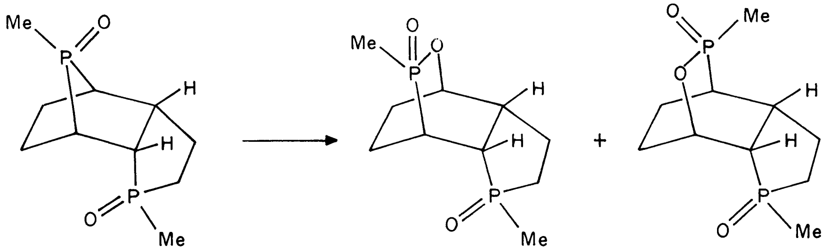
(120)	R^1	R^2	(121)	(122)
(120.1)	H	Me	72	3
(120.2)	Me	H	5	3

SCHEME 25

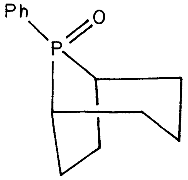


(123)

In the 7-phosphanorbornadiene system, oxygen insertion occurs readily and regiospecifically at the phosphorus bridge to give the compounds **123**. When the carbon skeleton is fully saturated, as in **124**, the insertion occurs non-regiospecifically to give a 1:1 mixture of the isomeric phosphinic ester **125** and **126**. Kashman and Awerbouch[178] were unable to carry out the insertion reaction with the saturated compound **127** and they also failed with examples of the 8-phosphabicyclo[3.2.1]octane series. 4-Methyl-4-(diphenylphosphinoyl)pentan-2-one also fails in the Baeyer–Villiger process[181].



(124) (125) (126)



(127)

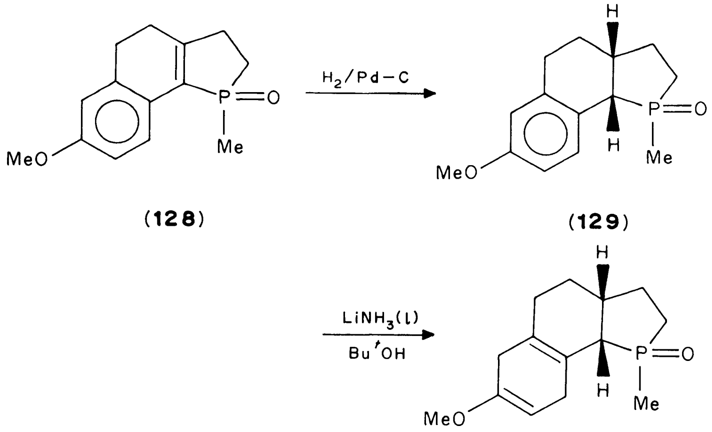
Other oxidation processes have received much less attention, but there are no apparent reasons why such processes should not occur in any manner other than that expected; thus, the secondary OH function in 3-hydroxy-2-phospholene 1-oxides is readily oxidised to the carbonyl group by CrO_3–pyridine with retention of optical activity[172], and the Jones reagent has been used for the same purpose for compounds in the 8-phosphabicyclo[3.2.1]octane series[177].

B. Reduction

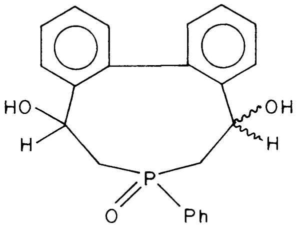
Hydrogenation of isolated double bonds in acyclic compounds such as diphenyl-(2-phenylethenyl)phosphine oxide or in cyclic systems, e.g. 8-methyl-8-phosphabicyclo-[3.2.1]octene 1-oxide[177], or in the tricyclic system **128**[182] occurs readily in the presence of ruthenium, palladium or platinum catalysts. In the case of the last compound, the dihydro compound has *cis* geometry at the ring fusion; further reduction of the methoxyphenyl group in **129** is possible under Birch conditions, when the phosphoryl group remains unchanged.

Hydrogenolysis at 100–200 atm and 100 °C in the presence of platinum reduces phenyl compounds to the cyclohexyl analogues, for example tribenzylphosphine oxide yields tris(cyclohexylmethyl)phosphine oxide[45,183]; a potential drawback to the process is the possible elimination of halogen from the initial aromatic ring. Polarographic reduction of phosphorylvinyl groups is accompanied by dimerization, and diphenylvinylphosphine oxide itself afford 1,4-bis(diphenylphosphinoyl)butane.

Ketone groups in ring systems containing phosphorus atoms can be reduced by conventional means, e.g. through a dithioketal intermediate. Partial reduction of carbonyl



(**128**) (**129**)



(**130**)

(ketone) groups to secondary alcohol functions is readily achieved using $NaBH_4$ and is of importance in the Horner reaction (Section V). The phosphoryl group is stable to the action of borohydride during the reduction of ring carbonyl groups in the preparation of the dialcohol **130**, which is of interest since it is a precursor to the unusual dibenzophosphonin ring system[184].

The widespread use of $LiAlH_4$ for the modification of organic ligands is rendered complicated by its ability to also remove the phosphoryl oxygen and give the parent phosphine although this could then be re-oxidized. The extent of its success in the reduction of the C=C bond in 3-methyl-1-phenyl-2-phospholene 1-oxide without at the same time removing P=O depends on the experimental conditions; relatively lower temperatures favour selective, but by no means specific, reduction of the C=C bond[185].

When treated with $LiAlH_4$, diaryl- and dialkyl-(alkynyl)phosphine sulphides yield the 1-alkenylphosphines in the *trans* form, which then undergo isomerization to the *cis* form. Deuteriation experiments demonstrate the initial addition of H^- (or D^-) to $C_{(2)}$ in a normal Michael fashion. Such phosphine sulphides are stable to $NaBH_4$, even in boiling thf, but the corresponding oxides are reduced to the *trans* olefinic phosphine oxide[186].

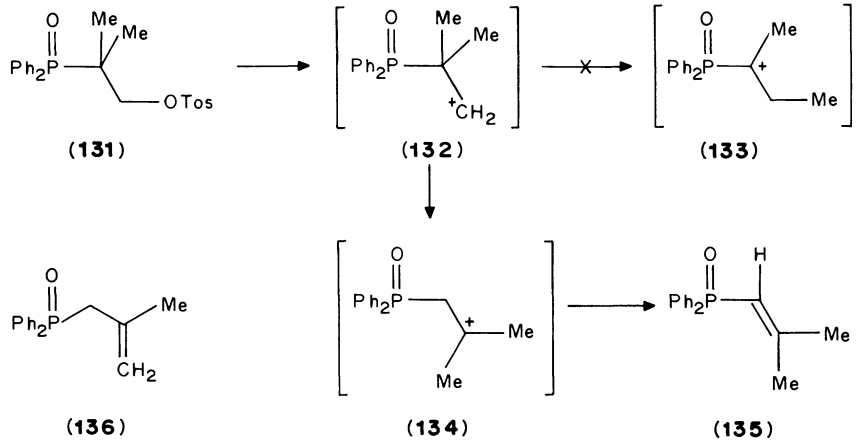
C. Dehydration: Phosphinoyl Carbocations

The diphenylphosphinoyl group appears to activate a process of spontaneous dehydration under appropriate conditions; thus the diketone $Ph_2P(O)CH(COPh)CH_2COPh$, presumably through its dienol, dehydrates to 2,5-diphenyl-3-diphenylphosphinoylfuran during crystallization. Dehydration of 1-(diethylphosphinothioyl)-1-hydroxycyclohexane has been reported to occur during its distillation[187]. Powerful dehydrating agents such as $KHSO_4$ and P_4O_{10} fail to dehydrate $Bu_2P(S)C(OH)Me_2$, and the compound readily decomposes into its precursors, dibutylphosphine sulphide and acetone.

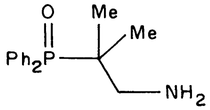
The diol **130** is dehydrated when treated with $POCl_3$–pyridine and affords *cis, trans*-1-phenyldibenzophosphonin 1-oxide; although dehydration of the 1-methyl compound may similarly be achieved, the stereochemistry of the product appears, as yet, to be unknown[181].

Extensive investigations have been carried out by Warren[188] into the dehydration of phosphinoylated alcohols in which the phosphinoyl group is placed β to the OH group, and hence to the site of cation formation under acidic conditions. One of the more important reactions accompanying the dehydration of the alcohol, or the solvolysis of an ester, e.g. a sulphonate, with tosOH or tfa in a solvent at either ambient temperature or at the boil, consists in the migration of the diphenylphosphinoyl group from the α-carbon atom (the migration origin) to an adjoining carbocationic site (the migration terminus). The roles of the two sites and their influence on the migrating ability of the phosphinoyl group, or indeed of any other nearby group, have been explored in a systematic manner. Although, in some cases, quenching of the reaction mixtures allows the isolation of an isomeric alcohol, the product(s) normally isolated consist of alkenes. Subject to the availability of an appropriately sited proton, these are either vinyl- or allyl-phosphine oxides; in practice the former are obtained comparatively rarely.

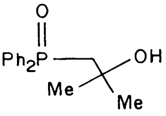
An example of the migration from a tertiary carbon origin to a primary carbocationic site occurs during the solvolysis, using formic acid at 120 °C, of the tosylate **131** of a primary alcohol, and which proceeds through a 'low-energy' cation. Here, the unstable primary cation does not isomerize through methyl group migration (Scheme 26), (**132** to **133**), but rather by phosphinoyl migration, (**132** to **134**), the product being the vinylphosphine oxide **135**. On the other hand, presumably the same, or a very similar, carbocation is formed when the primary amine **137** is diazotized, but the eventual products then consist of mixtures of the vinyl- and allyl-phosphine oxides **135** and **136**, together with some of the alcohol **138** and traces of the cyclopropylphosphine oxide **139**[181].



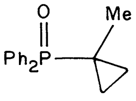
SCHEME 26



(137)

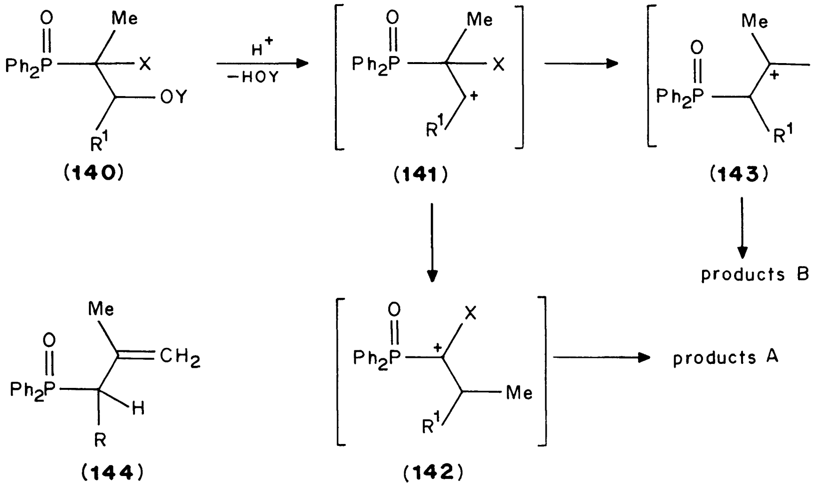


(138)



(139)

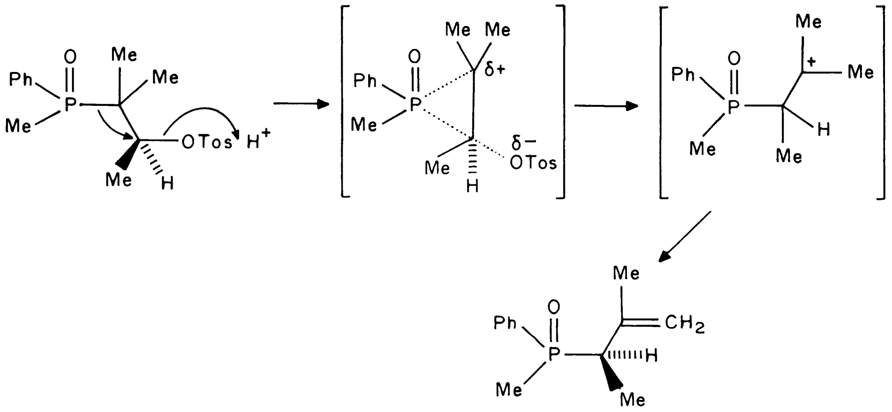
Scheme 27 depicts migrations from a substrate possessing a tertiary migration origin coupled with a secondary migration terminus. Essentially, dehydration or solvolysis of



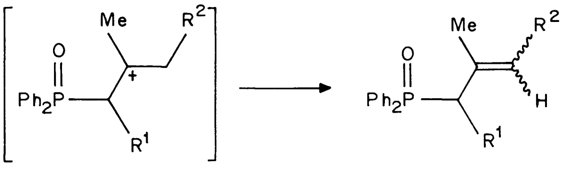
SCHEME 27

140 provides the initial carbocation **141**, which can isomerize by phosphinoyl migration to the relatively unstable carbocation **143** (positive charge adjacent to the electronegative phosphinoyl group) leading to products B, or it can isomerize by methyl migration to the isomeric cation **142** to give products A.

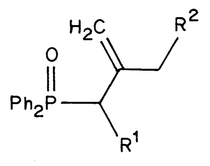
Not surprisingly, it has been argued that the choice, or balance, between the two routes represented in Scheme 27 will depend on electronic factors, in particular the relative stabilities of the carbocations **142** and **143** (and indeed **141**)[189]. For the solvolysis of the ester **140** ($X = R^1 = Me$; $Y = tos$), the preferred choice is the formation of the cation **143**, with the observed formation of the allylic phosphine oxide **144** ($R = Me$) rather than a vinylic isomer. However, a conformational argument based on the preferred antiperiplanarity of the relatively large $Ph_2P(O)$ and OTos groups in the most highly populated conformer (with a resultant boost to phosphinoyl migration) cannot be excluded. This latter argument has received some indirect support from the observation that the tosylate of 3-methyl-3-(methylphenylphosphinoyl)butan-2-ol undergoes solvolysis in acetic or formic acid with retention of configuration at phosphorus but with inversion of configuration at the migration terminus; the migration is thus pictured as a concerted process (Scheme 28) with very little epimerization[190]. The structure of the final olefinic product was confirmed by an X-ray crystallographic investigation.



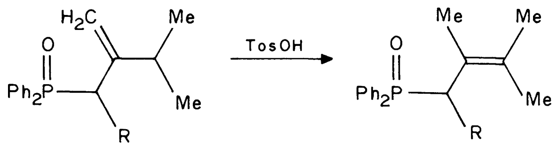
SCHEME 28



(145) (=**142**, $X = CH_2R^2$) **(146)**

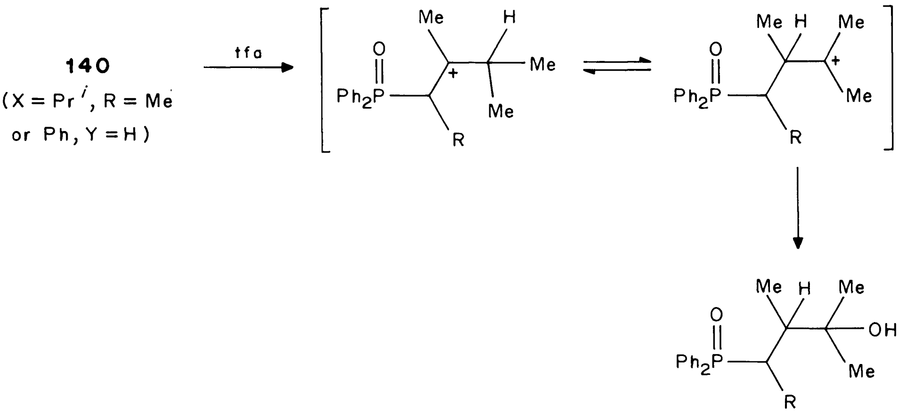


(147)



(148) **(149)**

When, in **140**, $X = CH_2R^2$ (R^2 = Me or Bu) and R^1 = Me or Ph, acidolysis of the alcohol (Y = H) yields a mixture of the *E* and *Z* forms (in a ratio >9:1) of the allylic phosphine oxide **146** via the carbocation **145**, but none of the allylic isomer **147** nor of an isomeric vinylphosphine oxide, was obtained[191]. When, however, X = Pr^i, acidolysis then afforded the allylic phosphine oxide **148**, i.e. a phosphine oxide of type **147**, although for R^1 = Me prolonged treatment with tosOH led to some isomerization to the more highly substituted alkene **149**[191]. However, when tfa was used as the acid catalyst, a further complicating feature then arose, viz. a double migration; this, consisting of a phosphinoyl migration followed by a hydride shift, led, following quenching, to the isomeric tertiary alcohol **150** (Scheme 29).



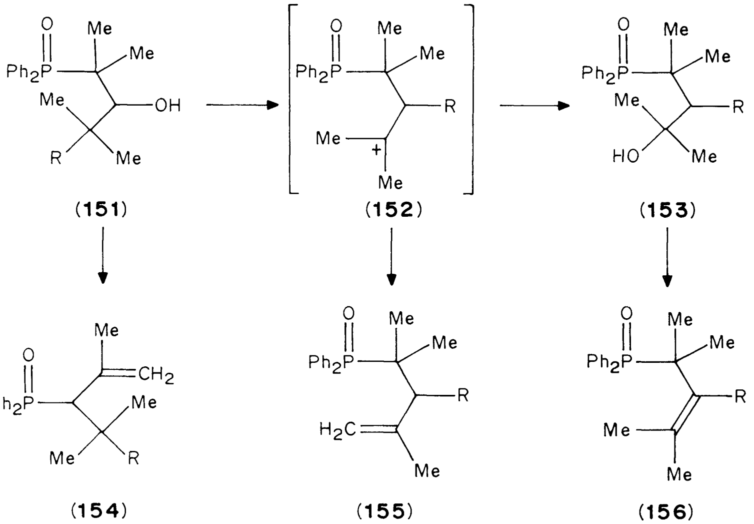
(150)

SCHEME 29

Tfa also brings about rapid dehydration of the secondary alcohols **140** (X = Me; Y = H) to give the allylic phosphine oxides **144**, which then isomerize to the more highly substituted alkene, in this case of the vinylic type. Dissolution of **140** (X = Me; R = Ph; Y = H) in 98% H_2SO_4, followed by quenching, yields **150** (R = Ph). With a primary alkyl group at the migration terminus, as in **140** (R = Me, Et or Pr), tosOH yields **150** as the only products[192].

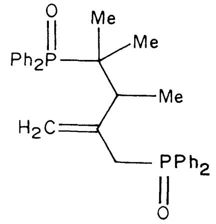
The picture regarding the migratory abilities of the diphenylphosphinoyl and alkyl(methyl) groups begins to change with an increase in the complexity of the alkyl group R^1 in **140** (X = Me; Y = H). Thus, acid-catalysed dehydration of **151** (R = H) (i.e. **140**, R^1 = Pr^i; X = Me; Y = H) yields only **154** (Scheme 30). Scheme 30 also indicates the various possible products which may be obtained from **151** (R = Me) (i.e. **140**; R^1 = Bu^t; X = Me; Y = H); treatment of the latter alcohol with H_3PO_4 at ambient temperature affords 90% of the isomeric alcohol **153** (R = Me)[193]. When **151** (R = Me) is treated with tosOH in benzene, there are produced 50% **155** (R = Me) and 27% **153** (R = Me), both obtained through the carbocation **152** (R = Me) and Me migration, in addition to 18% of the alkene **154** (R = Me), the product of phosphinoyl migration. Thus, for the alcohol **140** (R^1 = Bu^t, X = Me, Y = H), Me migration more than satisfactorily competes with phosphorus migration[192].

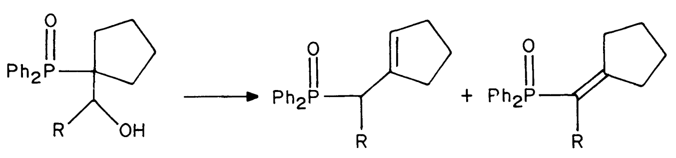
In an attempt to obtain a truer comparison of the migrating abilities of the Me and $Ph_2P(O)$ groups, Howells and Warren[193] prepared the two bis(diphenylphosphinoyl) compounds **151** [R = Ph_2PO or $Ph_2P(O)CH_2$]. When acidolysed in buffered acetic acid, the mesylate of the former gave **155** (R = Ph_2PO and **153** (R = Ph_2PO) in the ratio 9:1;



SCHEME 30

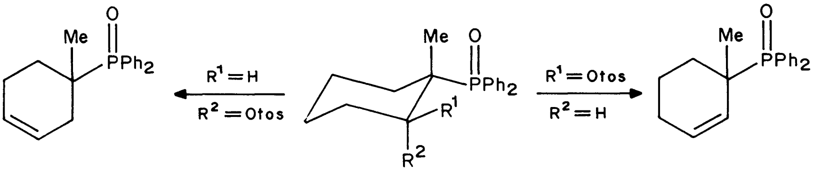
the latter alcohol dehydrates rapidly at ambient temperature to give the corresponding **156**. Under the same conditions, the second mesylate gave 70% of **154** (R = Ph_2PO) by phosphinoyl migration and 25% **157** (R = Ph_2PO) by Me migration[193].


(157)

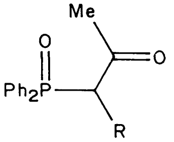


Tfa dehydrates the alcohol **158** (R = Ph) to give only **159** (R = Ph), but with tosOH a 1:9 mixture of **159** and **160** (R = Ph) is formed. The alcohol **158** (R = Me) is similarly dehydrated to a mixture of **159** and **160** (R = Me) in the ratio 2.5:1. The formation of the compounds **160** represents one of the comparatively few examples of the formation of vinylphosphine oxides from β-hydroxyalkylphosphine oxides by dehydration. The cyclobutane derivatives behave similarly, and the proportion of vinylphosphine oxide increases with the duration of the reaction contact time[192].

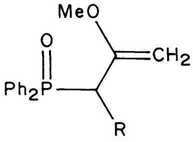
Within this group of substrates in which phosphinoyl migration from a tertiary origin centre to a secondary site might occur, evidence has been obtained which certainly points to the existence of conformational control. The isomeric tosylates **161** when solvolysed yield the isomeric phosphinoyl cyclohexenes **162** and **163** with no evidence for either Me or Ph_2PO migration.



(163) **(161)** **(162)**



(164)



(165)

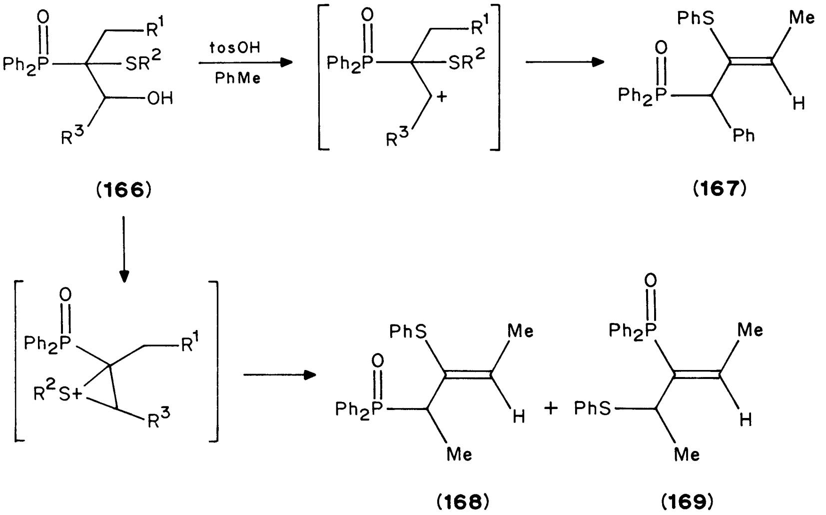
The presence of other functional groups is not restrictive to the migration of the diphenylphosphinoyl group. When treated with tfa, the alcohol **140** ($R^1 = Ph$; $X = OMe$; $Y = H$) yields the methyl ketone **164** ($R = Ph$) only. 3-(Diphenylphosphinoyl)butan-2-one (**164**; $R = Me$) is the only product obtained from **140** ($R^1 = Me$; $X = OMe$; $Y =$ tos-*p*); on the other hand, when $R^1 = \mathrm{Pr}^i$, both **164** and **165** ($R = \mathrm{Pr}^i$) are formed in the reaction in buffered acetic acid[194].

Slight structural modifications also bring about changes to the dehydration reaction course for the sulphides **166** (Scheme 31). Phosphinoyl migration appears to be the sole pathway for **166** ($R^1 = Me$; $R^2 = R^3 = Ph$), with **167** being the product, whereas the allylic olefins **168** and **169** are obtained from **166** ($R^1 = R^3 = Me$; $R^2 = Ph$) through migration of the PhS group, a process which also has useful synthetic potential[188]. Migrations of the MeS group have also been recorded[188,194].

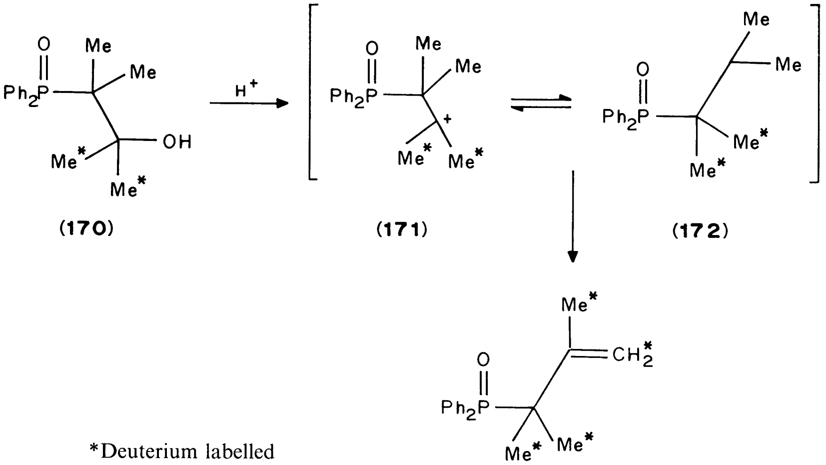
A special case exists when both migration origin and migration terminus are tertiary units (Scheme 32). The use of a deuterium-labelled substrate (**170**) has demonstrated equilibrium between the two carbocations **171** and **172**, and the overall reaction is very fast, occurring even during acylations under very mild conditions[191,195].

Reactions 15 and 16 exemplify phosphinoyl migrations from secondary carbon origins[191]. Here in reaction 15, the vinylphosphine oxide is not obtained when for **173** $R^1 = R^2 = Me$, but both vinyl- and allyl-phosphine oxides are obtained, in equal amounts, when $R^1 = Et$. A similar situation is found for reaction 16[196]. In neither of these reaction systems is phosphinoyl migration observed.

Warren's group also examined the behaviour of several silicon-containing phosphinoylated alcohols under acidolysis conditions; such substrates would be of interest since the silyl group can effectively act simply as a protecting group (Scheme 33)[191]. Following the action of tfa on the alcohol **174**, the nature of the product(s) is dependent on the reaction conditions. At ambient temperature phosphinoyl migration is followed

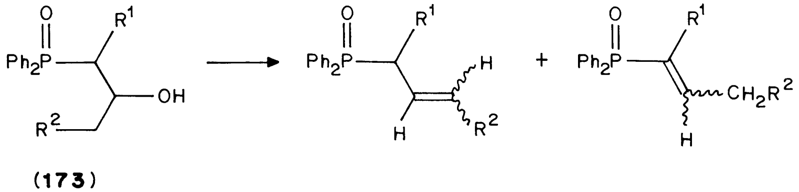


SCHEME 31

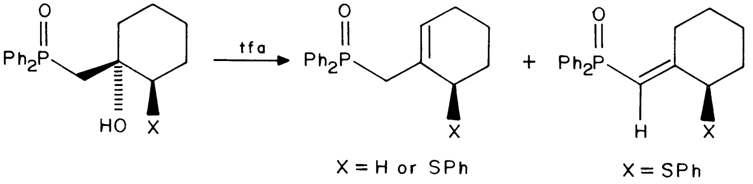


*Deuterium labelled

SCHEME 32

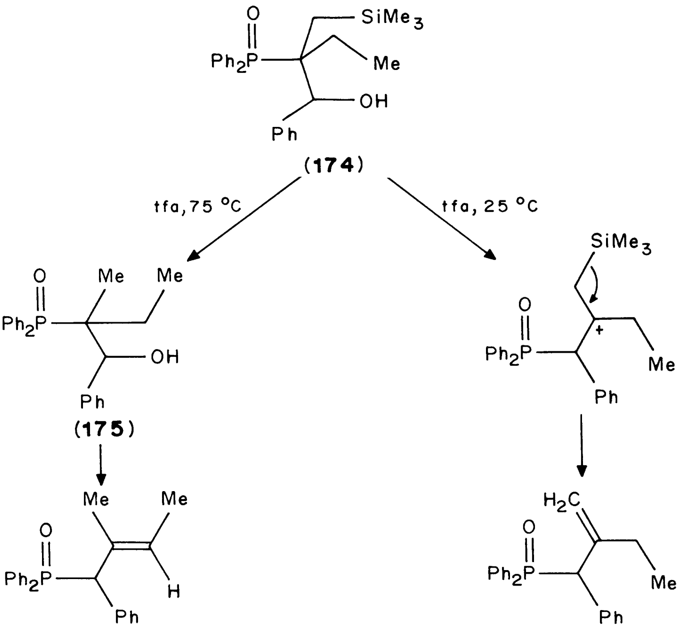


(15)

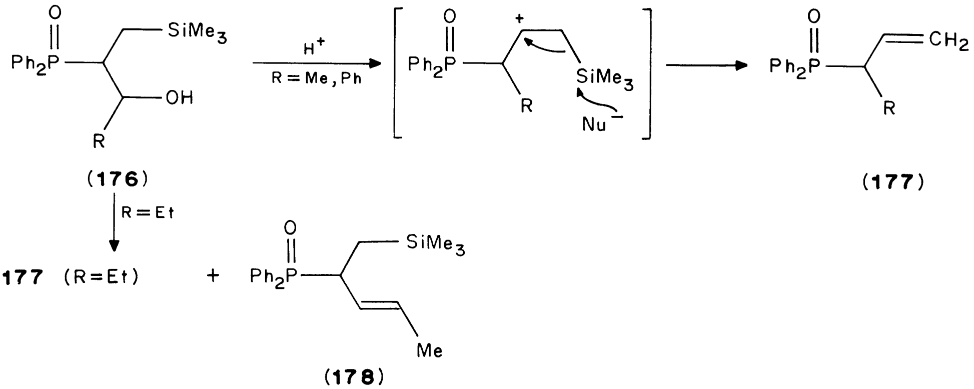


(16)

by desilylation, whereas at the higher temperature, desilylation to **175** evidently precedes phosphinoyl migration, and the product is an isomeric allylphosphine oxide (compare Scheme 27).



SCHEME 33

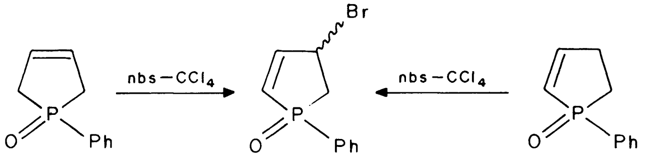


SCHEME 34

The group R in structure **176** is a controlling feature for the reactions of such compounds (Scheme 34), a single alkene being obtained when R = Me or Ph, but when R = Et a mixture of **177** (R = Et) and **178** is obtained in the ratio 2:1[191].

D. Halogenation

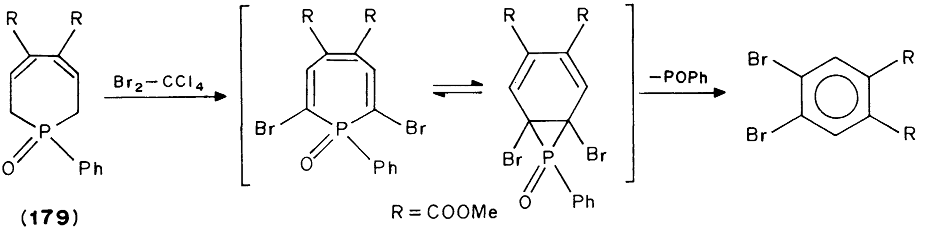
The reaction between benzyldiphenylphosphine oxide and *tert*-butyl hypochlorite affords 36% of the α-chlorobenzyldiphenylphosphine oxide in what is, presumably, a free-radical process; the α-bromo compound is similarly prepared and is also obtainable from α-diazobenzyldiphenylphosphine oxide and HBr in benzene. Other reported brominations of acyclic phosphine oxides using the same reagent include that of diphenyl-(2-phenylethyl)phosphine oxide in which substitution evidently occurs on $C_{(2)}$. The same mixture of stereoisomeric 4-bromo-1-phenyl-2-phospholene 1-oxides is obtained from isomeric 1-phenylphospholene 1-oxides (Scheme 35)[197].



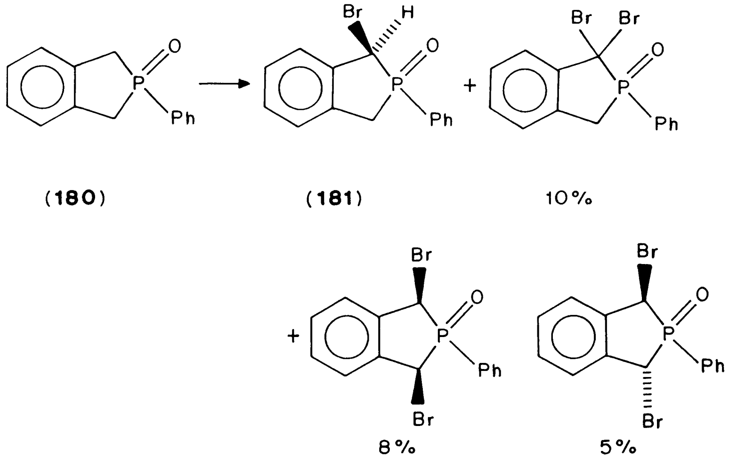
SCHEME 35

Direct bromination of the dihydrophosphepin 1-oxide **179** evidently occurs at the two allylic methylene positions to yield an unstable intermediate which extrudes phosphorus as PhPO and leaves dimethyl 3,4-dibromophthalate (Scheme 36)[198]. In the presence of dibenzoyl peroxide, nbs brominates 2-phenylisophosphindoline 2-oxide (**180**); the products (equation 17) consist of a mixture of isomeric and stereoisomeric mono- and di-bromo derivatives of which the monobromo compound **181**, following dehydrobromination, serves as the precursor in the synthesis of bridged compounds in the 7-norbornene series by cycloaddition reactions (Section III.H.3)[199]. Stereoisomeric α-mono- and α,α′-dibromo derivatives of dibenzylphenylphosphine oxide (**182**) ($R^1 = R^2 = \mathrm{Ph}$)[200] and of **182** ($R^1 = \mathrm{Ph}$, $R^2 = \mathrm{SOPh}$)[201] have been obtained following bromination with bromine/nbs in pyridine or with bromine in CCl_4 at 150 °C. Analogous chloro derivatives of the oxides **182** ($R^1 = \mathrm{Bu}^t$ or Ph, $R^2 = \mathrm{Bu}^t$) may be prepared by reaction with BuLi followed by CCl_4[200,202].

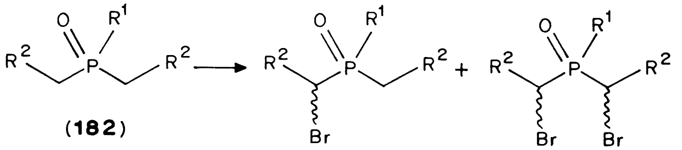
3-Oxo-1-phenylphospholane 1-oxide is brominated by nbs in a process akin to that encountered for acetone, and the brominated enol form, 2-bromo-3-hydroxy-1-phenyl-2-phospholene 1-oxide, is obtained[203]. Other halogenation and related reactions occurring by addition mechanisms are described later (Section III.H).



SCHEME 36



(17)



E. Dehydrohalogenation

Standard 1,2-elimination reactions have been performed on a variety of halogenated phosphine oxides using sodium alkoxides, thioalkoxides or, better, tertiary amines, to yield *trans*-alkenes (Scheme 37)[204]. Similar products have been obtained by the pyrolysis of acetate esters (equation 18).

$$(ClCH_2CH_2)_3PO \xrightarrow[\text{or } 3\,Et_3N]{3\,NaOEt} (H_2C{=}CH)_3PO$$

$$\xrightarrow{NaOEt} H_2C{=}CHP(O)(CH_2CH_2Cl)_2 + (H_2C{=}CH)_2P(O)CH_2CH_2Cl$$

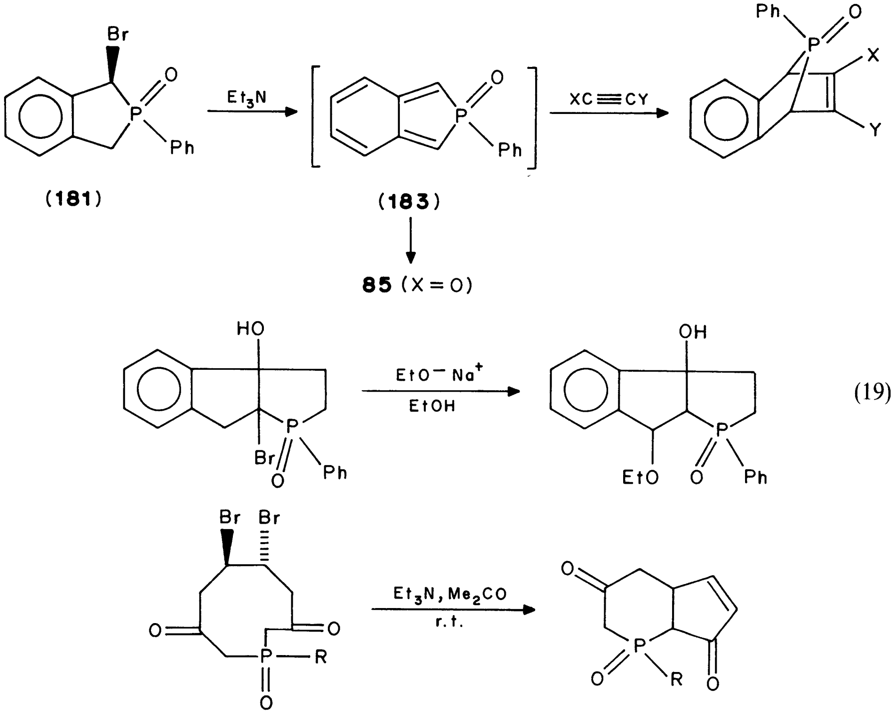
$$(ClCH_2CH_2)_2P(O)CH_2Cl \xrightarrow{NEt_3} ClCH_2P(O)(CH{=}CH_2)_2$$

SCHEME 37

$$(AcOCH_2CH_2)_2P(O)CH_2OAc \xrightarrow{heat} (H_2C{=}CH)_2P(O)OAc \qquad (18)$$

Other dehydrohalogenation reactions may be followed by rapid modification of the product, e.g. by the dimerization of the benzo[*c*]phosphole oxide (**183**) to give **85** (X = O), and the same reactive species can also be trapped by other dieneophiles[84,159] or through non-cycloaddition processes (equation 19)[74].

In the dehydrobromination of the dibromophosphonanedione oxides **184** (R = Me or Ph) with Et_3N, a normal 1,2-elimination is accompanied by a transannular process to give the fused system **185**[181]. The elimination of hydrogen halide from monohalogenated but otherwise symmetrical phosphine oxides leads to phosphiranes together with acyclic elimination products (equation 20)[201,202]. Here, the choice of base is critical. The best yields in the cyclization are achieved by the use of $LiNEt_2$ in Et_2O at −60 to +10 °C, and with the minimum of elimination to alkenephosphine oxide and reductive dehalogenation. By contrast, little if any phosphirane is obtained when lithium 2,2,6,6-tetramethylpiperidide in Et_2O or thf at −78 to +35 °C is used, and when reductive dehalogenation is at a maximum.

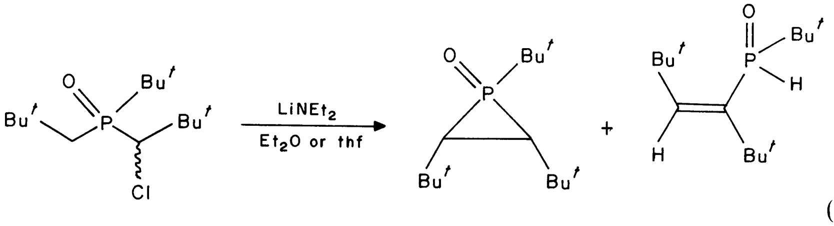


(181) **(183)**

85 (X = O)

(19)

(184) **(185)**



(20)

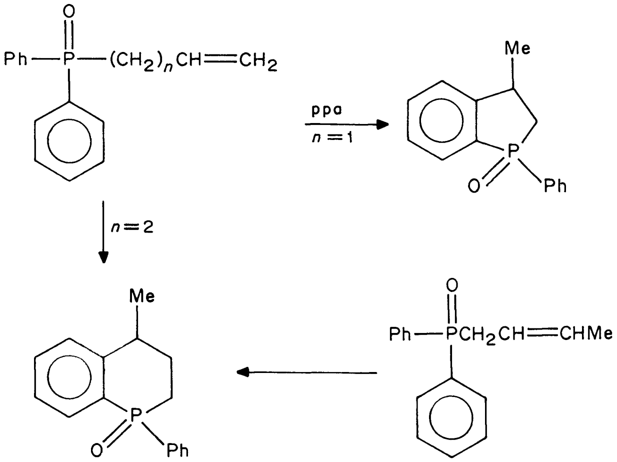
F. Electrophilic Aromatic Substitution

An early demonstration of the position that an electrophile occupies on entering an aromatic ring directly attached to the phosphoryl group in a phosphine oxide, was made by Challenger and Wilkinson who, in 1924, showed that the product from the nitration of triphenylphosphine oxide was tris(3-nitrophenyl)phosphine oxide, obtained originally by the same process by Michaelis in 1885, although without characterization[6–9]. The later identification consisted of reduction to tris(3-aminophenyl)phosphine oxide followed by diazotization and a Sandmeyer conversion into tris(3-chlorophenyl)phosphine oxide, identified by alternative synthesis. We thus have an early indication of the electron-withdrawing activity of the phosphoryl group. Similar procedures have been followed to show the marked preponderance of *meta* substitution during the nitration of bis(chloromethyl)phenylphosphine oxide and methyldiphenylphosphine oxide. Appreciable *ortho* substitution may also occur during conventional nitration. Thus, for the oxides $R_2P(O)Ph$, when R = Me, Et or Pr^i, the ratios of *meta* to *ortho* substitution are 90:10, 93:7 and 99:1, respectively; when R = CH_2Cl, only *meta* substitution was observed (see above)[205]. Russian workers obtained similar results with other simple oxides and noted that the corresponding phosphine sulphides gave the same products and product ratios. However, as might be expected, nitration of dialkyl(benzyl)phosphine oxides gave the dialkyl(4-nitrobenzyl)phosphine oxides[124].

Elsewhere, *meta* substitution has been assumed in nitration, sulphonation[206] and chloromethylation[207]. A recent study has demonstrated *meta*-sulphonation when triphenylphosphine oxide, or the sulphide, is dissolved in oleum, although in the case of the oxide the actual *meta*-directing group might then be $P^+—OH$[208].

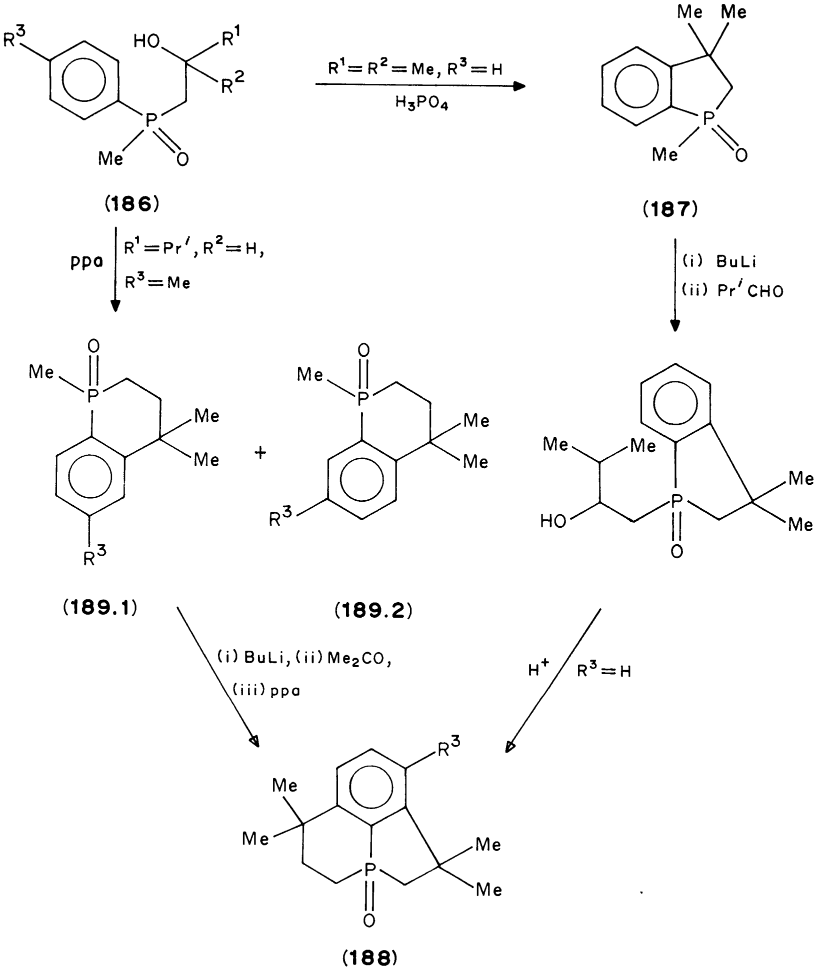
Although chloromethylation appears to be the only example thus far recorded of intermolecular alkylation of an aromatic ring directly attached to the phosphoryl group, and thus far to be of little interest, intramolecular alkylation is a process important in the synthesis of polycyclic phosphine oxides[209]. The alkylating function may consist, initially, of an olefinic bond or a hydroxyl group. In the reactions exemplified in Scheme 38 the cyclizations were achieved using polyphosphoric acid at 150–200 °C[210].

Two groups have synthesized tricyclic phosphine oxides using the methodology. Warren and coworkers started with **186** (R^3 = H), which yields the phosphindoline oxide **187** when treated with 98% H_3PO_4; further metallation, treatment with isobutyraldehyde and cyclization afforded **188** (R^3 = H)[211]. A similar sequence starting with **186** (R^3 = Me) proceeds through an inseparable mixture (**189**) of intermediates, although this provides no obstacle to the successful synthesis of **188** (R^3 = Me)[57].

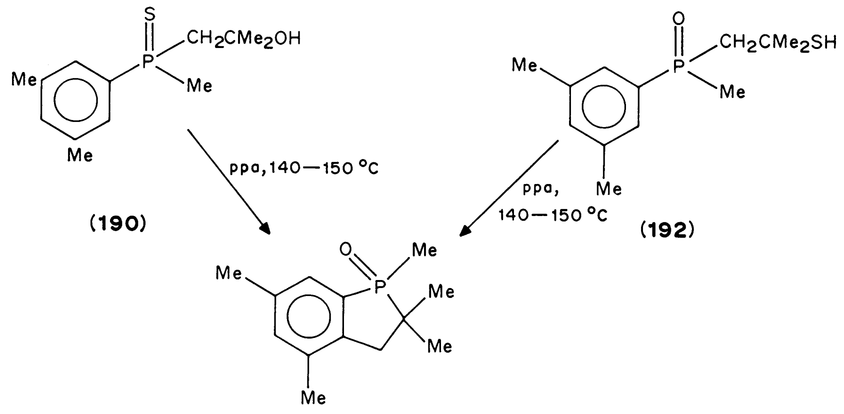


SCHEME 38

The phosphine sulphide **190** is acted on by ppa at 140–150 °C to give a 3:1 mixture of the phosphindoline oxide **191** and the corresponding sulphide. The phosphine oxide **192**, obtained through the isomerization of **190** with $MeSO_3H–P_4O_{10}$ at ambient temperature, loses H_2S when heated with ppa, and affords **191** only[212].



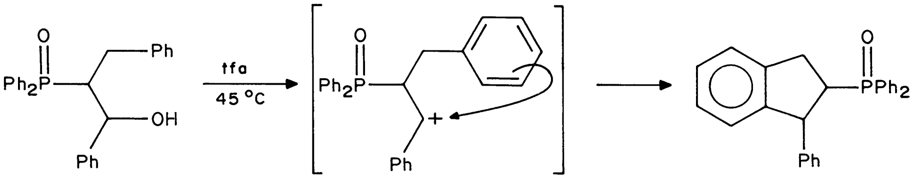
Acidity data for ω-phosphinoyl-alkanecarboxylic acids[213–215] and -benzoic acids[216], and also for other compounds, demonstrate the strong electron-withdrawing ability of the $R_2P(X)$ group (X = O or S), also proved by the course of electrophilic aromatic substitutions. If, in the latter, a carbocationic site is generated near to an aromatic ring distant from the phosphinoyl group, then it is that aromatic ring which will, in preference, react with the carbocation (Scheme 39)[211]. The deactivation is such that even an isolated carbon—carbon double bond will react in preference to the phosphinoyl-deactivated benzene ring (reaction 21).



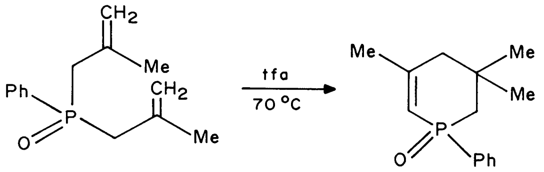
(190)

(192)

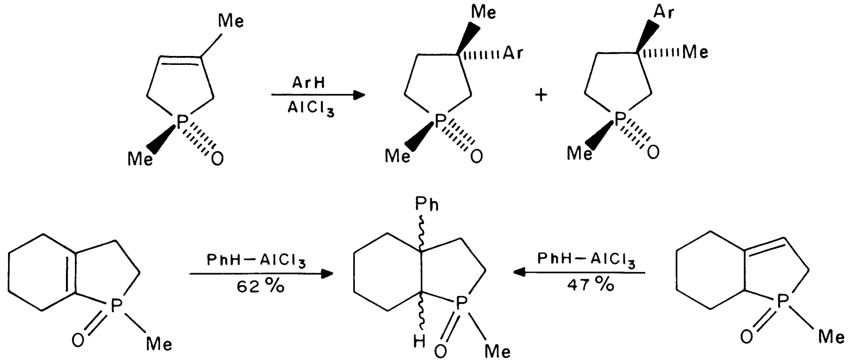
(191)



SCHEME 39



(21)

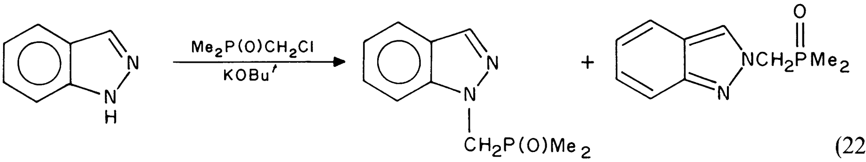


SCHEME 40

Friedel–Crafts arylation of phospholene derivatives has been accomplished readily (Scheme 40) using $AlCl_3$ as catalyst, although such reactions fail to occur in the presence of BF_3, $SnCl_4$, HCl or H_3PO_4[217].

G. Nucleophilic Substitution

Hydroxymethylphosphine oxides are converted into the corresponding chloromethyl compounds through reaction with $SOCl_2$ or PCl_5. The chloromethyl group is then reactive towards a wide range of nucleophiles. Reaction with dialkylamines is straightforward[218], as is that with the sodium salt of imidazole, or other azoles in the presence of KOBu^t, although tautomerism may then be the cause of mixed product formation (reaction 22)[219].

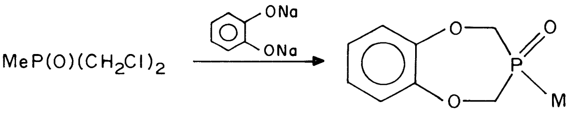


(22)

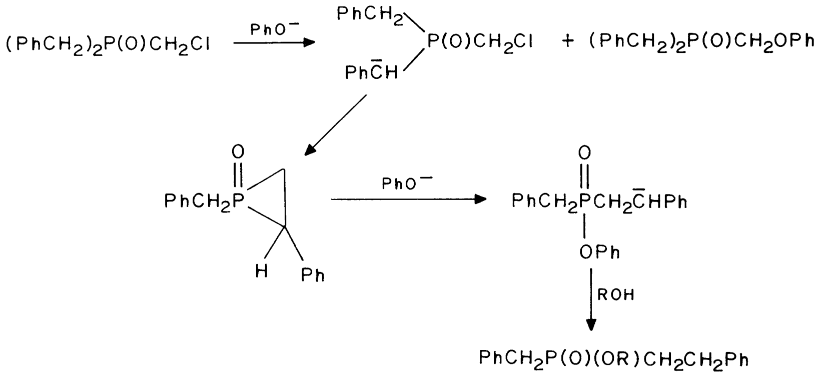
Reactions involving thiolate anions[218], alkoxide anions[218] or azides[220] are also without apparent problems. The chloromethyl group undergoes Arbuzov reactions with suitable esters of tervalent phosphorus acids as exemplified by reaction 23[221]; tertiary phosphines yield (phosphinoylmethyl)phosphonium salts[222]. The chlorine is replaceable by certain carboxylate (generally aromatic) anions (reaction 24) and in some cases straightforwardly by aryloxide anions (equation 25)[223,224].

$$(PhCH_2)_2P(O)CH_2Cl + (PhCH_2)_2POEt \longrightarrow (PhCH_2)_2P(O)CH_2P(O)(CH_2Ph)_2 \qquad (23)$$

$$(ClCH_2)_3PO \xrightarrow{\text{PhCOONa}} (PhCOOCH_2)_3PO \qquad (24)$$

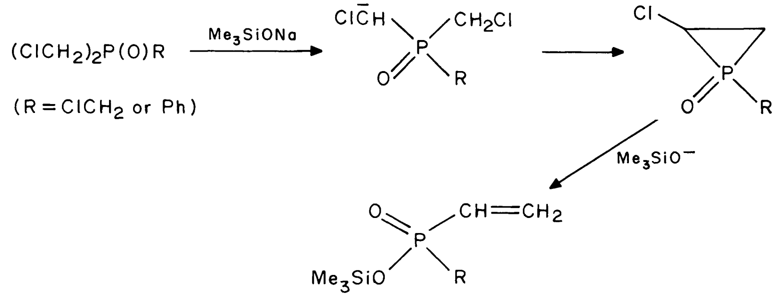


(25)



SCHEME 41

Other displacements by aryloxide anions may result in complications with the formation of 'normal' and rearranged products (Scheme 41)[218]. A novel reaction between bis(chloromethyl)phosphine oxides and Me_3SiONa has been afforded a similar interpretation involving initial deprotonation (Scheme 42)[225].



SCHEME 42

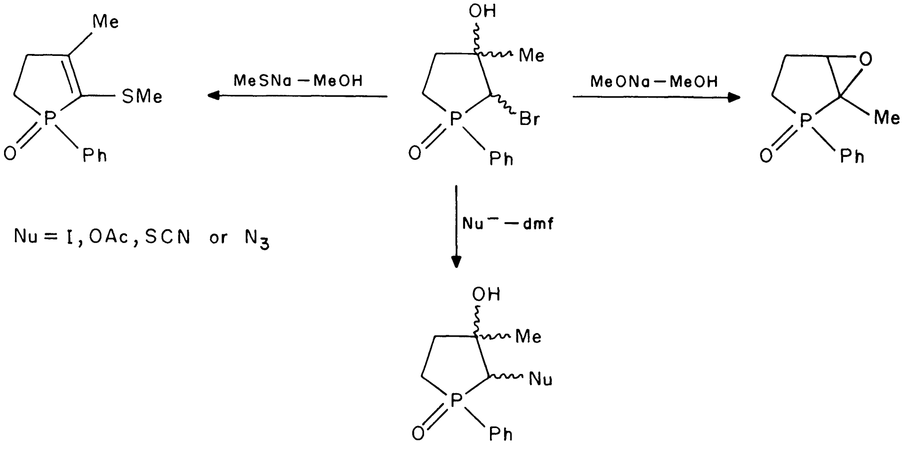
The halogen in 2- and 1-chloroethyl groups can be replaced directly (reaction 26)[226] or by consecutive elimination–addition processes as in reactions 27[222] and 28[204]. The results of an investigation[197] into displacements of a halogen attached to a phospholane ring are summarized in Scheme 43; the type of product depended on the nature of the attacking nucleophile. Observed nucleophilic displacements have not been restricted to those of halogen from sp^3 carbon, but include those of other groups, e.g. sulphonate anions (reaction 29)[227].

$$R_2P(O)CH_2CH_2Cl + (EtO)_2PSSNa \longrightarrow R_2P(O)CH_2CH_2SP(S)(OEt)_2 \qquad (26)$$

$$Ph_2P(O)C_6H_4CHClMe\text{-}4 + MeOH \longrightarrow Ph_2P(O)C_6H_4CHMe(OMe)\text{-}4 \qquad (27)$$

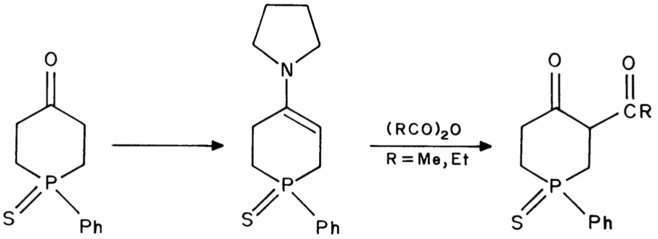
$$(ClCH_2CH_2)_2P(O)CH_2Cl \xrightarrow[X\,=\,O\text{ or }S]{2RXNa} (RXCH_2CH_2)_2P(O)CH_2Cl \qquad (28)$$

$$Ph_2P(O)CH_2Otos + Ph_3P \longrightarrow Ph_2P(O)CH_2P^+Ph_3\,tosO^- \qquad (29)$$



SCHEME 43

Reactions in which the functionalized phosphine oxide itself acts as the nucleophile include those reactions of hydroxyalkyl- and aminoalkyl-phosphine oxides towards acylating agents. Tris(hydroxymethyl)phosphine oxide is best acylated with the acyl chloride in $PhNO_2$, and attempts to acetylate tris(2-hydroxyethyl)phosphine oxide with ketene, acetyl chloride or acetic acid all failed, although the use of acetic anhydride was successful[204]. Aminoalkylphosphine oxides form the customary derivatives in their interactions with acyl halides, ureas, isocyanates[228] and ketenes[229]. Cyclic phosphaketones can be acylated on oxygen through their enol forms[203] or on carbon through an enamine intermediate (Scheme 44)[230].

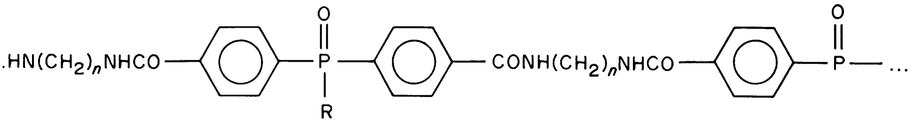


SCHEME 44

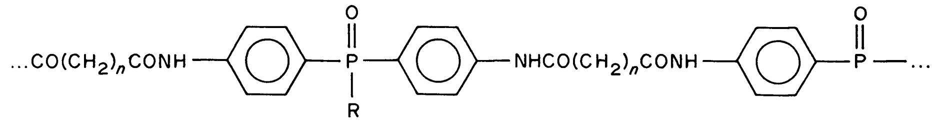
Tris(4-chlorophenyl)phosphine oxide is unreactive towards aqueous or ethanolic alkali, ammonia or aniline, but the positioning of NO_2 groups *ortho* to Cl renders the compounds increasingly reactive to these and similar nucleophiles[206,231]. Aromatic halogen (Cl, F) *para* to a phosphinoyl group is displaceable by MeO^- and the kinetics of the process for a series of 4-(dialkylphosphinoyl)-1-halogenobenzenes have been determined[222,232]. Methoxy groups in several 3- and 4-methoxyphenylphosphine oxides have been demethylated using 48% aqueous HBr, 50% aqueous HI or HBr in acetic acid.

$MeNH_2$ displaces only a *para* fluorine atom from either diphenylphosphinoyl- or diphenylphosphinothioyl-pentafluorobenzene in EtOH; in benzene, *ortho* substitution also occurs when, for the oxide, the *ortho*:*para* ratio is 46:54, whereas for the sulphide it occurs when the ratio is 82:18. With NaOMe in MeOH, *ortho* and *para* substitution again both occur for both oxide and sulphide; additionally, however, the sulphide undergoes phosphorus—carbon bond cleavage to give methyl diphenylphosphinothioate[233,234].

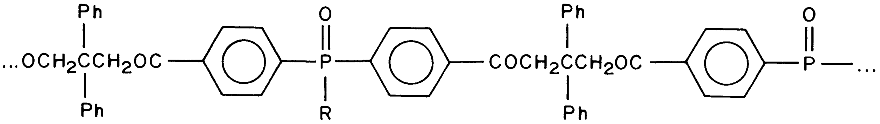
Phosphinoyl-substituted benzoic acids, conveniently obtained by the permanganate oxidation of tolylphosphine oxides, can be transformed via the acid chlorides into amides, aldehydes and alcohols[170]. Phosphinoylarylamines provide phosphinoyl isocyanates and thus phosphinoyl-ureas and -urethanes[235]. Bis(carboxyphenyl)phosphine oxides in their reactions with α,ω-alkanediamines yield phosphine oxide-based polyamides of type **193**, and the related polyamides (**194**) are obtainable from bis(aminophenyl)phosphine oxides and dicarboxylic acids and their derivatives. The condensation of bis(chlorocarbonyl)-phenylphosphine oxide with diphenylolpropane yields a polymeric ester **195**[6].



(**193**)



(194)



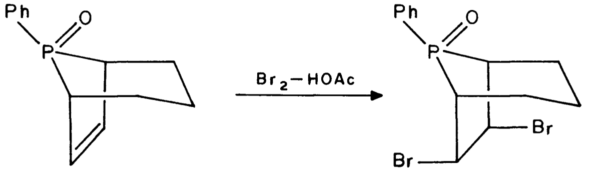
(195)

H. Addition Reactions

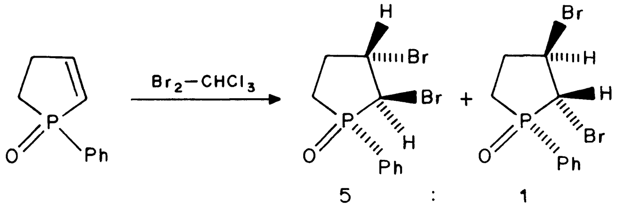
Unsaturated phosphine oxides undergo addition reactions with electrophiles, nucleophiles, free radicals and other species, with cycloaddition reactions playing a prominent role. Of particular interest is the involvement of the phosphinoyl group in such reactions, both indirect in its influence on the course of such reactions, but also by direct involvement in bond formation.

1. Electrophilic additions

The reaction of chlorine or bromine with either vinyl- or allyl-phosphine oxides yields products the natures of which are consistent with a *trans* addition shown for both acyclic and cyclic (phospholenes) phosphine oxides according to equations 30[177] and 31[236].

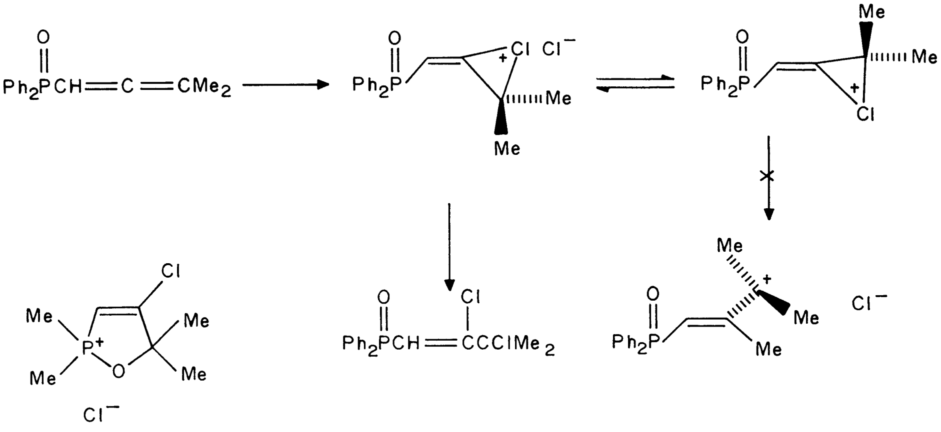


(30)



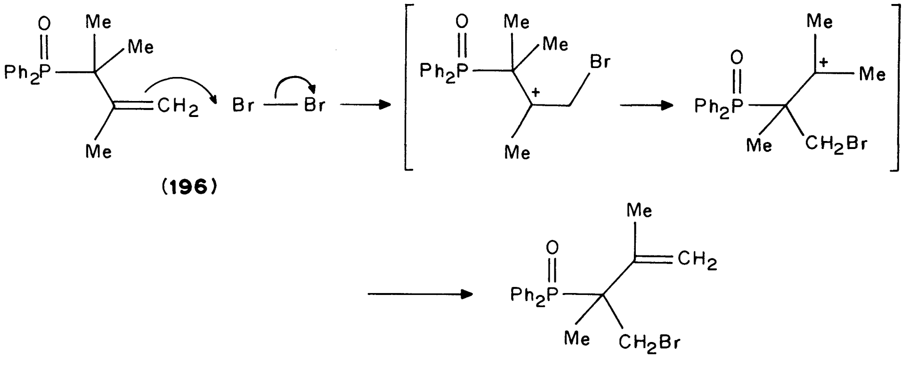
(31)

The addition of chlorine to allenephosphine oxides is a particularly interesting case of electrophilic addition. Although not so extensively examined as the additions of halogens and other electrophiles to structurally similar phosphonic esters, one notable feature is the fact that (3-methylbuta-1,2-dienyl)diphenylphosphine oxide adds the halogen to the terminal double bond whereas (3-methylbuta-1,2-dienyl)dimethylphosphine oxide yields a cyclic phosphonium salt (Scheme 45)[237].



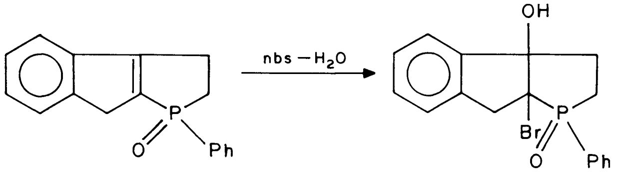
SCHEME 45

The addition of bromine to the phosphine oxide **196** is also unusual. Normal electrophilic attack is initiated but a faster phosphinoyl migration (Section III.C) occurs within the intermediate carbocation, and the product, isolated in quantitative yield is the monobromo compound **197**[193,195].



The formation of phosphinoylated bromohydrins when acyclic vinylphosphine oxides (equation 32)[238] and 2-phospholenes (equation 33)[74] react with nbs under aqueous conditions is probably the result of nucleophilic participation by the solvent. Diphenylvinylphosphine oxide itself fails to react[238]. Addition of a phosphorodithioic acid to a vinylphosphine oxide takes place under moderate conditions of heat in a suitable solvent (equation 34). Additions to vinylphosphine sulphides occur more slowly and even then only under more forcing conditions[226].

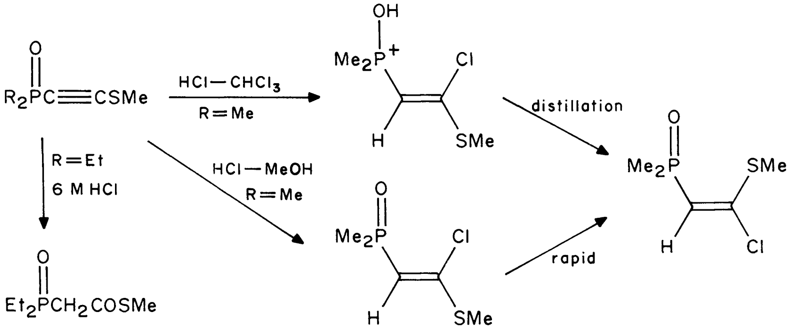
$$\mathrm{Ph_2P(O)CH{=}CR^2R^1 \xrightarrow[\mathrm{H_2O}]{\text{nbs or nba}} Ph_2P(O)CHBrC(OH)R^1R^2} \tag{32}$$



(33)

$$R^1{}_2P(X)CH{=}CH_2 + (R^2O)_2P(S)SH \longrightarrow R_2P(X)CH_2CH_2SP(S)(OR^2)_2 \quad (34)$$

The addition of hydrogen halides to acetylenic phosphine oxides has also been investigated to only a limited extent, but agreement seems to have been reached that both HCl and HI react, the latter faster, in a *trans* fashion to yield a *cis*-olefinic phosphine oxide, through a pseudophosphonium intermediate (depending on reaction solvent), and that isomerization may occur during final distillation (Scheme 46)[239,240].

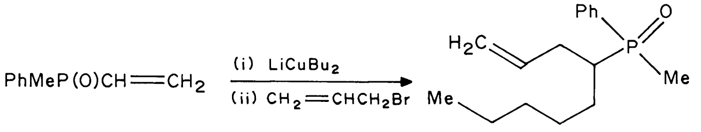


SCHEME 46

2. *Nucleophilic additions*

Reported Michael additions of carbanions to alkenephosphine chalcogenides include that of diethyl malonate (equation 35); equation 36 illustrates addition followed by alkylation with organolithium cuprates, $LiCuR_2$[241]. A similar addition to an allenephosphine oxide affords a mixture of products (reaction 37)[242]. Organometallic reagents have been used to effect anionic polymerization, with Grignard reagents acting on diphenylvinylphosphine oxide to obtain polymers with molecular weights of around 10000. Zinc–copper couple promotes the addition of alkyl halides to vinylphosphine oxides in an aqueous ethanolic medium; the scope of the reaction includes the use of sterically hindered alkyl halides[243].

$$Ph_2P(O)CH{=}CH_2 + CH_2(COOEt)_2 \xrightarrow{Na} [Ph_2P(O)CH_2CH_2]_2C(COOEt)_2 \quad (35)$$



(36)

$$Ph_2P(O)CH{=}C{=}CH_2 \xrightarrow{LiCuMe_2} \underset{70\text{–}93\%}{Ph_2P(O)CH_2CMe{=}CH_2} + \underset{7\text{–}30\%}{Ph_2P(O)CH{=}CMe_2} \quad (37)$$

Acetylenic phosphines, $R^1{}_2PC{\equiv}CR^2$, cannot be alkylated by nucleophilic additions of Grignard reagents, whereas the corresponding reactions of the oxides and sulphides take place readily in the presence of a trace of copper(I) halide (equation 38) in high yields; the stereochemistry of addition appears, as yet, to be undecided. Further addition to the alkene products also does not take place[244].

$$R^1{}_2P(X)C{\equiv}CR^2 + R^3MgY \xrightarrow[Y = Br \text{ or } I]{X = O \text{ or } S} R^1{}_2P(X)CH{=}CR^2R^3 \qquad (38)$$

$$R^1 = \text{Me or Ph}; \; R^2 = R^3 = \text{Me, Et or Ph}$$

The additions of protic substances possessing the X—H bond, where X = N, O, S or P, have been investigated far more extensively than those of active methylene C—H acids. In general, the additions reactions involving vinylphosphine oxides are much faster than those of the parent phosphines, if indeed the latter react at all, but they are slower than those same reactions of esters of vinyl-phosphonic or -phosphinic acids. The additions take place in a manner contrary to the Markownikoff rule and the heteroatom adds to the β-carbon atom. There is the direct analogy between the modes of additions to C=CP=O and C=CC=O[245].

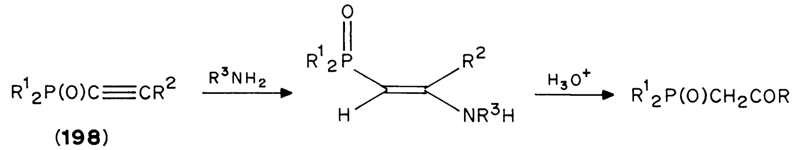
Successful addition of an amine to a vinylphosphine oxide requires that for the amine pK_B be less than 3[246] and in the case of primary amines a two-stage process is possible (Scheme 47). From the phosphorus reactant point of view, the addition of amines to vinylic or allylic diphenylphosphine oxides succeeds when substituents on the sp^2 carbon are lacking or when there is only one substituent on $C_{(2)}$, but the presence of one substituent α or two β to phosphorus prevents addition. Benzamide also adds to diphenylvinylphosphine oxide in the presence of NaH under thf[247,248]. Additions have been carried out with optically active chiral phosphine oxides[249] and with optically active amines, e.g. L-prolinol[246].

$$Ph_2P(O)CH{=}CH_2 \xrightarrow{RNH_2} Ph_2P(O)CH_2CH_2NHR$$

$$\xrightarrow{Ph_2P(O)CH{=}CH_2} [Ph_2P(O)CH_2CH_2]_2NR$$

SCHEME 47

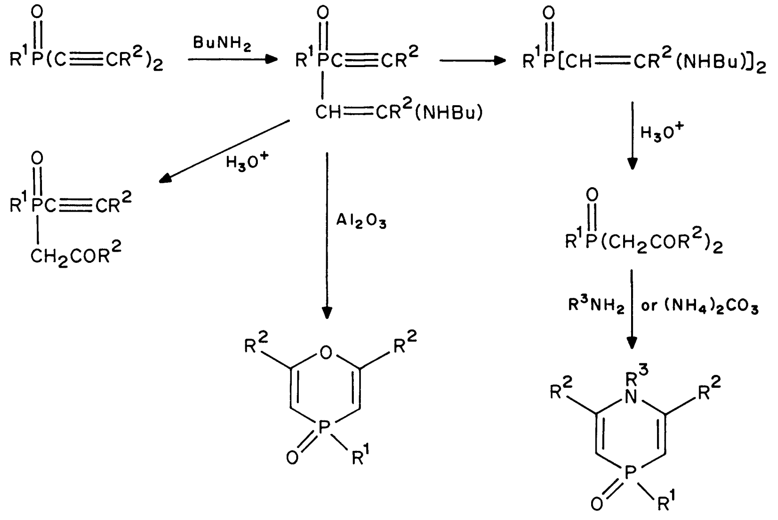
Conclusions differ as to the stereospecificity of additions of amines to acetylenic phosphine oxides (but again, additions to acetylenic phosphines do not occur), but do agree on regiospecificity. Additions to **198** (R^1 = Ph; R^2 = H, primary alkyl, cyclohexyl, Bu^t or Ph) have been stated to occur in a *cis* fashion to yield *trans*-enamine products which do not then isomerize to the *cis* forms (Scheme 48)[250,251]. The enamines are hydrolysable (aqueous oxalic acid) to β-ketoalkylphosphine oxides. On the other hand, further studies using **198** (R^1 = Me or Bu) have suggested that the stereospecificity of addition depends on the experimental conditions but appears to be initially *trans* followed by isomerization to the *cis* form: at −20 °C Et_2NH adds to **198** (R^1 = Bu) to give the *cis*-enamine, but at 60 °C the product has *trans* geometry. When Me_2NH is used, a mixture of *cis* and *trans* products is formed even at −20 °C[239].



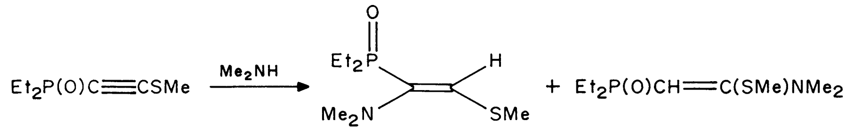
(198)

SCHEME 48

Additions to bis(acetylenic)phosphine oxides are of particular interest and value since they provide an acceptable route to several heterocyclic systems, as exemplified in Scheme 49[252,253]. The regiospecificity of addition of amines can be modified by the presence of appropriate substituents at the acetylenic $C_{(2)}$ and also by change in experimental conditions (equation 39)[240].

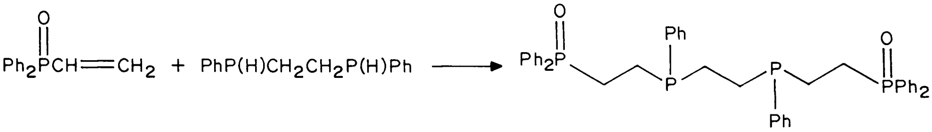


SCHEME 49

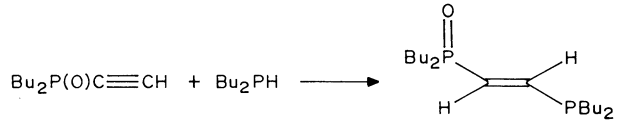


(39)

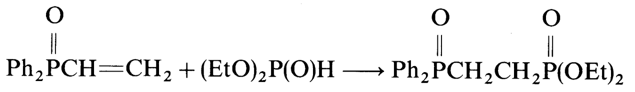
The additions of primary or secondary phosphines to vinylphosphine oxides or sulphides constitute well authenticated reactions for the synthesis of polyphosphine chalcogenides (e.g. reaction 40)[254] and thus polyphosphines themselves following deoxygenation or desulphurization (Section II.A.1.2)[90,91]. Phosphines which have been examined in connection with reaction 40 include phosphine itself, RPH_2 (R = Me or Ph), R_2PH (R = Me or Ph), $H_2PCH_2CH_2PH_2$ and $Ph(H)PCH_2CH_2P(H)R$ (R = H or Ph). The additions of phosphines to acetylenic phosphine oxides (equation 41)[255] and dialkyl phosphonates to unsaturated phosphine oxides (e.g. reaction 42) have also been recorded.



(40)



(41)



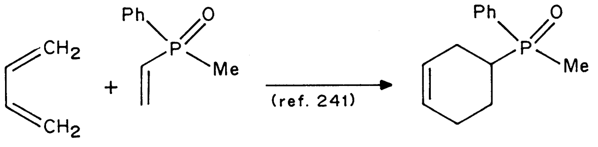
$$Ph_2\overset{O}{\overset{\|}{P}}CH{=}CH_2 + (EtO)_2P(O)H \longrightarrow Ph_2\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}(OEt)_2 \qquad (42)$$

The addition of alcohols to vinylphosphine oxides and sulphides occurs regiospecifically with the RO group adding to $C_{(2)}$[238,239]; reactions have been carried out with chiral phosphine oxides[27] and with optically active alcohols such as borneol and menthol[256], but the reaction may be complicated by nucleophilic substitution at phosphorus. Thus, the products from the interaction of $Bu_2P(O)C{\equiv}CH$ and NaOEt in EtOH for 2 h at 75 °C include both *cis*- and *trans*-$Bu_2P(O)CH{=}CH(OEt)$ together with $Bu_2P(O)CH_2CH(OEt)_2$ (the total yield of the three products was 30%) and $Bu_2P(O)OEt$ (47%) and acetylene[239]. Both mono- and bis-addition, as well as cleavage, have also been observed in the reaction between NaOMe and $Me_2P(O)C{\equiv}CSMe$[240]. Hydration of vinylphosphine oxides has been achieved by exploiting the hydroboration process; the stereochemistry of reaction for rigid cyclic systems is unaffected by the stereochemistry at phosphorus[177].

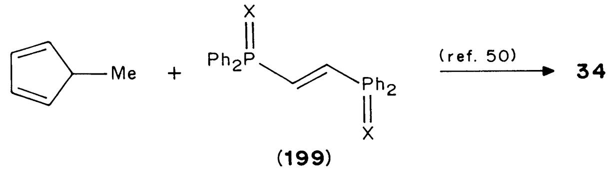
In competition experiments, thiols have been shown to be more selectively reactive in additions to diphenylvinylphosphine oxide than are either primary alcohols or amines[257]; the additions are regiospecific with the sulphur adding to $C_{(2)}$, but a mixture of (*E*)- and (*Z*)-vinylic thioethers results from acetylenic phosphine oxides[239,240]. Additions have also been observed to occur slowly under free-radical conditions.

3. *Cycloaddition reactions*

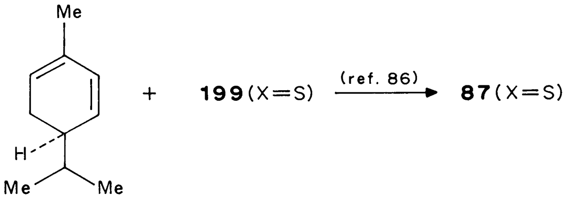
Acyclic unsaturated phosphine oxides are able to react as either dienes or dieneophiles in intermolecular Diels–Alder reactions. The complexity of such reactions ranges from the very straightforward, such as the addition of diphenylvinylphosphine oxide to cyclopentadiene, through to reactions which build up phosphorus-containing analogues of well known natural product molecules. A selection of reactions which illustrate the dieneophilic behaviour of vinylphosphine oxides and sulphides is given in equations 43–49. Reference has already been made to the removal of the chalcogen from **34**, **87** (X = S) and **88** (X = S) to give the tervalent phosphorus compounds, useful as chiral ligands (Section II.1.2). The reaction represented by equation 47 is a complete reversal of the usual reaction direction, and is the result of the negation of the influence of the carbonyl group by the diphenylphosphinoyl group. Reaction 48 illustrates the instability of the initial Diels–Alder adduct, always a possibility, and which, by the rapid loss of CO_2 in a retro-reaction, affords ultimately 1,2-bis(diphenylphosphinoyl)benzene. Reaction 49 exemplifies the synthesis of a 17-phosphasteroid analogue; a similar reaction with 1-phenyl-2-phospholene 1-oxide and 2,3-disubstituted buta-1,3-dienes yields hexahydro-phosphindolines as their oxides[77].



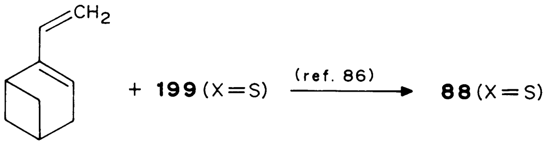
(43)


Me
+
X
Ph2P
Ph2
X
(199)
(ref. 50)
34

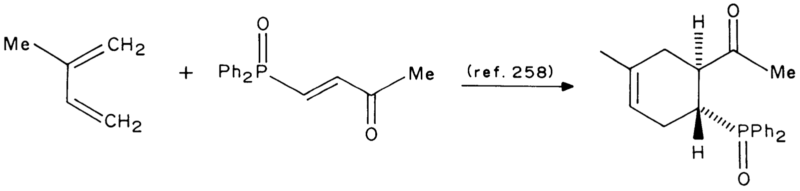
(44)


Me
H
Me
Me
+
199(X=S)
(ref. 86)
87(X=S)

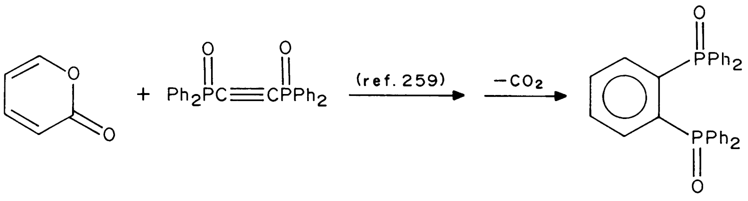
(45)


CH2
+ 199(X=S)
(ref. 86)
88(X=S)

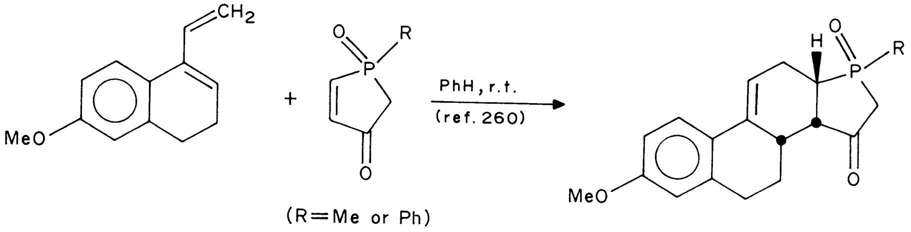
(46)


Me
CH2
CH2
+
O
Ph2P
Me
O
(ref. 258)
H
O
Me
PPh2
O
H

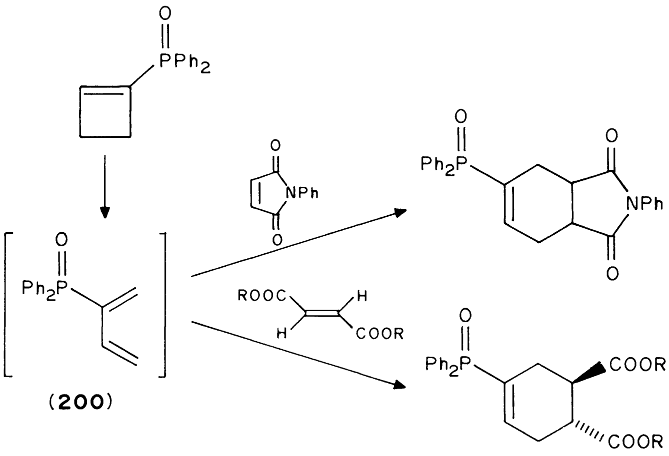
(47)


O
O
+
O
O
Ph2PC≡CPPh2
(ref. 259)
−CO2
O
PPh2
PPh2
O

(48)


CH2
MeO
+
O
R
P
O
(R=Me or Ph)
PhH, r.t.
(ref. 260)
H
O
P
R
O
MeO

Thermolysis of 1-(diphenylphosphinoyl)cyclobutene affords the very reactive 2-(diphenylphosphinoyl)buta-1,3-diene (**200**), which acts as an activated diene and can be trapped with the customary dieneophiles in reactions illustrated in Scheme 50[261]. Monomeric phospholes can also act in the dual capacity as either dienes or dieneophiles. The 1-oxides and 1-sulphides of phospholes exhibit a marked propensity to dimerize, although there are some exceptions to such behaviour, and they include 1,2,5-triphenylphosphole 1-oxide, penta-substituted phosphole 1-oxides, including the pentaphenyl derivative, and 3,4-dimethyl-1-phenylphosphole 1-sulphide. When operational, the dimerization process yields the *endo* isomer products. Scheme 51 illustrates the ready formation and dimerization of a highly reactive phosphole, which can also be trapped by added dieneophiles[262,263].

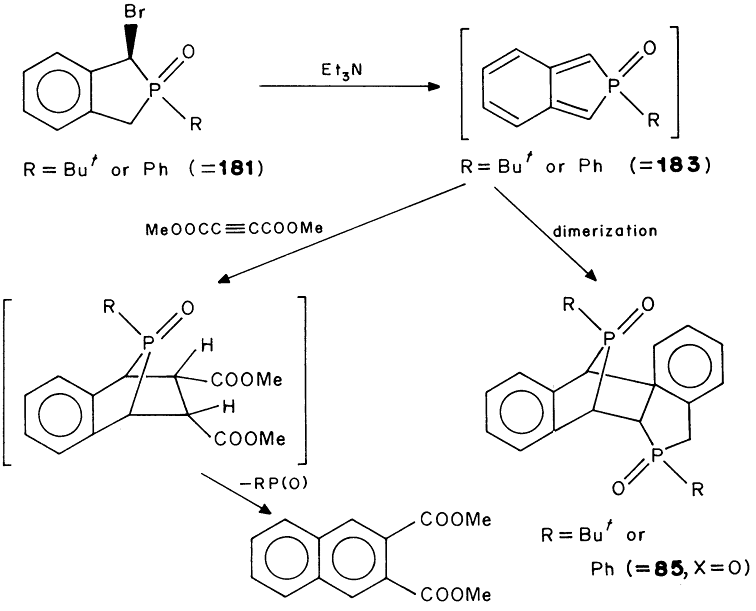


SCHEME 50

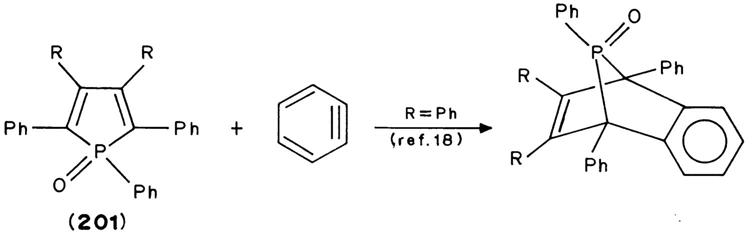
Reactions which illustrate the intermolecular diene behaviour of phosphine chalcogenides are illustrated in equations 50–53. The reactions indicated in Scheme 52 illustrate the diene behaviour of 1,2-dihydrophosphorin 1-oxides and their value in syntheses of 2-phosphabicyclo[2.2.2]oct-5-enes[267] and -octa-5,7-dienes[268]. Once again, the initial [4 + 2] adducts often break down when heated gently.

The capacity of phosphole 1-chalcogenides to act as dieneophiles is illustrated by reactions 54–56. Reaction 56 results in a 15-phosphasteroid analogue. The reaction with tropone should be considered as [2 + 4] rather than a [4 + 6] addition. Thioacetophenone undergoes a [4 + 2] cycloaddition to give **203**; other examples of compounds possessing the same bicyclic system have been obtained by the interaction of phosphole oxides or sulphides with oxyallyl cations, when the coproducts are 8-phosphabicyclo-[3.2.1]octanes[265].

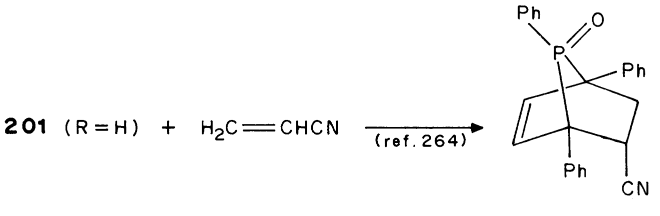
A useful study[271] has demonstrated the catalytic activity of Lewis acids in reaction systems comprising vinylphosphine oxides and dienes. In the absence of catalyst, diphenylvinylphosphine oxide and cyclopentadiene react to give a 19% yield of a 42:58 mixture of *endo* and *exo* products. With the addition of 10 mol% of catalyst the yields of mixed adducts ranged from 23% (with $SnCl_4$) to 47% (using $TiCl_4$), but with generally little change in the stereochemical ratios, which ranged from 48:52 {for $[Cl_2Ti(OPr^i)_2]$} to 60:40 (using $TiCl_4$), with $AlCl_3$, $FeCl_3$ and $SnCl_4$ producing intermediate effects. More notable, however, were the significantly higher yields with *endo*:*exo* ratios of 3:1



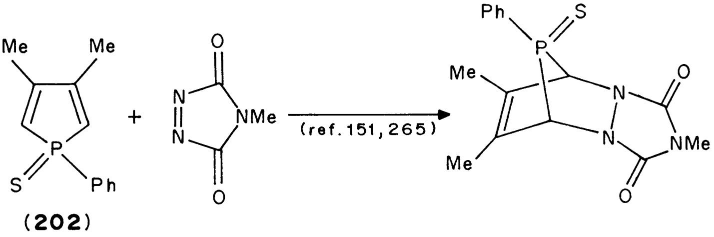
SCHEME 51



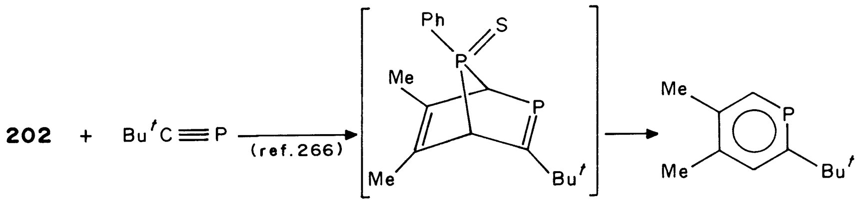
(50)



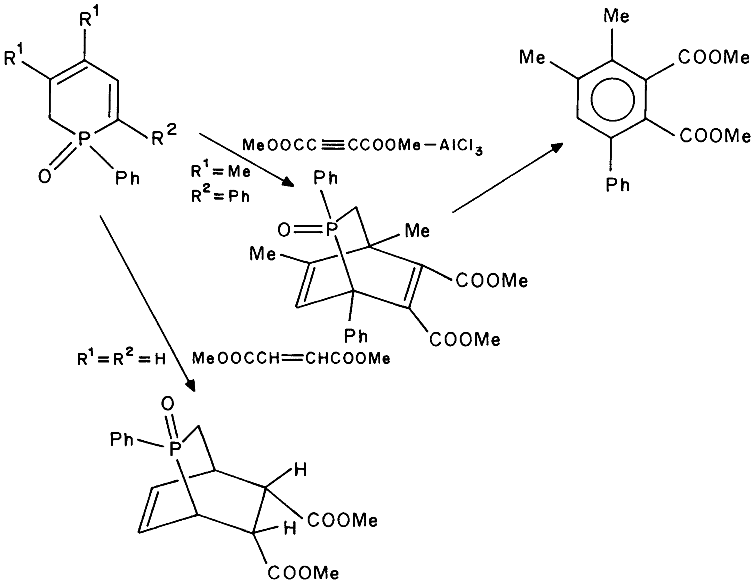
(51)



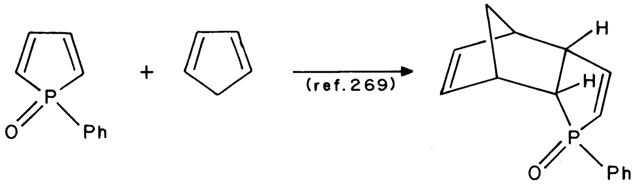
(52)



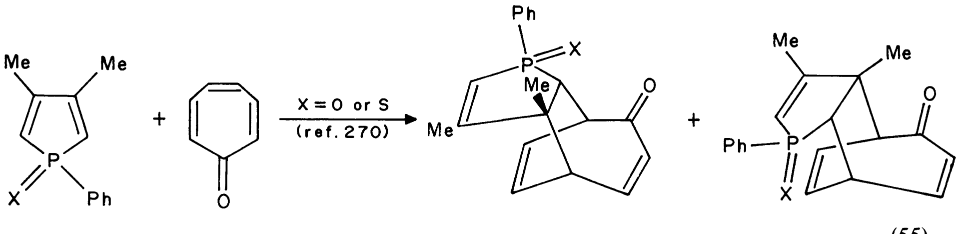
(53)



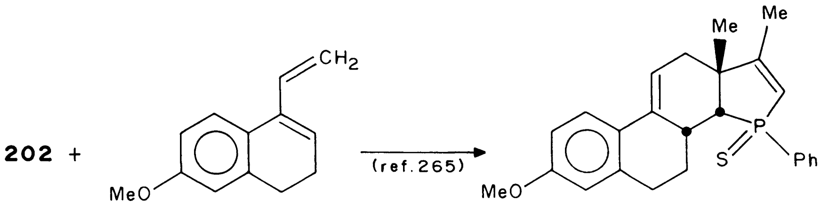
SCHEME 52



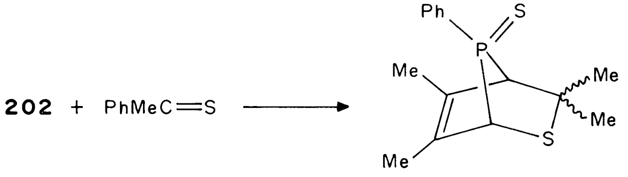
(54)



(55)

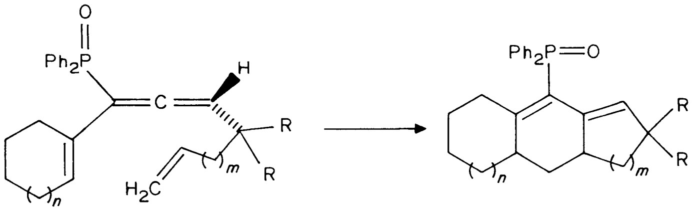


(56)

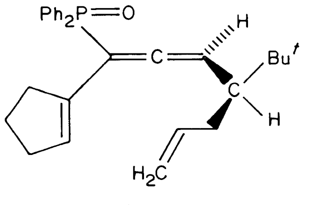


203

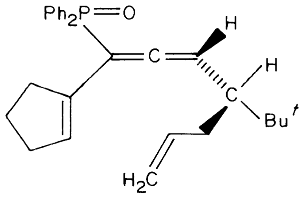
to 4:1 when 1 mol equiv. of catalyst ($AlCl_3$, $FeCl_3$ or $TiCl_4$) was employed. The same Lewis acids also produced worthwhile changes in the diastereoisomer ratios for the products from (2-methoxyphenyl)phenylvinylphosphine oxide and cyclopentadiene, and for which titanium-containing reagents were particularly valuable for obtaining more of the *endo* products.



(204)

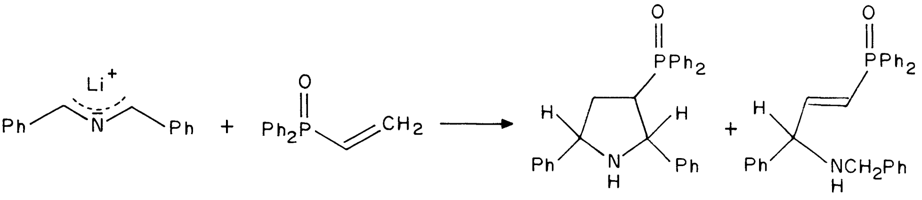


(205)



(206)

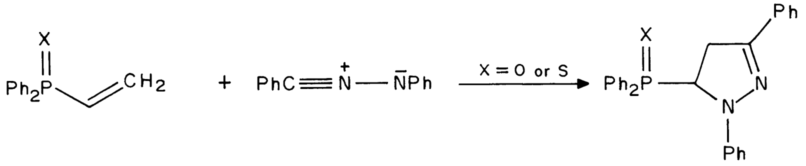
Some interesting activation effects have been found in connection with the unusual intramolecular Diels–Alder reaction of the allene phosphine oxides **204**[272]. Relative to the reaction rate observed for **204** ($n = 0$; $m = 1$; R = H), substitution by alkyl groups increased reaction speeds by factors of 4.6 (R = Me), 21.1 (R = Et) and 27.8 (R = Pr). On the other hand, increasing n from 0 to 3 (with $m = 1$) produced relatively little change in reactivity. Much more pronounced was the effect of change in stereochemistry, as demonstrated by **205** and **206**, which showed accelerations of 70 and 205 times that of **204** ($n = 0$; $m = 1$; $R = H$); increasing m from 1 to 2 in **204** ($n = 0$; $R = Me$) caused a decrease in the rate of cyclization by a factor of 850. The diphenylphosphinoyl group (and also the diphenylphosphino and analogous diphenylarsino and diphenylarsinoyl groups) activates ethene to cycloaddition with the lithium derivatives of Schiff bases as in reaction 57[273].



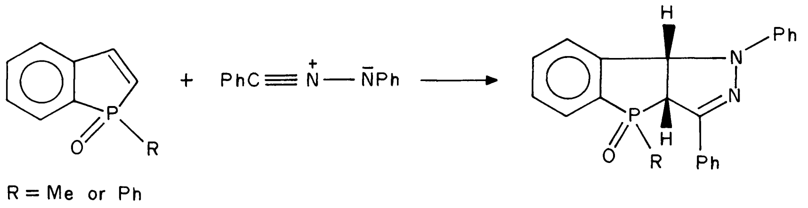
(57)

Vinylphosphine chalcogenides react with dipolarophiles in [2 + 3] cycloadditions with nitrones, nitrilimines, nitrile oxides, azides and diazoalkanes; such reactions result in the synthesis of diphenylphosphinoylated heterocyclic systems, but they appear to take place more slowly than those reactions for similar vinylphosphinic and vinylphosphonic acid derivatives.

In the reactions of vinylphosphine oxides or sulphides with nitrilimines, Kolokol'tseva *et al.*[274] have argued that the resultant pyrazolines are phosphinoylated at $C_{(2)}$ (equation 58) but this conclusion regarding regiospecificity has been disputed by other workers, e.g. for reaction 59[275].

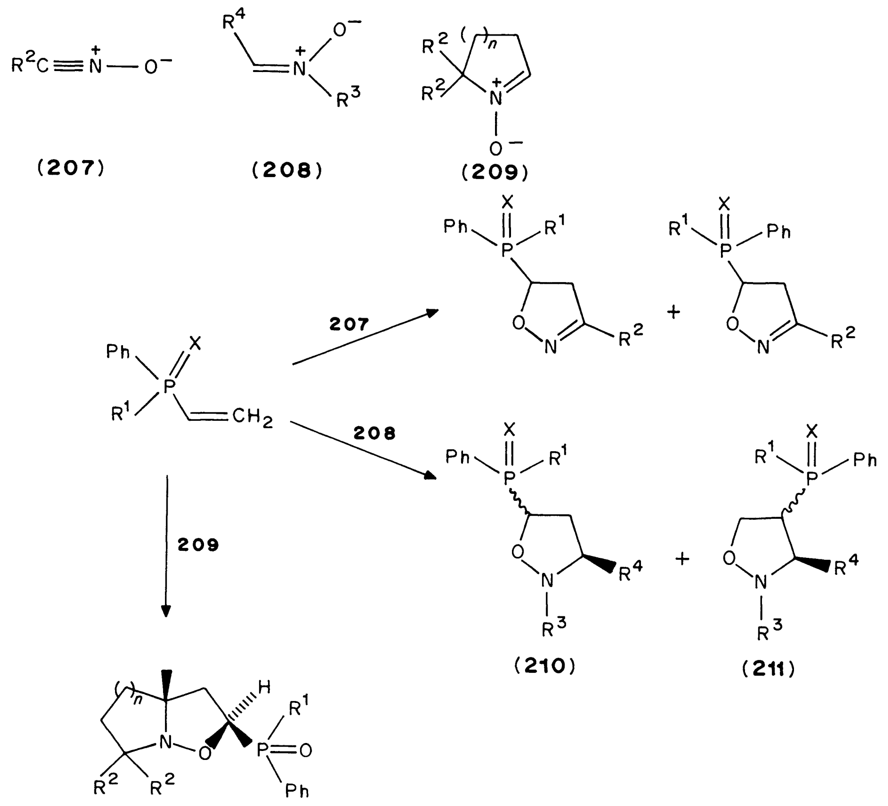


(58)



(59)

The same Russian authors have likewise described the formation of 5-phosphinoyl-1,2-oxazolines from vinylphosphine oxides or sulphides and nitrile oxides (Scheme 53), with conclusions regarding regiospecificity not being disputed by others[51,276]. Interestingly, the phosphine oxides are less reactive than the corresponding sulphides, and the 5-substituted regioisomers either prevail in the product mixtures or are the only products. Considerable diastereofacial selectivity is indicated by the dependence of the nature of the products on R^2, the diastereoisomeric ratios being 2.6:1 for $R^2 = Me$ and 1.6:1 for $R^2 = Ph$.



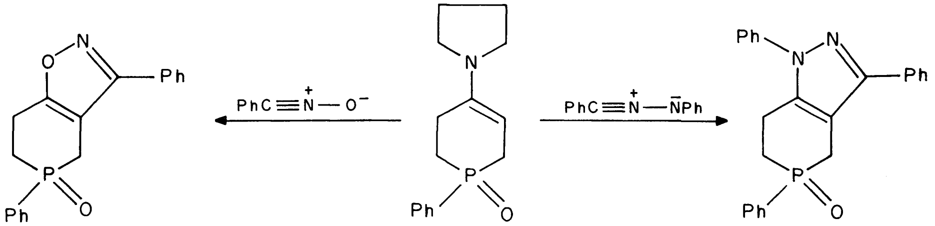
SCHEME 53

Reactions involving nitrones (**208**) yield the analogous 1,2-oxazolidines in non-regiospecific additions (Scheme 53)$^{276-278}$. In all those cases examined, the composition of the product mixtures depended on the structure of the nitrone, but the reactions were highly specific for the cyclic nitrones **209** which produced regioisomer ratios of >95:5. When the nitrone **208** ($R^3 = R^4 = Ph$) reacts with diphenylvinylphosphine oxide, the regiospecificity is represented in a **210**:**211** ratio of ca 40:60, whereas for nitrone **208** ($R^3 = Me$; $R^4 = Ph$) the ratio is ca 60:40, both figures being in contrast to the ratio 86:14 obtained for **209** ($n = 1$; $R^2 = Me$).

The principal regioisomer obtained from diphenylnitrone and diphenylvinylphosphine oxide has been shown by X-ray diffraction experiments to have the *trans* arrangement between the phosphinoyl and $C_{(3)}$ phenyl groups^{278}.

Cycloadditions of the same reagents to carbon—carbon double bonds which are not activated by adjacent phosphinoyl groups are but poorly exemplified (Scheme 54)^{279}.

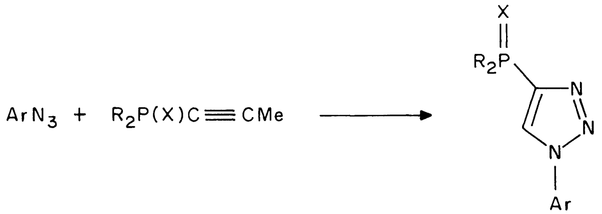
The influence of the chalcogen atom on the regio- and stereo-chemistry of addition of various nitrones to diphenylvinylphosphine chalcogenides has been examined in a recent study which showed that, for the acyclic nitrones **208** ($R^3 = R^4 = Ph$) undergoing reaction with $Ph_2P(X)CH{=}CH_2$ in benzene at 80 °C, a more equitable regioisomer distribution was obtained for X = O, but for X = S or Se the regioisomer ratio was 10:90; the regiochemistry was reversed when $R^3 = Me$. When the cyclic nitrone **209** ($n = 1$;



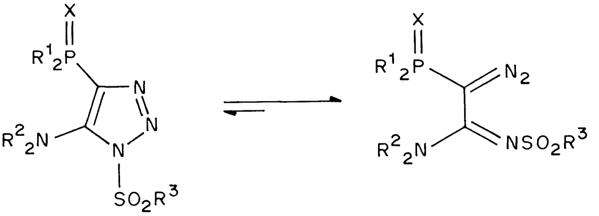
SCHEME 54

$R^2 = Me$) was employed in benzene at ambient temperature, the regiochemistry was unaffected by a change in X[280].

The addition of aryl azides to 1-propynylphosphine chalcogenides yields 4-phosphinoyl-1,2,3-triazoles (equation 60) in a process accelerated by either electron-donor or -acceptor substituents in the dipolarophile[281,282]. In a similar reaction between (2-aminoethynyl)-phosphine chalcogenides and sulphonyl azides, the resultant 5-amino-4-sulphonyl-5-phosphinoyltriazoles are tautomeric with the predominant linear 2-diazoalkyl from (equation 61)[283].



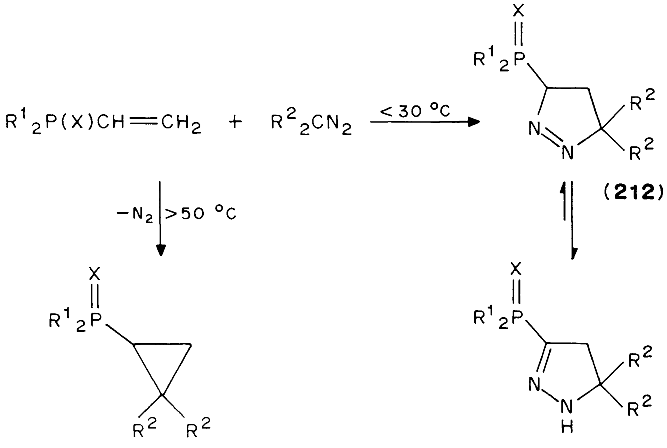
(60)



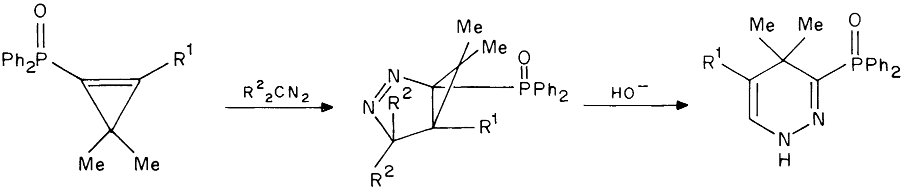
(61)

The addition of diazoalkanes $R^1{}_2CN_2$ ($R^1 = H$ or Ph) to olefinic phosphine oxides takes place under very mild conditions, and indeed needs to so as to prevent loss of nitrogen[51,284] and allow the isolation of the pyrazolines (**211**) which readily isomerize, the tautomerism being faster in MeCN than in benzene[285]. At higher temperatures loss of nitrogen occurs during the initial reaction with the formation of phosphinoylcyclopropanes, a process for which a carbene mechanism has been excluded.

Reactions of a similar nature involving 1-alkynylphosphine oxides yield products which aromatize by prototropy when the diazoalkane is of the type $RCHN_2$[286]. The reactions between 1-(diphenylphosphinoyl)cyclopropenes (**213**) and diazoalkanes are generally regiospecific, and give the adducts **214** except when R^1 = Ph and R^2 = H. The adducts **214** (R^2 = H) may be converted readily into the phosphinoylated 1,2-pyridazines **215**[287].



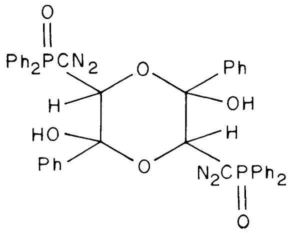
(212)



(213) **(214)** **(215)**

That the phosphinoyl group has an activating effect on the cycloadditions to the vinyl group does not appear to be in doubt; thus, for example, diphenyldiazomethane does not react with allyldiethylphosphine oxide at lower temperatures, and at temperatures higher than 120 °C yields only very small amounts of (cyclopropylmethyl)diethylphosphine oxide, probably through a carbene mechanism[285].

α-Diazo(diphenylphosphinoyl)alkanes undergo cycloadditions to α,β-unsaturated ketones[288] and with acetylenes[289]. Reactions between α-diazobenzyl(diphenyl)phosphine oxide and aldehydes lead to (2-hydroxy-1-diazoalkyl)diphenylphosphine oxides (by aldol addition); in the case of glyoxal, the initial product dimerizes to give the 1,4-dioxan derivatives **216**[290].

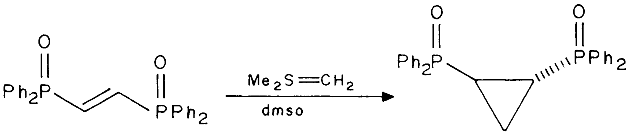


(216)

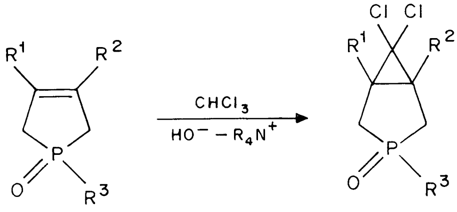
4. *Reactions involving ylides or carbenes*

Under thermal or photolytic conditions, (α-diazoalkyl)diphenylphosphine oxides and sulphides are reactive and yield products suggestive of the formation of carbene intermediates; they are also subject to attack by nucleophiles, e.g. during their treatment with hydrogen halides with the formation of (α-halogenobenzyl)diphenylphosphine oxides, and also during hydrolysis. Similarly, when (α-diazobenzyl)diphenylphosphine oxide is heated in ethanol, (α-ethoxybenzyl)diphenylphosphine oxide and (benzhydryl)-phenylphosphinic acid result[291].

Representative examples of the additions of ylides or carbenes to unsaturated phosphine oxides are given in equations 62[48] and 63[292]. The adducts **217** can be made to undergo rearrangement to 4-chloro-1,2-dihydrophosphorins through the action of heat, water or alcoholic $AgNO_3$[293].



(62)



(63)

(217)

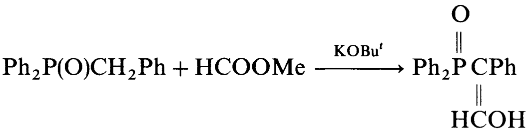
IV. PHOSPHINOYL CARBANIONS

A. Formation

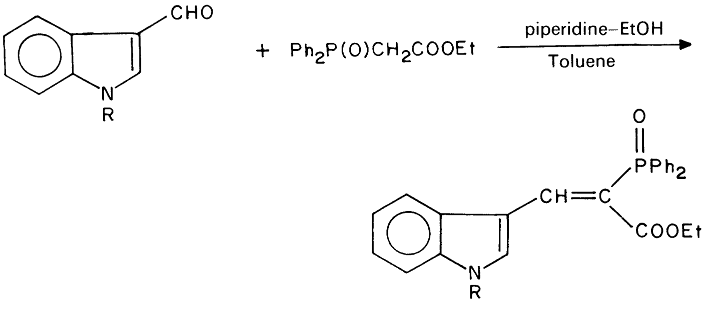
Data on the acidities of phosphine oxides, including (dialkylphosphinoyl)alkane-carboxylates and (diarylphosphinoyl)alkanecarboxylates[214,215] and phosphinoyl-substituted benzoic acids[216] as well as other phosphinoylmethylene compounds[213,294] demonstrate that the groups R_2PO and Ar_2PO are electronegative, with little difference between the electron attracting power of these and the corresponding phosphinothioyl groups. Their place in the general order of electron attracting power is $Ph_3P^+ > PhCO > MeCO > CN > COOR > R_2P(S) \approx R_2P(O) > Ph_2P > Ph > H > Me$.

Carbon—hydrogen bonds are thus activated towards proton removal by a suitable base. Bis(diphenylphosphinoyl)methane undergoes rapid exchange with deuterium but requires the presence of a weak base, and hence the use of a substance such as $PhND_2$ is satisfactory for the purpose. The introduction of a *p*-diphenylphosphinoyl group into toluene raises the acidity in dmso by ca 14 orders of magnitude; in other solvents the electronic effects of the diphenylphosphinoyl group are similar to those displayed by a *p*-CN group. In the presence of $KOBu^t$, 4-diphenylphosphinoyltoluene condenses with aromatic aldehydes (compare *p*-nitrotoluene) to give 4-diphenylphosphinoyl-4′-substituted stilbenes[295].

Activation of methylene groups has also been demonstrated by several condensation reactions such as those illustrated by equations 64[288] and 65[296]. α-Phosphinoyl carbanions can be generated when phosphinoylalkanes or their derivatives are treated with an appropriate base; the more activated the methylene protons by the presence of

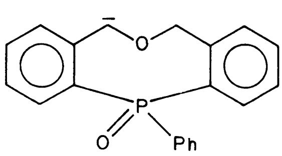


$$Ph_2P(O)CH_2Ph + HCOOMe \xrightarrow{KOBu^t} Ph_2\overset{\overset{O}{\|}}{P}\underset{\underset{HCOH}{\|}}{C}Ph \qquad (64)$$

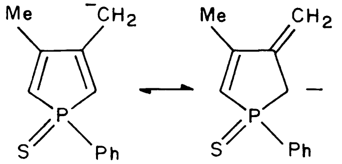


(65)

more than one phosphinoyl group attached to a common CH group, or alternatively aided by the presence of one of the common electron-attracting groups such as Ph, COOR, COR, CN or SO_2, the weaker the base needed, and a wide range of bases has been employed. For phosphine oxides, PhLi, $NaNH_2$, $KOBu^t$, PhNa, NaH (this has also been used to generate dianions from 2-oxoalkylphosphine oxides[297]), lithium diisopropylamide[47,55,298] and, most commonly, BuLi, have all been used in combination with Et_2O or, better, thf. The same reagents are often satisfactory with mono- or di-methylphosphine oxides[299] and even Et_3PO. The carbanion **218** has been generated by the use of $NaN(SiMe_3)_2$ or $NaNHCH_2Ph$[65]. Bu^tLi was used to generate the mesomeric anion from $[Me_2P(S)]_3CH$[300] and also the mesomerically stabilized anion **219**[301], although BuLi itself was sufficient for some mono- and di-methyl arylphosphine sulphides[95,212].

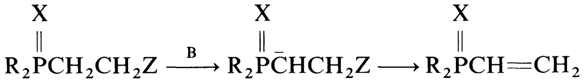


(218)



(219)

Two difficulties may arise during the generation of the carbanion. The first relates to the site of carbanion generation. Thus, with BuLi, EtMePhPO loses a proton from the Me group, whereas $Me(Me_2NCH_2CH_2)PhPO$ loses a proton from the α-carbon of the substituted ethyl group[302]. The second point arises from the stability of the generated carbanion; that of **220** depends on the leaving ability of the group Z, and fragmentation of the carbanion into the vinylphosphine oxide will be enhanced by a group Z easily stabilized as an anion.



$$R_2\overset{\overset{\displaystyle X}{\|}}{P}CH_2CH_2Z \xrightarrow{B} R_2\overset{\overset{\displaystyle X}{\|}}{P}\bar{C}HCH_2Z \longrightarrow R_2\overset{\overset{\displaystyle X}{\|}}{P}CH{=}CH_2$$

(220)

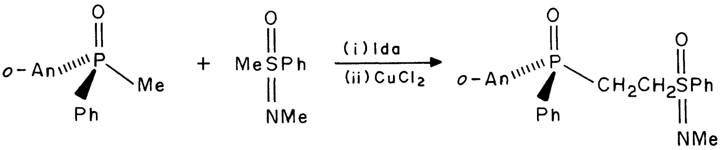
B. Reactions

1. Coupling

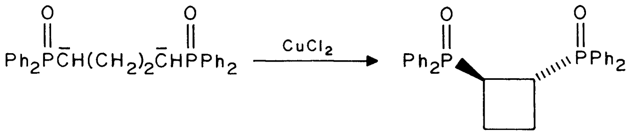
In the presence of $CuCl_2$, phosphinoyl carbanions **221** couple ('dimerize') to give ethanebis(phosphine oxides)[303]. A mixture of diastereoisomers may result from appropriate starting materials; (*R*)-EtMePhPO affords a mixture of 3% *meso*-EtPhP(O)-$CH_2CH_2P(O)PhEt$ together with 34% of the same dioxide in its (*S*,*S*)-form.

$$\underset{\textbf{(221)}}{R^1R^2P(O)CH_2^-} \xrightarrow{\text{Cu salts}} R^1R^2P(O)CH_2CH_2P(O)R^1R^2$$

Interaction with other anions can take place (equation 66)[55] and an interesting application is the intramolecular coupling with the formation of cycloalkanebis(diphenylphosphine) dioxides as illustrated by equation 67[49].



(66)

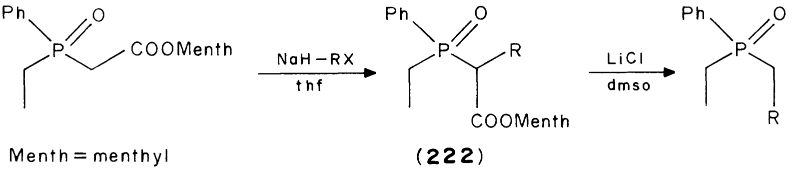


(67)

2. Alkylation

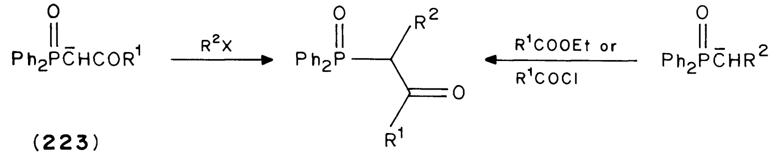
Alkylation of a phosphinoyl carbanion has been widely employed to build up more highly substituted alkyl groups attached to a diphenylphosphinoyl moiety, but such an apparently simple reaction may not always be so convenient from the practical standpoint. Thus, bis(diphenylphosphinoyl)methane, as its sodium salt, does not alkylate straightforwardly and, when acted upon by hexyl bromide in dmso, the salt affords a mixture of cleavage products, namely methyldiphenylphosphine oxide and hexyl diphenylphosphinate[304]. On the other hand, the corresponding potassium salt alkylates in the expected fashion.

L-Menthyl $(S)_P$-(ethylphenylphosphinoyl)acetate, when alkylated, gives the $(R)_P$ product (**222**), from which the ester group is easily removable[241].



(222)

The carbanions from (2-oxoalkyl)phosphine oxides **223** (R = Me or Ph) are readily alkylated by methyl, benzyl or prenyl halides, as well as by α-halogenocarbonyl compounds, but even a simple alkyl halide such as BuBr may fail to react, so that alkylation of an acylmethylphosphine oxide may only sometimes be an alternative to the acylation (see next section) of an alkylphosphine oxide (Scheme 55)[297].

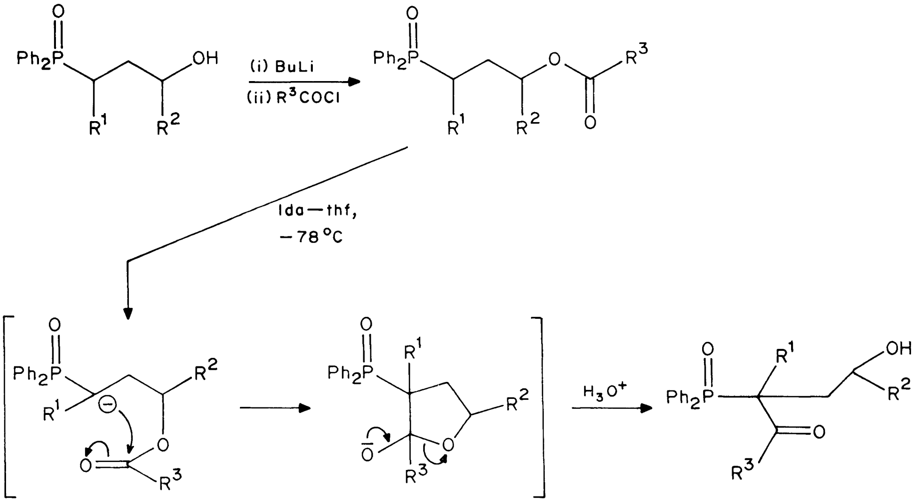


(223)

SCHEME 55

3. *Acylation*

Acylation of phosphinoyl carbanions has normally been carried out using carboxylic esters (Scheme 55)[292,305,306], but lactones[297,307] and carboxylic acid chlorides[305,306] have also been employed. Acylation at the α-carbon atom can also be achieved through acyl transfer in an intramolecular process (Scheme 56), resulting from the influence of lda at low temperature[308]. Other carbanions have been phosphorylated with a variety of halides of acids of either tervalent or quinquevalent phosphorus (reactions 68–71).



SCHEME 56

$$Ph_2P(O)CH_2Li + R_2P(O)Cl \xrightarrow[\text{(ref. 305)}]{} Ph_2P(O)CH_2P(O)R_2 \tag{68}$$

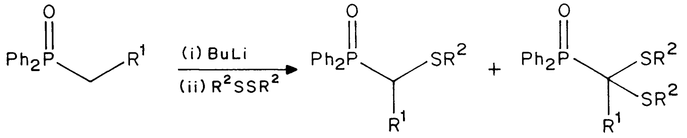
$$R = \text{hex, oct, Ph}$$

$$Ph_2P(S)CH_2Li + R_2PCl \xrightarrow[\text{R = Ph (ref. 309), Bu}^t\text{(ref. 104)}]{} Ph_2P(S)CH_2PR_2 \tag{69}$$

$$Ph_2P(S)CH_2Li + PhPCl_2 \xrightarrow[\text{(ref. 309)}]{} [Ph_2P(S)CH_2]_2PPh \tag{70}$$

$$[Me_2P(S)]_2CHLi + Me_2P(S)Cl \xrightarrow[\text{(ref. 300)}]{} [Me_3P(S)]_3CH \tag{71}$$

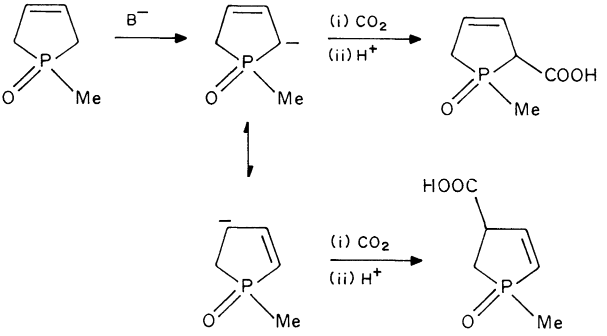
A widely exploited example of acylation is that of sulphenylation since this, through the Horner reaction (Section V), provides a route to vinyl sulphides and thence, through their hydrolysis, to ketones. Sulphenylation is achieved through reaction of the phosphinoylcarbanion with a disulphide (equation 72)[306,310,311]; monosulphenylation may, under certain circumstances, be accompanied by disulphenylation. Oxidation of phosphinoylalkylsulphides with mCPBA yields the corresponding sulphinyl or sulphonyl derivatives[311].



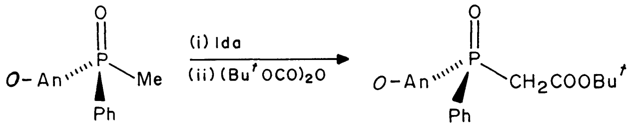
(72)

4. *Carboxylation and decarboxylation*

The treatment of the phosphinoyl or phosphinothioyl carbanions with an excess of CO_2 yields a carboxylic acid[305]. Those carbanions which are capable of resonance may yield mixtures of carboxylic acids (Scheme 57)[62].



SCHEME 57

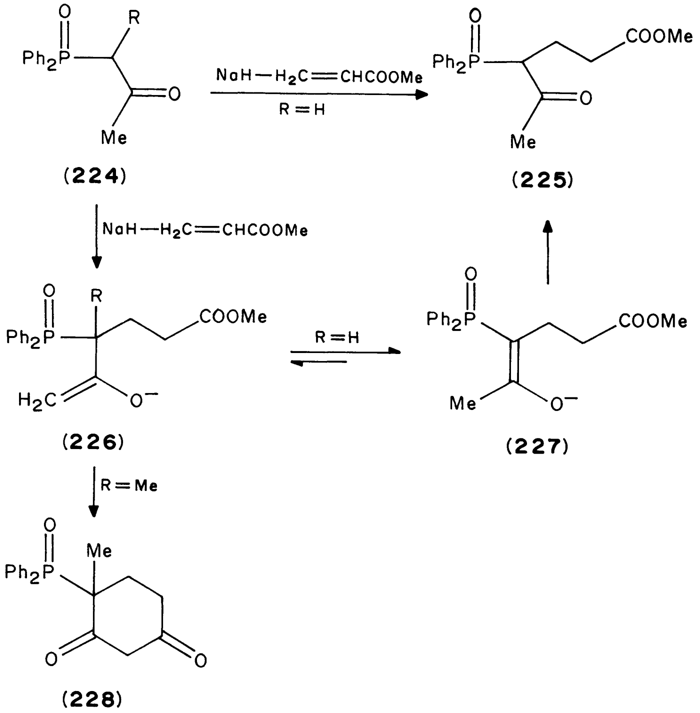


(73)

Reaction 73 illustrates a useful direct synthesis of the *tert*-butyl ester of a carboxylic acid; as in more conventional organic reactions, the *tert*-butyl group is a useful protecting group removable, after any further reaction at the active methylene group, with *p*-tosOH in xylene (see the next section)[55]. The decarboxylation of (di)carboxylic acids follows the patterns observed for active methylene dicarboxylic acids and related compounds, e.g. $R_2P(O)CH(COOH)CH_2COOH$ is decarboxylated to $R_2P(O)CH_2CH_2COOH$.

5. Addition reactions

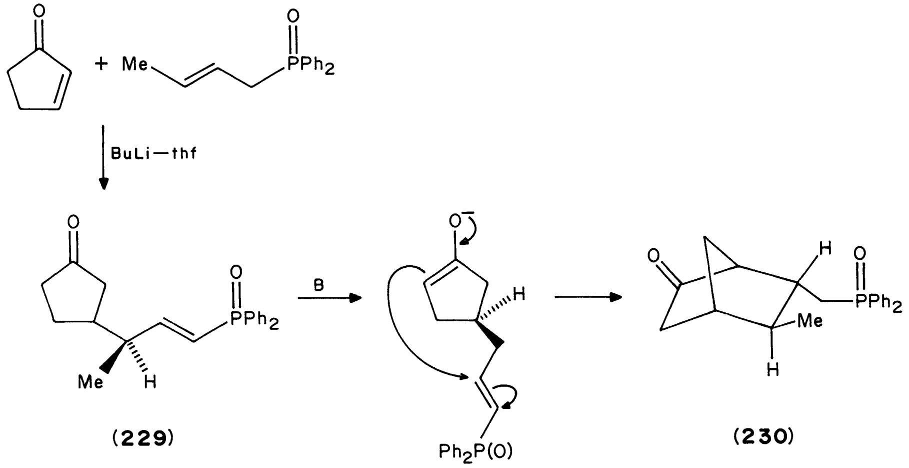
Torr and Warren[297] have reported Michael additions of phosphinoyl carbanions to acrylic esters (Scheme 58). A base-catalysed reaction between the latter and the ketone **224** (R = H) gave the expected adduct **225**, whereas the product from the ketone **224** (R = Me) was the cyclohexadione **228**. The reason for this difference in behaviour resides in the anions **226** (R = H or Me); when R = H, conversion to **227** occurs and hence formation of **225** is facile, but when R = Me an equilibration occurs, resulting in cyclization to **228**[297].



SCHEME 58

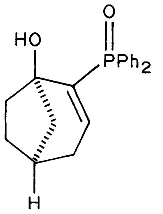
Haynes and coworkers[312,313] exploited the already recorded Michael addition of the carbanions from (*E*)- and (*Z*)-but-2-enyldiphenylphosphine oxides to cyclopent-2-enone to yield the diastereoisomers of the vinyldiphenylphosphine oxide **229** in a route to diphenylphosphine oxides possessing the bicyclo[2.2.1]heptanone and bicyclo[3.2.1]-octanol moieties through the intramolecular conjugate addition depicted in Scheme 59[312,313]. Treatment of the oxide **229** with $KOBu^t$ in thf at room temperature gave **230** in 90% yield as a single diastereoisomer; similarly, the product from (*Z*)-but-2-

enyldiphenylphosphine oxide gave the diastereoisomer of **230** with *endo*-Me and *exo*-$CH_2P(O)Ph_2$ groups. Compound **231** was the product which resulted from the treatment of **229** with 2.5 equiv. of lda in thf at −78 °C in a reaction which evidently involved the deprotonation of a vinylic phosphine oxide.



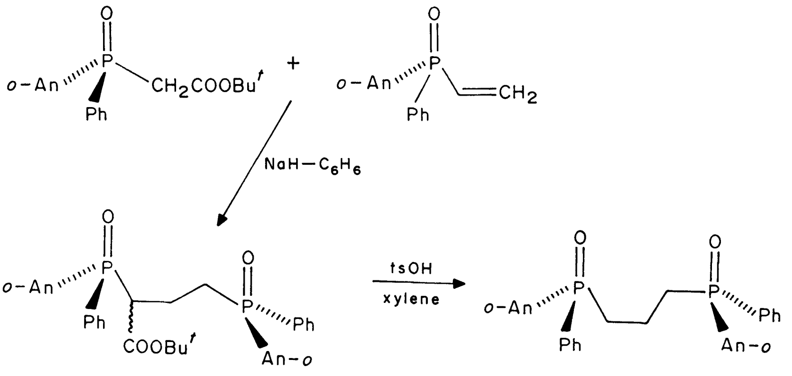
(229) **(230)**

SCHEME 59



(231)

Scheme 60 exemplifies the potential of Michael addition reactions in the synthesis of precursors to valuable chiral ligands[55].



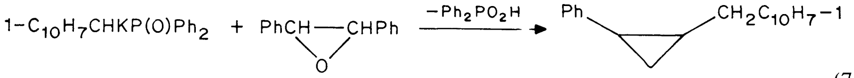
SCHEME 60

6. Reactions with aldehydes, ketones and epoxides

The original reports on the interaction of phosphinoyl carbanions with aldehydes or ketones were those given by Horner[314]. Benzyldiphenylphosphine oxide, treated initially with $NaNH_2$ in benzene, reacted with benzophenone to give diphenylphosphinic acid and triphenylethene; a similar reaction took place between the potassium salt of the same phosphine oxide and benzaldehyde to give stilbene. The latter was also obtainable by oxygenation of the same potassium salt followed by acid hydrolysis, and by the decomposition of (α-hydroxybenzyl)diphenylphosphine oxide (obtainable from the lithium salt of benzyldiphenylphosphine oxide by oxygenation and acid hydrolysis) using $KOBu^t$.

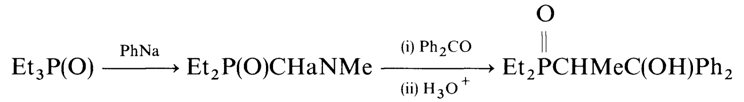
In competition experiments involving benzyldiphenylphosphine oxide and benzyltriphenylphosphonium bromide (the latter acting as a source of the ylide $Ph_3P{=}CHPh$) in the presence of a base, phosphinoyl-activated olefination of benzaldehyde or benzophenone occurred preferentially. When both phosphorus-containing functions were present in the same substrate, loss of Ph_2PO (as diphenylphosphinic acid) always occurred in preference to loss of Ph_2PS or of Ph_2P. Unusually, α,α-bis(diphenylphosphinoyl)toluene anion reacts with PhCHO, but affords $Ph_2P(O)CHPhCHPhP(O)Ph_2$ rather than a phosphinoylstilbene[315].

Coupled with the foregoing observations are those relating to the formation of cyclopropane derivatives from alkali metal salts of activated phosphine oxides through their reactions with epoxides, and again associated with the expulsion of phosphorus as diphenylphosphinic acid (e.g. reaction 74); such a reaction was thought to proceed through a β-hydroxyalkylphosphine oxide.



(74)

Other workers have observed that the use of phosphine oxides with less acidic α-hydrogen atoms coupled with the use of stronger bases allowed the actual isolation of β-hydroxyalkylphosphine oxides (Scheme 61).



$$Et_3P(O) \xrightarrow{PhNa} Et_2P(O)CHNaMe \xrightarrow[(ii)\ H_3O^+]{(i)\ Ph_2CO} Et_2\overset{\overset{\displaystyle O}{\|}}{P}CHMeC(OH)Ph_2$$

SCHEME 61

The sequence phosphine oxide → phosphine oxide carbanion → phosphinic acid plus alkene bears a formal resemblance to the base-initiated reaction phosphonium salt → ylide → phosphine oxide plus alkene upon, in each case, the addition of an aldehyde or ketone at an intermediate stage. The second of these sequences is based on the work of Staudinger from the 1920s, but developed later by Wittig, under whose name it is now known; it was followed by still further developments using base-activated esters of phosphonic acids. Although in some ways not developed to the same extent as the original Wittig reaction or its later modifications for the convenient synthesis of alkenes, nevertheless, the reaction between phosphine oxide carbanions and aldehydes or ketones ('phosphine oxide olefination') offers considerable potential for future development. Because of both its present importance and the future potential in organic synthetic application, the reaction is considered in greater detail in a separate section.

V. REACTIONS BETWEEN PHOSPHINOYL CARBANIONS AND ALDEHYDES OR KETONES: THE HORNER REACTION

For the sake of clarity, the formation of alkenes through the interaction of aldehydes or ketones with carbanions from phosphine oxides is, in this chapter, referred to as the Horner reaction[316]. In this way, it is clearly distinguishable from the parent Wittig reaction which employs phosphonium ylides, generally of the type $Ph_3P{=}CR^1R^2$, as the phosphorus-containing reactant, the Wadsworth–Emmons modifications, which uses phosphonic acid esters, $(RO)_2P(O)CHR^1R^2$, for the same purpose, and the Corey modification, which employs phosphonic acid bisamides, e.g. $(Me_2N)_2P(O)CHR^1R^2$ (ref. 316). In principle, all three of these series of compounds would interact with the carbonyl compound R^3COR^4 after suitable treatment with a base to yield the olefin $R^1R^2C{=}CR^3R^4$.

The Horner reaction uses phosphorus reactants of the general type $R_2P(O)CHR^1R^2$, where, for convenience, R is nearly always Ph, and differs from the three other named reactions in allowing the use of reagents which afford, by the action of the base, a carbanion which need not necessarily be stabilized by the presence of a second electronegative group on $C_{(1)}$. All four reactions have undoubted advantages over many more conventional alkene syntheses in being highly regiospecific.

Essentially, the Horner reaction consists in the generation of a phosphinoyl carbanion (Section IV.A) in a solvent and generally at low temperature (0 to −78 °C) followed by the addition of the carbonyl reactant, again at fairly low temperature, although this might be allowed to rise during the course of the reaction. A metal salt (Li, Na or K) of the adduct is generated, and this may be allowed to decompose directly at a higher temperature; alternatively, an appropriate aqueous work-up often allows the isolation of a (β-hydroxyalkyl)phosphine oxide. The latter can then be made to decompose into the required alkene(s) by treatment with a strong base in a hot solvent; NaH in dmf or thf or $KOBu^t$ in dmso have been used extensively. The trimethylsilyl ethers of (β-hydroxyalkyl)diphenylphosphine oxides also decompose in the presence of sodamide-type bases to give alkenes[299].

A. The Reactants

The general availability of the carbonyl reactants need not be discussed here, and it is sufficient to say at this stage that, generally, aldehydes tend to undergo the Horner reaction more readily than ketones, but this is a very broad generalization which may not necessarily hold in specific cases; thus, $Ph_2P(O)CH_2OMe$ reacts equally easily with aldehydes or ketones, whereas $Ph_2P(O)CHMe(OMe)$ in unreactive towards ketones[317]. Enolizable ketones tend to afford poor yields of alkenes.

The phosphine oxide reactants are readily available by synthesis through the use of one of several fairly conventional reactions which include (i) application of the Arbuzov reaction between the ester Ph_2POR and an alkyl halide of a more reactive type, (ii) the alkylation of the anion Ph_2PO^- (generated from $Ph_2P(O)H$ by the action of an alkali metal or organic base), (iii) the alkylation (Section IV.B.2) or acylation (Section IV.B.3) of the carbanions from simpler phosphine oxides, (iv) the alkaline hydrolysis of alkyltriphenylphosphonium salts, $Ph_3PR^+X^-$, and (v) the cleavage of Ph_3PO with alkyllithium reagents, e.g. RCH_2Li, when the products are PhH and $Ph_2P(O)CHLiR$.

When the isolation of the intermediate (β-hydroxyalkyl)phosphine oxide is considered desirable, they can also be synthesized by other routes, more details of which will also be considered in a later section.

B. Advantages of the Horner Reaction

The various modifications to the original Wittig reaction each have advantages over the latter and also over more conventional approaches to the synthesis of a particular alkene.

Unlike those reagents used in the Wadsworth–Emmons modification, Horner reagents are generally crystalline compounds and are relatively easily purifiable. Also of distinct practical significance is the relative ease of separation of the Horner reaction products—typically a liquid or solid water-insoluble alkene and the water-soluble metal diphenylphosphinate; in this respect, the Wadsworth–Emmons reaction is similar in that it generates a water-soluble salt of a phosphoric acid. The Wittig reaction can easily generate mixtures of products that are completely water insoluble.

The phosphinoyl carbanions in Horner reactions are capable of extensive modification through alkylation or acylation; they are considered to be non-nucleophilic, although allylic phosphine oxide carbanions have been reported to dealkylate phosphoryl chlorides[318]. Such modifications may be further expanded through appropriate migration sequences involving Me, MeS, PhS or MeO groups, or even of the phosphinoyl group itself. The order of sequential modifications can be utilized to achieve desirable and specific results.

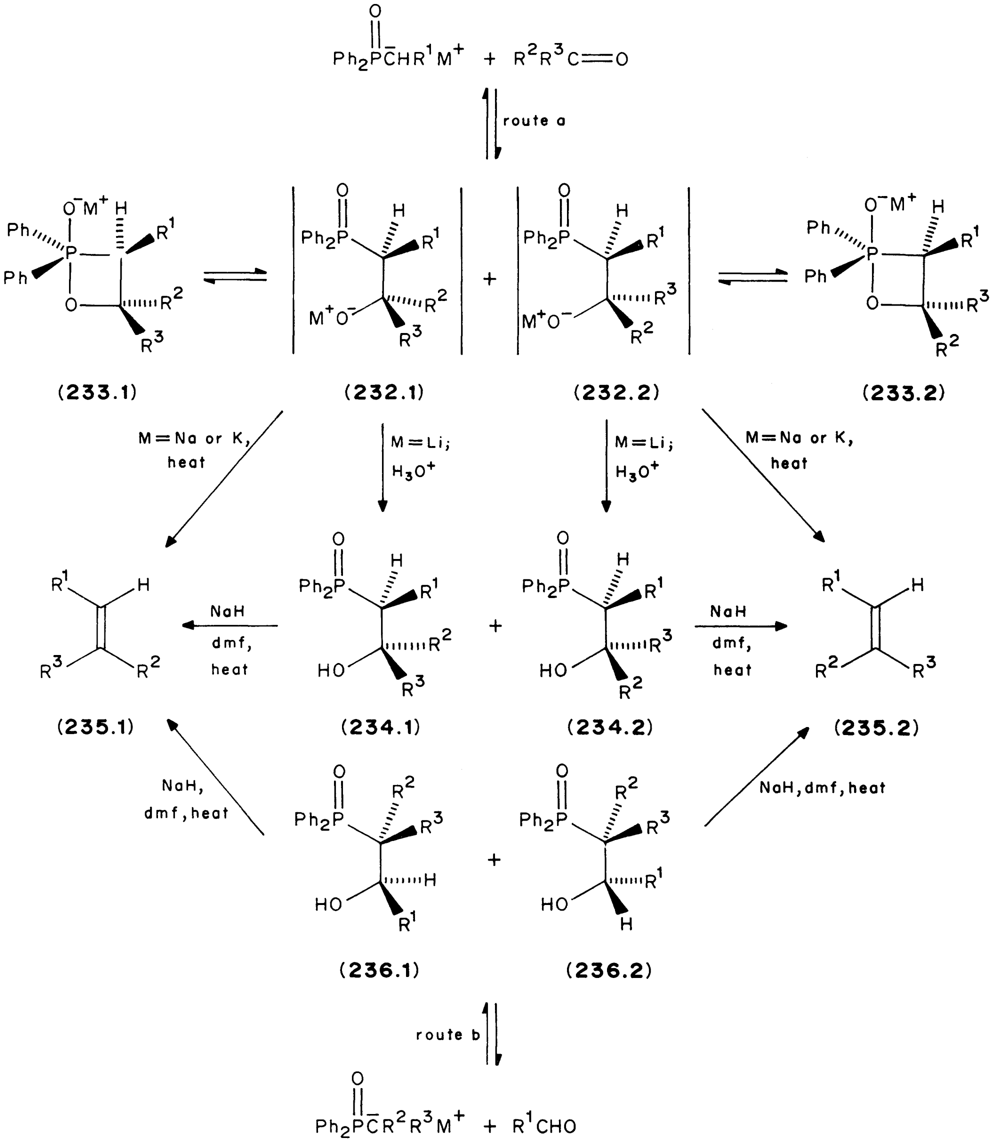
The very high regiospecificity of the Horner reaction, and of other Wittig modifications, and the consequent advantage over 'non-phosphorus' methodology, has already been commented upon. In many cases the Horner reaction also has advantages over the other Wittig modifications with regard to stereospecificity within a particular reaction. For example, the use of $Ph_2P(O)CH_2CN$ rather than $(EtO)_2P(O)CH_2CN$ in reactions with ArCHO or Pr^iCHO not only achieves higher yields of alkene, but also a much higher degree of stereoselectivity. In the reaction between $Ph_2P(O)CH_2SMe$ and PhCHO, the alkene *E*/*Z* ratio for the product is 20:1, whereas the use of the Wadsworth–Emmons reagent, $(EtO)_2P(O)CH_2SMe$, is stereochemically non-selective.

C. Mechanism, Stereochemistry and Regiochemistry

Scheme 62 outlines our present knowledge of the mechanism of the Horner reaction and its associated methodology, assembled, to some extent, through analogy with the original Wittig reaction and the Wadsworth–Emmons modification, but with additional evidence. The upper part of the Scheme (route a) indicates the mode of interaction of a phosphinoyl carbanion with a ketone to give, initially, a pair of diastereoisomeric salts (**232**); these may indeed exist in the acyclic form or they may exist as, or be in equilibrium with, pentacoordinate dioxyphosphorane species possessing oxaphosphetane rings (**233**); the latter feature would restrict the possibilities in isomerization.

The fate of either of the species **232** or **233** depends to a large extent on the metal counter ion. With care, appropriate work-up of the lithium salts can provide the free alcohols (**234**)[192,193,211], but the corresponding Na or K salts suffer ready *syn* elimination to give the product alkenes (**235**). Separation of the stereoisomeric alcohols **234** is often feasible, but the individual isomers can be recognized in mixtures by the application of ^1H NMR spectroscopy; individual diastereoisomers have also been structurally characterized using X-ray diffraction techniques, and they include *erythro*-(1*RS*,2*RS*)-2-diphenylphosphinoyl-1-phenylpropan-1-ol[319] and (2*RS*,3*RS*,4*RS*)-4-benzamido-3-diphenylphosphinoylpentan-2-ol[248].

The lower part of Scheme 62 (route b) indicates how the same products (**235**) might be obtained using an aldehyde together with a branched-chain phosphine oxide through alcohols (**236**) isomeric with **234**. In the event of R^2 being hydrogen (route a), i.e. the carbonyl reactant being an aldehyde, then structures **234.1** and **234.2** are those of the



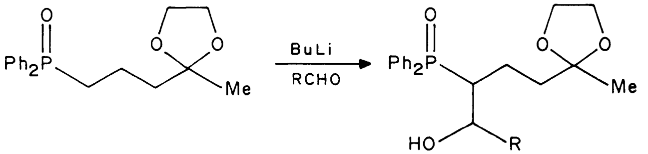
SCHEME 62

erythro and *threo* forms of the alcohol, and decomposition of the *erythro* alcohol or its salt would thus be expected to yield the (*Z*)-alkene with the (*E*)-alkene being obtainable from the *threo*-alcohol or its salt.

The question of stereoselectivity arises at two points in Scheme 62, namely with regard to the formation of the diastereoisomeric alkoxides **232** (and thus of the alcohols **234**, and also with the decomposition of these into the target alkenes.

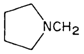
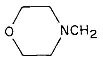
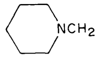
In an extensive and systematic investigation into reactions summarized by equation 75, Buss and Warren[320] showed that when R^2 was Ph or $MeOC_6H_4$, a variation in R^1 maintained the *erythro*:*threo* ratio of alcohols at ca 6:1 unless there was branching at $C_{(1)}$, when the ratio could become 2:1. There was, however, a greater lack of diastereoselectivity when $R^2 = Me$. The stereoselectivity was sensitive to the size of R^2 when $R^1 = Me$ or an aromatic nucleus. No selectivity was observed when the size of the groups R^1 or R^2, e.g. cyclohexyl, competed with that of the diphenylphosphinoyl group. No variation in the diastereoisomer ratio was observed when the position of the aromatic MeO substituent was changed[320]. For reaction 76[306] a systematic decrease in the chain length of the group R from butyl to methyl caused an increase in the *erythro*:*threo* ratio from 1.7:1 to 3.2:1, but when R was branched at $C_{(1)}$, as in Pr^i or cyclohexyl, complete stereorandomness was observed. For R = Ph, the ratio was 3.8:1. Some additional data are given in Table 1. From the wealth of available data it would thus appear that reactions between unfunctionalized or simply functionalized phosphine oxide carbanions and aldehydes are either non-stereoselective or are biased towards the *erythro* product.

$$Ph_2P(O)CH_2R^1 + R^2CHO \xrightarrow{\text{BuLi}} \underset{\textbf{(237)}}{Ph_2P(O)CHR^1CH(OH)R^2} \tag{75}$$

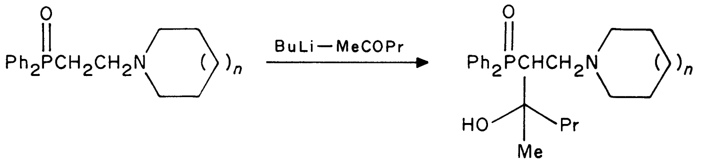


(76)

TABLE 1. Reaction 75: *erythro*:*threo* ratios for the products **237**

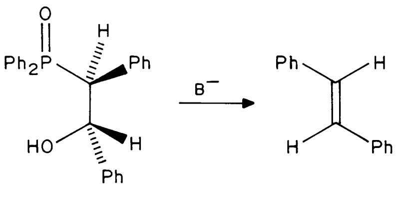
$Ph_2P(O)CH_2R^1$: R^1	R^2CHO: R^2	*erythro*:*threo* ratio	Ref.
MeO	$4\text{-}MeOC_6H_4$	45:55	317, 320
$LiOCH_2CH_2$	Ph	75:25	321
Pr^iCH_2	Ph	80:20	320
	Me	51:49	248, 322
	Ph	52:48	322
	Me	50:50	248
	Ph	66:34	248
	Me	49:51	248
	Ph	48:52	248
$PhCH_2CH_2$	Me	58:42	320
$Bu^tMe_2Si(CH_2)_5$	Et	64:36	321

On the other hand, reactions involving ketones may be much more stereoselective and biased towards the *threo* product, as for reaction 77, when the *erythro*:*threo* product ratios are 28:72 and 20:80 for $n = 0$ and 1, respectively[248]. The simple theoretical prediction that *erythro* intermediates lead to (*Z*)-alkenes and that *threo* intermediates afford (*E*)-alkenes is not always borne out in practice, and the question of reversibility of one or more of the steps in Scheme 62 must therefore be considered.

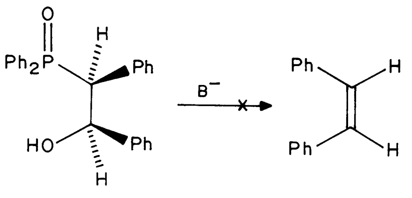


(77)

A simple case illustrates the nature of the problem. When treated with base, *threo*-1,2-diphenyl-2-(diphenylphosphinoyl)ethanol (**238.1**) yields only (*E*)-stilbene, the predicted



(238.1)

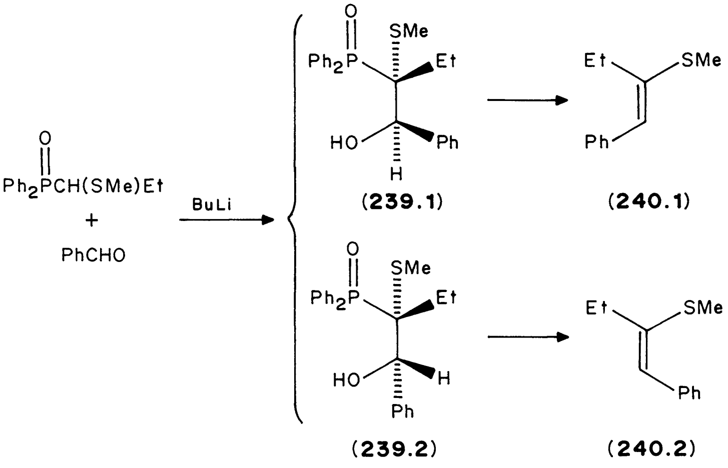


(238.2)

outcome. Under the same conditions, the *erythro* alcohol ought to give (*Z*)-stilbene but, although some of this is formed, the main products are (*E*)-stilbene and benzyldiphenylphosphine oxide. Warren and coworkers[323] were unable to corroborate Horner's original report on the formation of (*Z*)-stilbene.

Exploratory decompositions of the *erythro* alcohol were performed with a variety of bases including PhLi in diethyl ether, BuLi in diethyl ether or thf [which at 0 °C afforded the highest yields of (*Z*)-stilbene] or thf–TMEDA [this solvent system gave the highest observed yield of (*E*)-stilbene], NaH–dmso [no formation of (*Z*)-stilbene], $Bu_4N^+OH^-$ (benzyldiphenylphosphine oxide not formed), DBU in thf [which gave the lowest yield of (*E*)-stilbene but, at 66 °C the highest yield of benzyldiphenylphosphine oxide] and DBU–CaH_2 or KOH in dmso[323]. These results were attributed to the known decomposition of **238** into PhCHO and the observed benzyldiphenylphosphine oxide. In the presence of base, interchange of benzaldehyde with *p*-chlorobenzaldehyde from **238** was possible, but only for the *erythro* isomer. Further evidence for equilibration in Horner reactions comes from reactions such as that depicted in Scheme 63. The lithium salt of [1-(methylthio)propyl]diphenylphosphine oxide and benzaldehyde react at -78 °C to give a mixture of diastereoisomeric alcohols **239.1** and **239.2** in the ratio 4:1, a value correlating well with the ratio of alkenes **240.1** and **240.2** when these were obtained in a one-step process. However, whereas **239.2** afforded only (*Z*)-alkene when decomposed by NaH, the isolated **239.1** gave a mixture of (*E*)- and (*Z*)-alkenes in the ratio 10:1.

In general, *threo* adducts tend to give (*E*)-alkenes with total stereospecificity and in high yields. For the *erythro* adducts, pure (*Z*)-alkenes may be obtained when R^1 and R^2 (equation 75) are both alkyl; adducts from aromatic aldehydes also tend to afford largely the *Z* hydrocarbon together with less than 5% of the *E* isomer, but when R^1 is aryl, both poor stereoselectivity and low yields are observed[320,321,324].

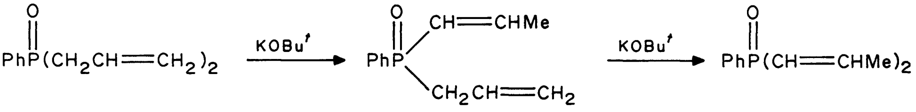


SCHEME 63

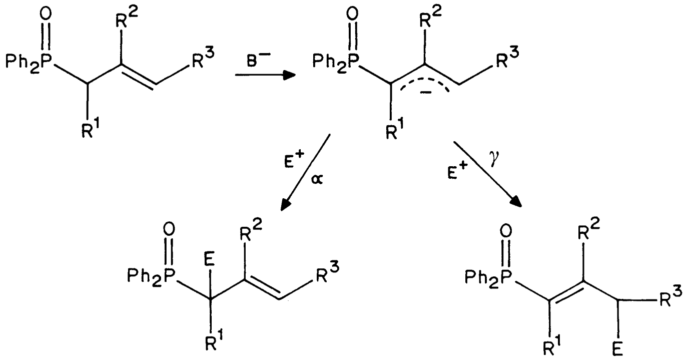
Route a (Scheme 62) has been employed to prepare alkenes with α-PhS or α-OMe substituents, β-Me_2N and γ-ketal substituents, all with poor stereoselectivity but which is generally in favour of the *threo* adducts. Treatment of the adducts **234** ($R^1 = R^3 =$ Me, $R^2 = p$-Tol; R^1 = Ph, R^2 = Et, R^3 = Me; $R^1 = R^3$ = Me, $R^2 = PhCH_2$) with NaH yields only traces of alkenes, the main products being the ketones R^2R^3CO. In addition, the adduct **234** ($R^1 = PhCH_2$; R^2 = Et; R^3 = Me) has been separated into its diastereoisomers but, when treated with NaH, each gives (*E*)-3,4-dimethyl-1-phenylpent-2-ene, presumably through reversion to the starting materials[307,323].

Route b (Scheme 62) has been employed for the synthesis of dienes, vinyl sulphides and unsaturated ketals with little stereoselectivity. For the particular case with R^1 = cyclopentyl, $R^2 = Pr^i$ and R^3 = Me, the bias towards the *threo* alcohol adduct is probably the result of equilibration.

Regiospecificity in the Horner reaction does not normally pose problems, but the problem does arise when the phosphine oxide is of the allylic type. Allylic phosphine oxides undergo prototropic rearrangement into 1-propenylphosphine oxides when acted on by strong bases (Scheme 64)[247,325,326]. The reverse reaction (e.g. as in equation 78) has also been observed. Because of resonance, anions from allylic phosphine oxides can react with an electrophiles at either the α- or the γ-position (Scheme 65). Normally, reactions with electrophiles occur at the α-position[327]. Those between cyclohexanone and allylic phosphine oxide carbanions have demonstrated complete regiospecificity towards the α-position together with essentially complete retention of double bond stereochemistry (equation 79)[328]. However, there are many instances where the reaction takes place, at least partially, at the γ-position. Thus, the cyclohexenyl compound **241** reacts with PhCHO at the α-position whereas the analogous cyclopentenyl compound **242** reacts at the γ-position giving **243**. A lack of substituents at the γ-position renders the allylphosphine oxide particularly susceptible to attack at that position. Thus, reactions between **245** (R^1 = Me) and R^2CHO (R^2 = Me or Ph) afford mixtures of α- and γ-adducts; when $R^1 = Pr^i$ virtually no γ-product is observed[192]. A series of (1-methoxyallyl)diphenylphosphine oxide carbanions (Scheme 65; R^1 = OMe) has been extensively investigated; here the carbon electrophiles PhCHO and MeCHO react at the γ-position to give the (*E*)-alkenes when R^2 and R^3 are either H or Me, or both are H, but when R^1 = H and R^2 = Ph the regiochemistry is a function of the electrophile, since MeCHO again reacts

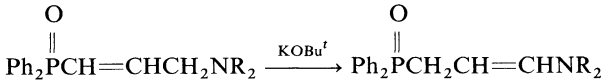


SCHEME 64

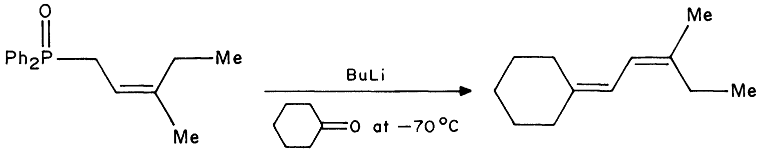


SCHEME 65

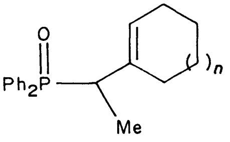
at the γ-position, but PhCHO gives a mixture of α-substituted stereoisomers[311,329]. Other compounds which react as electrophiles at the γ-position include $RSSO_2Me$ (R = Me or Ph) and PhSSPh, as sulphenylating agents, and also Me_3SiCl and $Ph_2P(O)Cl$[318].



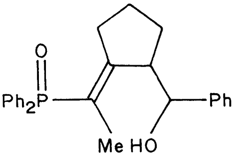
$$Ph_2\overset{O}{\overset{\|}{P}}CH{=}CHCH_2NR_2 \xrightarrow{KOBu^t} Ph_2\overset{O}{\overset{\|}{P}}CH_2CH{=}CHNR_2 \qquad (78)$$



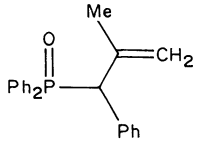
(79)



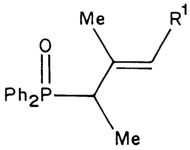
(241) n = 1; **(242)** n = 0



(243)

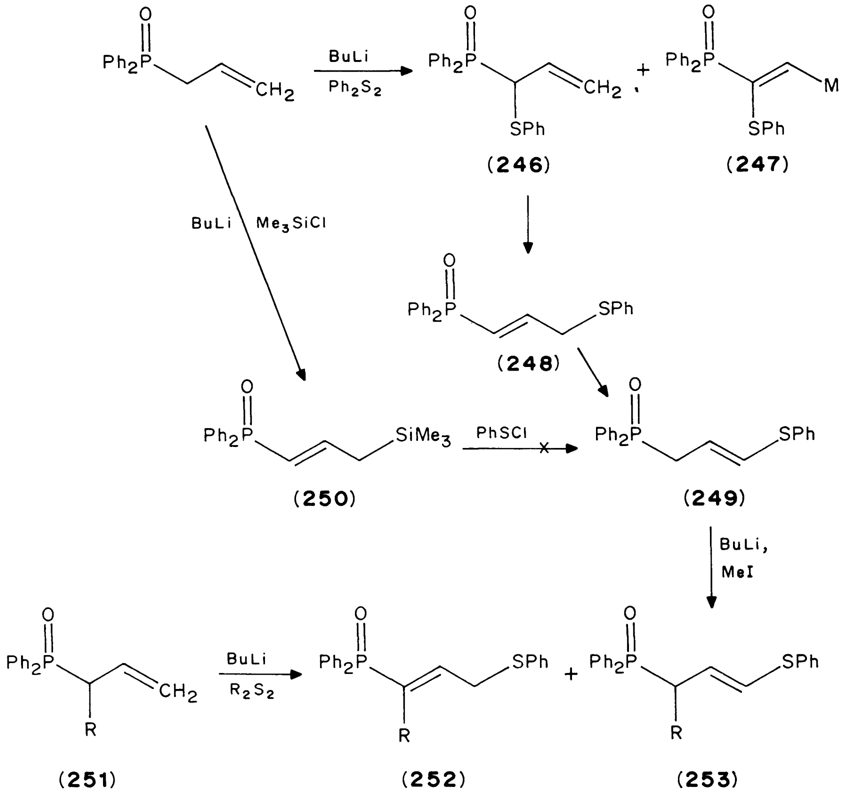


(244)



(245)

Allyldiphenylphosphine oxide anion itself is sulphenylated (Scheme 66) at the α-position to give a mixture of allyl (**246**) and vinyl (**247**) isomeric products, but the γ-substituted compounds **248** and **249** are also found to be present, and are thought to result from rearrangements commencing with **246**. Silylation occurs at the γ-position to give **250**, which reacts at the γ-position with iodine, but with D_2O at the α-position. In view of the known propensity of allyl sulphide anions to react with electrophiles at the position γ to the S atom, it is perhaps not surprising that **249** is methylated at the position which is α to phosphorus to give a 1:1 mixture of the *E* and *Z* isomers of **253** (R = Me); this and its vinyl isomer (**252**) are also obtained by the direct sulphenylation of **251** (R = Me, or Ph).



SCHEME 66

Once again, substituents exert a pronounced effect on the course of the reactions; the carbanion from **251** (R = Me) is deuteriated or methylated at the α-carbon atom, but gives the γ-adduct with PhCHO, whereas the anion from **251** (R = Ph) fails to react with PhCHO, and gives mixtures of α- and γ-products when deuteriated or methylated[311].

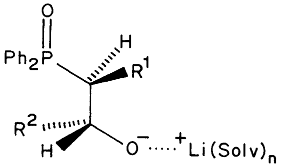
D. Control

Stereoselectivity in the Horner reaction depends on the rates of formation and decomposition (including, where appropriate, reversion to starting materials in equilibria) of alkoxides in Scheme 62. Attempts to control stereoselectivity, and so increase the potential synthetic value of the Horner reaction, have thus been partly concerned with those experimental factors which might govern the kinetics of such reactions.

One of the first systematic attempts to discern possible solvent effects on the course of the Horner reaction was a study[330] of the reactions between benzyldiphenylphosphine oxide and PhCHO or EtCHO, and between diphenylpropylphosphine oxide and PhCHO in either dmf or cyclohexane; all these reactions, and also similar ones using diethyl benzylphosphonate, favour the formation of the (*E*)-alkene, by contrast to the use of Wittig reagents. Generally, the change from the polar to the non-polar solvent produced little change in the (*E*)-/(*Z*)-alkene ratio, but the more pronounced effects (but then only moderate) were found for the combinations $Ph_2P(O)CH_2Ph$ with EtCHO and $Ph_2P(O)Pr$ with PhCHO, an increase in solvent polarity favouring the (*Z*)-alkene.

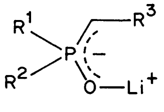
Poor stereoselectivity in the formation of the intermediate (β-hydroxyalkyl)phosphine oxide is often a result of the use of a non-polar solvent: thus, the reaction at −78 °C between diphenylpropylphosphine oxide carbanion (Li^+ as counter ion) and PhCHO in hydrocarbon solvents is non-stereoselective. When Et_2O is used as the solvent, a 6:4 bias towards the *erythro* alcohol is observed, and an almost 6:1 bias towards the same diastereoisomer was found with the use of dme or thf; the addition of tmeda still further increased the bias[320].

It has been suggested that the nature and degree of solvation of the metal counter ion present in the alkoxide **232**, and its consequent size, are important factors in the control of the course of the Horner reaction[320]. Lithium is the counter ion commonly employed in the first stages of the Horner reaction; the use of thf saturated with LiBr or LiCl retards the final stages in the sequence (Scheme 62), and the use of lithium often allows the isolation of the intermediate β-alcohols[194,320]. Even with the relatively small Li^+ ion (in contrast to Na^+ or K^+), conformational control within the complex **254** may well be governed by a tendency for the larger $Ph_2P(O)$ and $O \cdots Li(Solv)_n$ groups to position themselves antiperiplanar with respect to each other in the most highly populated conformer and hence govern the spatial relationship between R^1 and R^2.

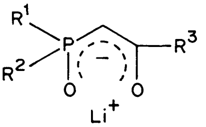


(254)

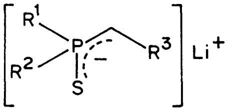
Irrespective of the degree of solvation, a further complicating feature is the nature of the bonding between metal and phosphine oxide ions. When basic groups other than the P=O are absent from the phosphine oxide, bonding between Li^+ and phosphoryl oxygen possesses a high degree of covalence (as in **255**) and the cation may be non-solvated, whereas in a more highly stabilized carbanion possessing a second electronegative group, the lithium cation might well be highly solvated, as in diglyme (structure **256**). In the case of phosphine sulphides, which lack both the more basic P=O group and a second stabilizing group, the salt contains only contact ion pairs (**257**). Alkoxides containing other Group I metal counter ions decompose more readily, and in practice NaH is used widely to bring about the decomposition of isolated *β*-phosphinoylated alcohols to the alkenes. When the counter ion is K^+ or Cs^+ in dmso, there would appear to be no subdivision into the types **255**–**257**, regardless of the presence, or otherwise, of other groups present in the phosphine chalcogenide[331].



(255)

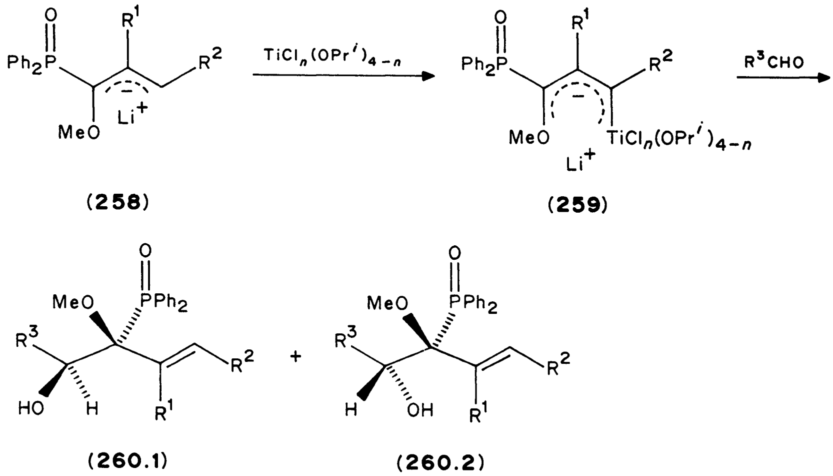


(256)



(257)

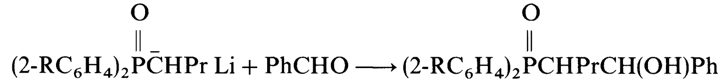
In reactions between the lithiated phosphine oxides **258** (R^1, R^2 = H, H; H, Me; or Me, H) and PhCHO (R^3 = Ph) (Scheme 67) only *γ*-products are obtained. A modification to the anion by its pretreatment with a titanium reagent $[TiCl_n(OPr^i)_{4-n}]$ resulted, in the case of **259** ($R^1 = R^2 = H$; $n = 0$) in mixed regiochemistry with a *γ*:*α* adduct ratio of 2:1 to 3:1, and with the (*S*,*R*)- and (*R*,*R*)-*α*-adducts **260.1** and **260.2** formed in the ratio 2.5:1. When $n = 1$ or 2, reaction occurs regiospecifically at the *α*-position, with the diastereoselectivity strongly biased towards the form **260.1**, although this is lower if R^3 is alkyl, and either or both R^1 and R^2 is (are) alkyl[332]. Reactions of the anions of the phosphine oxides **251** in the presence of $[Ti(OPr^i)_4]$ are slow in comparison with those of the corresponding phosphines, although this effect can be overcome by incorporating hmpa into the solvent system, when the reaction becomes useful in the synthesis of alka-1,3-dienes[333].



SCHEME 67

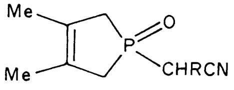
A lower reaction temperature not only disfavours the decomposition of an intermediate alkoxide to the alkene, thus making it easier to isolate the intermediate β-phosphinoyl alcohol, but it can also aid in controlling the diastereoisomeric composition thereof; for a reaction between $Ph_2P(O)Pr$, BuLi and PhCHO, the *erythro*:*threo* ratios for the intermediate alcohol were 2:1, 6:1 and ca 11:1 at 10, -78 and $-100\,^{\circ}C$ respectively[320].

Yet another factor capable of altering the rate of collapse of the intermediate alkoxide ions **232** with expulsion of diphenylphosphinic acid, and thus allowing for better equilibration between the individual diastereoisomeric ions and the starting materials, is the electronic charge distribution within the phosphoryl group. This effect has been explored, albeit to only a very limited extent, through reaction 80. As one ortho hydrogen is replaced successively with Me and MeO, the *erythro*:*threo* ratio, initially 74:26, is raised to 81:19, and then to 97:3[334].

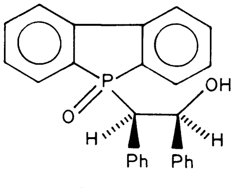


$$(2\text{-}RC_6H_4)_2\overset{O}{\overset{\|}{P}}\bar{C}HPr\ Li + PhCHO \longrightarrow (2\text{-}RC_6H_4)_2\overset{O}{\overset{\|}{P}}CHPrCH(OH)Ph \qquad (80)$$

Phosphorus is also considered to be more electrophilic when present in a five-membered ring than in an analogous acyclic compound and hence, when in compounds such as **261** and **262**, should be capable of modifying the rate of collapse of the alkoxide ion resulting therefrom. The reaction between **261** (K^+ as counter ion) and PhCHO is stereoselective with a (*E*)-/(*Z*)-alkene product ratio of 80:20, but those reactions between **262** and either PhCHO or Pr^iCHO (and with Li^+ or K^+ as counter ions) are, unfortunately, completely non-stereoselective[335].



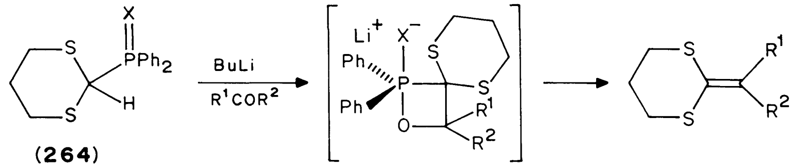
(261) R=H
(262) R=Me



(263)

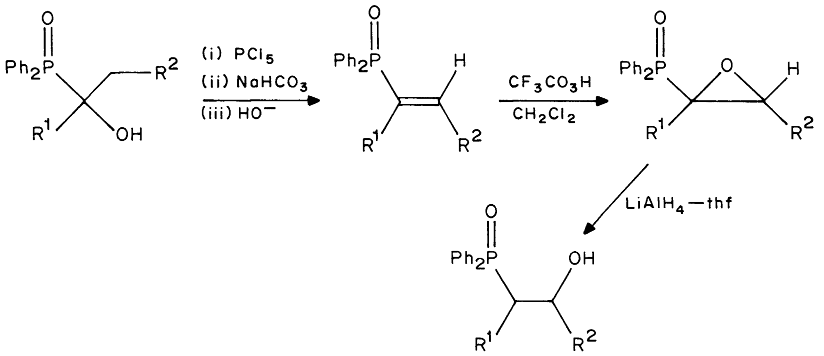
The failure of *erythro*-1,2-diphenyl-2-(diphenylphosphinoyl)ethanol to yield (*Z*)-stilbene on normal decomposition has been attributed to the combined influence of unfavourable Ph–Ph eclipsing interactions in a *syn*-elimination pathway from **238.2** and the relatively high acidity of benzyldiphenylphosphine oxide. Other *erythro* compounds afford (*Z*)-alkenes when acted on by base. When treated with NaH–dmso under the same conditions as **238.2**, the *erythro* alcohol **263** gives a 91% yield of stilbene with a *Z*/*E* ratio of 89:11, modified only slightly by using DBU in dmso at 60 °C. Here the combined influence of using an organic base, rather than NaH, and a phosphole derivative completely reversed the normal stereoselectivity, a result considered as indirect evidence for the participation of an oxaphosph(V)etane intermediate[336].

The role that diphenylphosphinothioyl derivatives take in the Horner reaction has been but little exploited. The diphenylphosphinothioyl-1,3-dithiane **264** ($X = S$) is unreactive to MeCHO, Ph_2CO and cyclohexanone, and is thus less reactive than the diphenylphosphinoyl analogue, a fact attributed to the relative stabilities of the pentacoordinate intermediates (Scheme 68) with their dependence on the relative apicophilicities when $X = O$ or S, rather than on an explanation based on steric crowding[337].



SCHEME 68

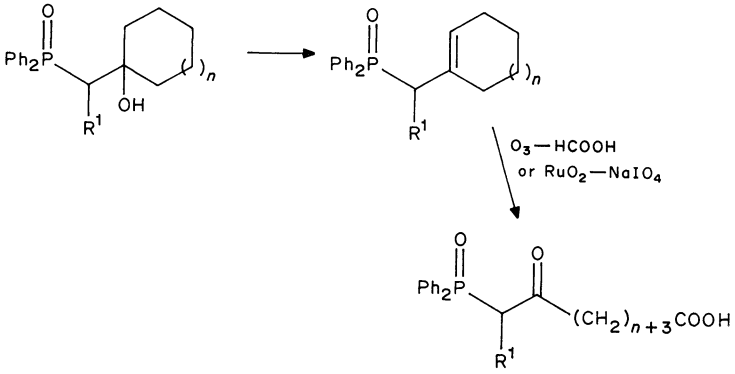
In the second method of approach to the control of the stereochemical outcome of the Horner reaction, the importance of the intermediate (β-hydroxyalkyl)phosphine oxides is taken into consideration, and in particular their synthesis by other reactions. β-Phosphinoyl alcohols have been prepared by the regiospecific ring opening of epoxides with Ph_2PLi followed by treatment with acetic acid–H_2O_2[189,338,340] or by treatment of the epoxide with $Ph_2P(O)K$[341]. In a second procedure, the readily obtainable (α-hydroxyalkyl)phosphine oxides are dehydrated, epoxidized and the β-alcohol obtained by ring opening with $LiAlH_4$ (Scheme 69)[173].



SCHEME 69

By far the most widely exploited synthesis of β-phosphinoyl alcohols by a different route consists in the reduction of (β-ketoalkyl)phosphine oxides. The latter can be obtained, in turn, by the oxidation of (β-hydroxyalkyl)phosphine oxides isolated from the Horner process, or by acylation of a phosphine oxide carbanion (Section IV.B.3). Other (β-ketoalkyl)phosphine oxides can be obtained by specific reactions, one example of which is illustrated in Scheme 70[324].

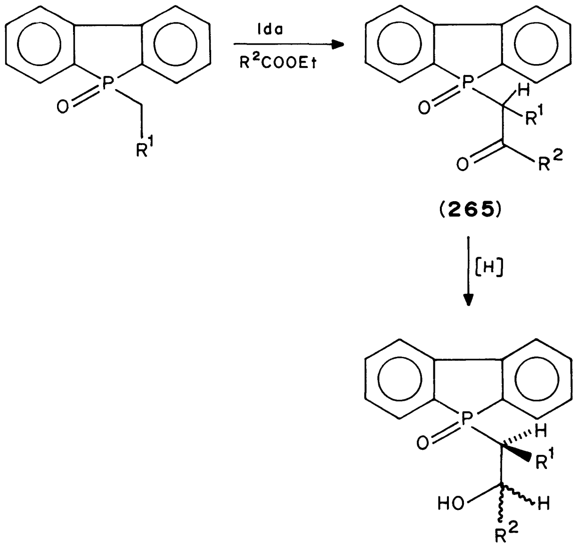
The usefulness of the (β-ketoalkyl)phosphine oxides as precursors to the (β-hydroxyalkyl)phosphine oxides obviously depends on the stereospecificity with which they can be reduced. Unfortunately, high reaction stereospecificity tends to be associated with low reaction yields. Thus, in the reduction of $Ph_2P(O)CHMeCOPh$, the use of H_2–PtO_2–MeOH or $LiAlH(OBu^t)_3$–PhMe at 100 °C gives only 40–50% yields of the alcohol but the *threo*:*erythro* ratio is 90–100:10–0. On the other hand, $LiAlH_4$ in thf at 0 °C or B_2H_6 in thf at −78 °C give 98% yields of the alcohol, with diastereoisomer ratios of ca 1:1 and 3:1, respectively. The reagent of choice for most reductions is $NaBH_4$, which affords satisfactory yields and acceptable diastereoisomer ratios of ca 80–90:20–10[320]. Buss and Warren[320] coworkers prefer to use the Felkin model[342] rather than Cram's rule to explain the stereoisomer ratios in borohydride reductions.



SCHEME 70

In the borohydride reduction of the oxides $Ph_2P(O)CHR^1COR^2$, variation in R^1 from Me to Bu^i (and including Pr^i) has little effect on the diastereoisomer ratio when $R^2 = Ph$; a change in the size of R^2 has a more pronounced effect on the stereoisomer ratio when $R^1 = Me$, and with a bias towards the *threo* alcohol.

The reduction of the dibenzophosphole derivatives **265** with $NaBH_4$ produced alcohol diastereoisomer ratios very similar to those for the analogous diphenylphosphinoyl compounds. In the particular case of **265** ($R^1 = Me$, $R^2 = Ph$), the diastereoisomer ratio obtained with $NaBH_4$–MeOH was very similar to those obtained with some other reducing agents, e.g. $Bu^s{}_2BHK$ in thf at −78 °C, but in complete contrast to those obtained with $Zn(BH_4)_2$ in diethyl ether or $NaBH_4$–$CeCl_3$–MeOH when, in each case, the *erythro* alcohol becomes the main product[343,344].



(265)

E. Applications

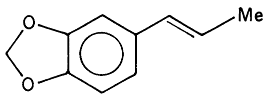
Table 2 lists many general types of compounds, other than simple alkenes, that have been synthesized using the Horner reaction, either directly, or indirectly through a single simple modification to the original Horner product. The list is not intended to be complete, but is intended to emphasize the broad scope of this versatile reaction.

The Wittig reaction between piperonal and an appropriate ethyltriphenylphosphonium salt provides a mixture of (*E*)- **266** and (*Z*)-isosafrole in 57% yield; the Horner reaction between ethyldiphenylphosphine oxide anion and piperonal gives a mixture (9:1) of *erythro* and *threo* β-alcohol adducts, the separated components of which provide *Z* and *E* isomers of isosafrole containing at most, only traces of the geometric isomers. A similar situation occurs in the synthesis of isomers of anethole (**267**)[307]. The same paper[307] also reports the synthesis of (*E*)-feniculin (**268**), a constituent of fennel. (*Z*)-α-Bisabolene (**269**) has also been prepared, using the anion from $Ph_2P(O)CH_2CH_2CH{=}CMe_2$, and also (*E*)-non-6-en-1-ol and (*E*)-dec-5-en-1-ol, insect pheromone constituents, from propyl- and pentyl-diphenylphosphine oxide anions, through acylation with lactones. Other applications in the natural product field include an approach to avermectin[373] and a synthesis of the oudemansins A (**270**; $R^1 = R^2 = H$) and B (**270**; $R^1 = OMe$, $R^2 = Cl$)[374].

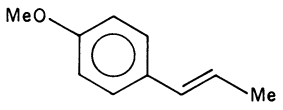
1,1-Difluoroalk-1-enes have been prepared from $Ph_2P(O)CHF_2$[375]. A particularly interesting study concerns the syntheses of cyclic alkenes of medium ring size, prepared from phosphine oxides using the epoxide route. (*1R*, 2*R*)-2-Diphenylphosphinoylcyclooctanol (**271**) with NaH in dmf affords (*S*)-(+)-*trans*-cyclooctene (**272**), with the (*R*)-(−)-hydrocarbon being obtainable from the enantiomeric alcohol. (*S*)-(+)-*cis,trans*-Cycloocta-1,5-diene has the oxide **273** as its precursor[376]. (1*RS*,4*SR*,5*SR*,8*RS*)-5-Diphenylphosphinoylbicyclo[6.4.0]dodecan-4-ol (**274**) with $KOBu^t$ in dmso leads to the (1*RS*,4*RS*,5*RS*,8*RS*)-hydrocarbon **275**; the (1*RS*,4*RS*,5*RS*,8*RS*)-alcohol is converted into the (1*RS*,4*RS*,5*SR*,8*RS*)-alkene using NaH in dmf[339]. The bis(phosphine oxide) **276** is a source of (*E*, *E*)-cycloocta-1,5-diene (**277**)[340]. These various procedures have also been used in the preparation of cyclononadienes[377]. The phosphine oxide **278** has been used to prepare *trans*-cyclooctene by decomposition with NaH[336].

TABLE 2. Types of compounds (other than monosubstituted ethene) preparable by the Horner reaction

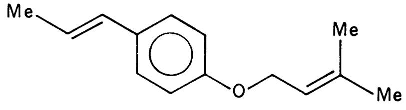
Compound type	Ref.
Di- and tri-substituted alkenes	307, 320
Dienes and polyenes	191, 320, 327–329, 345–351
Unsaturated acids and esters	324, 352
Unsaturated alcohols	176, 192, 307, 308, 321, 353–355
Unsaturated amines and amides	248, 322, 356
Unsaturated ketones	174, 306, 310, 357
Unsaturated keto esters	358
Vinyl ethers	194, 317, 359–361
Vinyl sulphides	196, 310, 311, 337, 362
Vinyl cyanides and isocyanides	363, 364
Vinyl amines (enamines)	365–367
Vinyl isoxazoles	368
Saturated ketones	353, 362, 365, 369
Saturated hydroxy ketones	308, 353
Saturated aminoketones	370
Ketals	306, 360, 371, 372



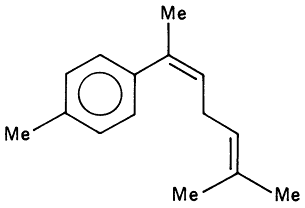
(266)



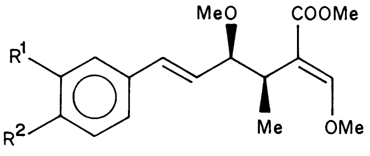
(267)



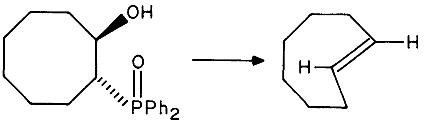
(268)



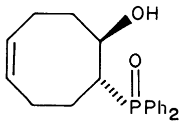
(269)



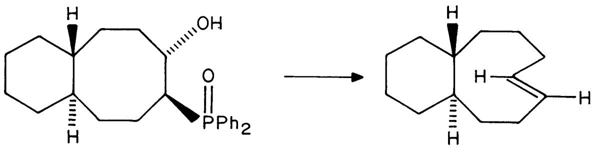
(270)



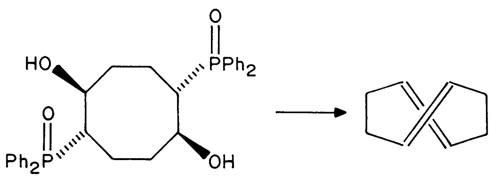
(271) **(272)**



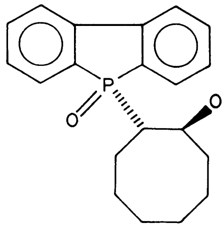
(273)



(274) **(275)**

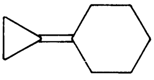


(276) **(277)**



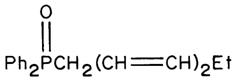
(278)

Treatment of the diphenylphosphinoylcyclopropane anion with appropriate aldehydes or ketones yields hydrocarbons of the type **279**[378]; 1,2-bis(diphenylphosphinoyl)ethane with $KOBu^t$ and the appropriate dicarbonyl reactant yield the polyene **280**[350]. Other polyenes, e.g. **282**[346] and **284**[345], have been obtained from the anions of the phosphine oxides **281** and **283** using standard procedures. Syntheses of 25-keto-vitamin-D_3 have employed phosphine oxides such as **285**[347–349].



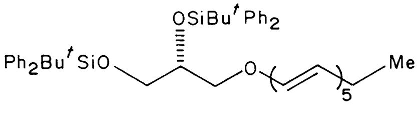
(279)

(280)

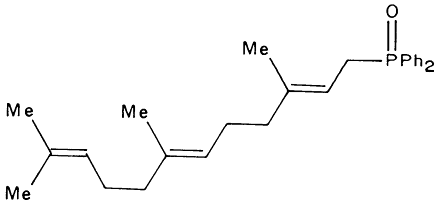


$Ph_2\overset{O}{\overset{\|}{P}}CH_2(CH{=}CH)_2Et$

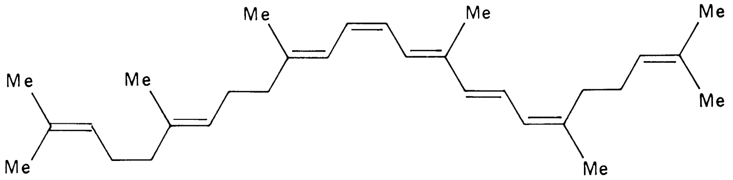
(281)



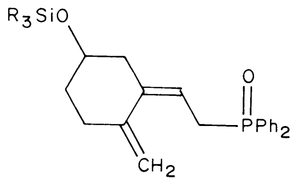
(282)



(283)

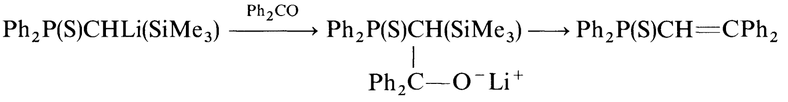


(284)



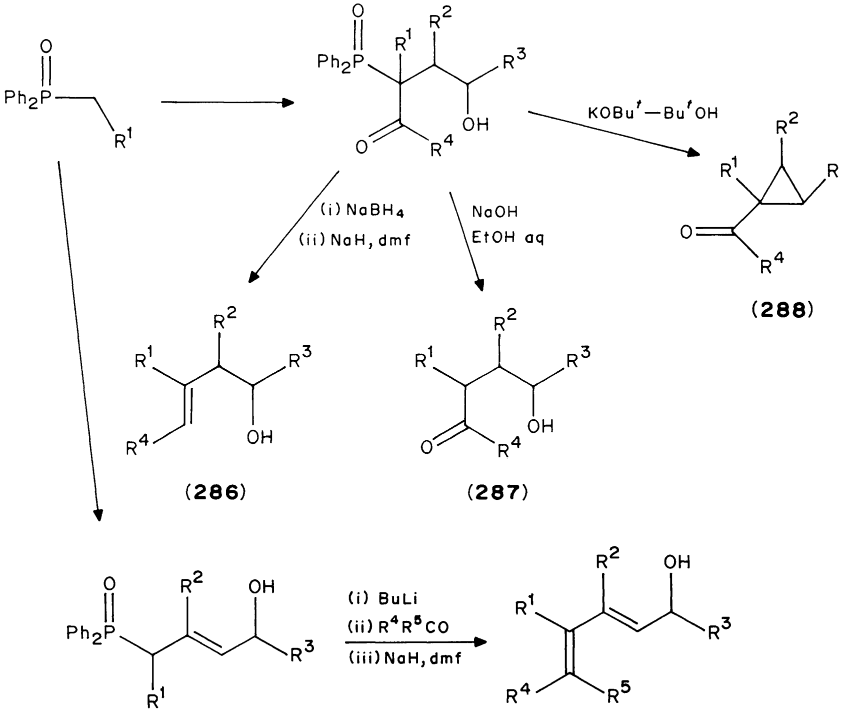
(285)

Returning to the possible use of phosphinothioyl compounds as intermediates in he Horner reaction, it is interesting to note an alternative reaction route (Scheme 71) for a silylated compound[379]. The versatility of the Horner reaction is well illustrated in Scheme 72, in which a single, simple, phosphine oxide as its anion acts as a source of unsaturated alcohols (**286**), hydroxy ketones (**287**) and cyclopropyl ketones (**288**)[353], and also of hydroxydienes (**289**)[354].



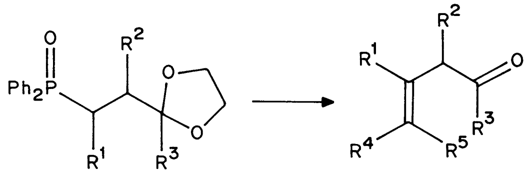
$$\mathrm{Ph_2P(S)CHLi(SiMe_3)} \xrightarrow{\mathrm{Ph_2CO}} \underset{\displaystyle \mathrm{Ph_2C{-}O^-Li^+}}{\mathrm{Ph_2P(S)CH(SiMe_3)}} \longrightarrow \mathrm{Ph_2P(S)CH{=}CPh_2}$$

SCHEME 71

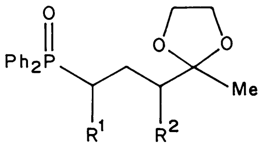


SCHEME 72

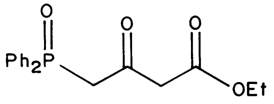
β,γ-Unsaturated ketones (**291**) are derived from the ketals **290**[371] and γ,δ-unsaturated ketones similarly from the ketals **292**[306] in either *E* or *Z* forms. The use of **292** (R^1 = PhS) allows a synthesis of α,δ-diketones after hydrolysis of the initial Horner product[306]. β-Keto-γ,δ-unsaturated esters have been prepared from the oxide **293** using two equivalents of NaH in thf–hmpt with the high selectivity biased towards the *E* isomers[358]. The many reported syntheses of vinyl ethers and thio ethers allow, by hydrolysis of the



(290) **(291)**



(292)

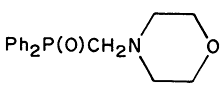


(293)

initial products, the preparation of a wide range of saturated ketones[310]. Carbonyl compounds are also readily obtainable by the hydrolysis of enamines; the latter have been prepared with only poor to moderate stereoselectivity from the oxide **294** via the β-alcohol route[365,366,368]; a similar reagent, **295**, is useful in the homologenation of aldehydes[380].

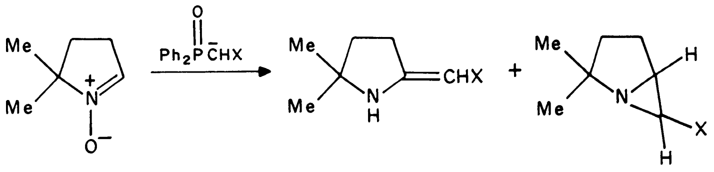
$Ph_2P(O)CH_2NMePh$

(294)



(295)

A modification to the normal Horner procedure involves the interaction of phosphine oxide carbanions with nitrones. In particular, the anions $Ph_2P(O)\bar{C}HX$ (X = CN or COOR) have been made to react with 3,4-dihydroisoquinoline *N*-oxide to give 1-(substituted)methylene-1,2,3,4-tetrahydroisoquinolines, but the cyclic nitrone **209** (R^2 = Me; $n = 1$) yields a mixture of 2-(substituted)methylenepyrrolidines and the bicyclic isomers **296**[381].

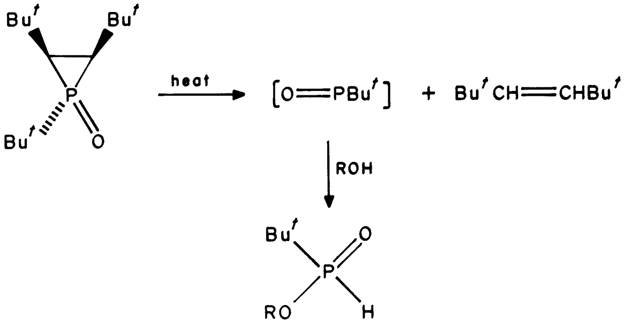


(296)

VI. PROPERTIES OF THE P—C (LIGAND) BOND

A. Thermal Stability

As might be expected, the thermal stability of tertiary phosphine chalcogenides depends on a number of structural features including the particular chalcogen atom and the

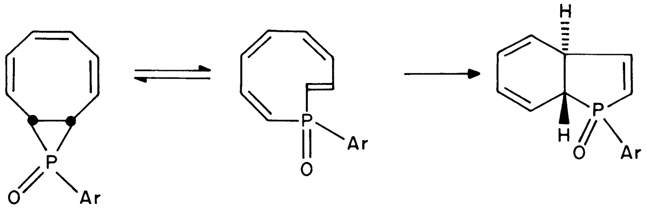


SCHEME 73

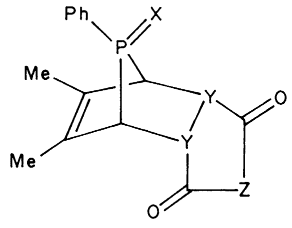
ligands, the general order of stability conferred by the chalcogen—phosphorus bond being oxide > sulphide > selenide > telluride. Ph_3PO decomposes at ca 450 °C and the sulphide at ca 380 °C. Trialkylphosphine oxides with no β-hydrogen atoms are even more stable, sometimes up to ca 600 °C, and most tertiary phosphine oxides appear to decompose at temperatures higher than those of the corresponding amine oxides, often by as much as 300 °C. When a β-hydrogen atom is available, elimination reactions may then occur during thermolysis (equation 81).

$$\mathrm{Me_2P(O)Et} \xrightarrow{330\text{–}670\,^{\circ}\mathrm{C}} \mathrm{H_2C{=}CH_2 + Me_2P(O)H + Me_2PH + Me_2POOH} \tag{81}$$

An important feature of the chemistry of smaller ring cyclic phosphine oxides is their tendency to fragment, particularly under thermolysis conditions. Thus, when heated, *r*-1,*t*-2,*t*-3-tri-*tert*-butylphosphirane 1-oxide eliminates *tert*-butylphosphinidine oxide, which can be trapped by reaction with alcohols or with a suitable *o*-benzoquinone



(297) **(298)** **(299)**



(300) X=S; Y=N; Z=NMe or NPh

(301) X=Se; Y=CH; Z=O or NPh

(Scheme 73)[382]. The 1,8-bond in 9-phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene 9-oxide (**297**; Ar = Ph) is particularly susceptible to fission, and when the oxide is obtained by direct oxidation of the corresponding phosphine even at −20 °C, it is accompanied by its valence tautomer **298**, which then rearranges to the dihydrophosphindole **299**[30]. The analogous **297** (Ar = 2,4,6-$Bu^t{}_3C_6H_2$) readily decomposes in $CHCl_3$ to yield cyclooctatetraene and *P,P′*-bis[(2,4,6-tri-*tert*-butyl)phenyl]phosphinic anhydride[383]. Extrusion of phenylphosphinidine oxide is assumed to account for the course of the bromination of the dihydrophosphepins **179** (Scheme 36).

Elimination of the phosphinidene fragments $RP{=}X$ (X = O or S) occurs from bridging positions when phosphole dimers and other Diels–Alder adducts are heated, e.g. **300**[384,385], or photolysed, e.g. **301**[384] (see also equations 52 and 53 and Schemes 51 and 52).

B. Cleavage by Metals

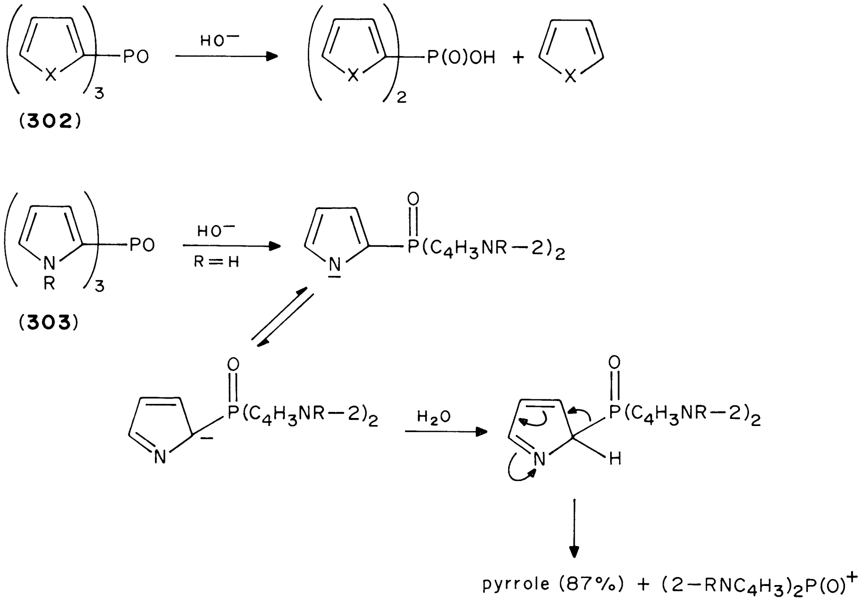
The older literature quotes several instances of the cleavage of P—C bonds by the action of metals, particularly the alkali metals. Trialkylphosphine oxides (butyl, octyl) and sodium have been shown to produce dialkylphosphines in ca 50% yields, but the oxide most widely investigated has been Ph_3PO. The latter is cleaved by two equivalents of sodium, and subsequent treatment with benzyl chloride gives benzyldiphenylphosphine oxide (77%); a similar reaction with potassium afforded [(3-benzyl)phenyl]diphenylphosphine oxide, probably through a biphenyl radical ion. The formation of a paramagnetic species is suspected as a result of the interaction of Ph_3PO and potassium or rubidium in ethereal solvents[386]. Benzyldiphenylphosphine oxide is also formed, together with benzene and diphenylphosphinic acid, from Ph_3PO and sodium under toluene, probably via $PhCH_2Na$.

C. Cleavage by Nucleophiles

Dialkylphosphine oxides are said to be formed when trialkylphosphine oxides interact with NaH; Ph_3PO and $LiAlH_4$ under thf or dioxane yield diphenylphosphine. The most widely studied examples of the cleavage of the phosphorus—carbon(ligand) bond by nucleophiles concern their behaviour towards alkali. The ready removal of a benzyl group from a benzylphosphine oxide is well authenticated. When fused with KOH, tribenzylphosphine oxide yields dibenzylphosphinic acid (about 10%), but higher yields of phosphinic acids are obtainable from substituted benzylphosphine oxides; under the same conditions the analogous tris(cyclohexylmethyl)phosphine oxides are unaffected[387]. Enantiomers of $MePh(PhCH_2)PO$ with KOH in dmso yield racemic $MePhP(O)OH$[388], and the same reagents remove the benzyl group from $PhCH_2P(O)Ph_2$[389], but fusion with NaOH at 250° will remove *n*-alkyl groups from the oxides $Ph_2P(O)R$. Tris(3-nitrophenyl)phosphine oxide is hydrolysed to nitrobenzene by 50% aqueous KOH[231].

When heated with alkali in 50% dioxane[390] or even with 10% aqueous NaOH solution[391], the oxides **302** (X = O or S) are cleaved to the free heterocycle and the phosphinic acid. Tris(2-pyrrolyl)phosphine oxide (**303**; R = H) was thought originally to hydrolyse to the pyrrolylphosphonic acid via the phosphinic acid, and ultimately to give pyrrole itself, following attack of HO^- at phosphorus. The failure of **303** (R = Me) to undergo hydrolysis under the same conditions rules out a mechanism involving such a process, and the currently favoured mechanism involves deprotonation at nitrogen (Scheme 74)[391,392].

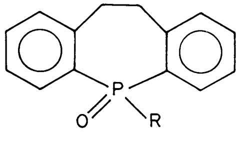
The attachment of strongly electronegative groups directly to phosphorus facilitates the fission of the phosphorus—carbon bond by nucleophiles. Tris(trifluoromethyl)phosphine oxide undergoes the fluoroform reaction with aqueous NaOH (and even with



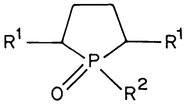
SCHEME 74

water only over an extended period); dimethylamine also removes one trifluoromethyl group very easily to give CHF_3 and $(CF_3)_2P(O)NMe_2$[393]. (Pentafluorophenyl)diphenylphosphine oxide loses the perfluorophenyl group by the action of NaOMe in MeOH; the corresponding sulphide behaves likewise[233,234]. Acetylenic phosphine chalcogenides are cleaved by boiling aqueous KOH and by ethanolic $AgNO_3$[394].

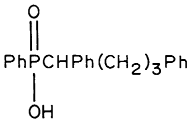
Some of the more interesting situations arise when the phosphorus atom is part of a ring system. The dihydrodibenzophosphepin **304** loses the exocyclic Ph group and gives the cyclic phosphinic acid **305** when acted upon by NaOH at 250 °C[395]; with $LiAlH_4$ or NaH, the principal reaction is one of ring fission, and with MeMgI both replacement of Ph by Me, and ring fission, occur[396].



(304) R = Ph
(305) R = OH



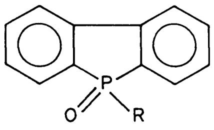
(306) R^1 = Cy; R^2 = Ph
(307) R^1 = Cy; R^2 = OH
(308) R^1 = R^2 = Ph



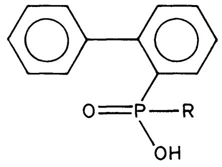
$\mathrm{Ph\overset{O}{\underset{OH}{P}}CHPh(CH_2)_3Ph}$

(309)

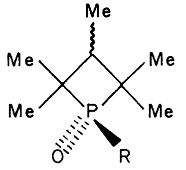
1-Methylphospholan-3-one 1-oxide is hydrolysed by NaOH solution to MeP(O)(OH)CH_2CH_2COMe[203]. The oxide **306** yields the phosphinic acid **307**, whereas **308** gives the acyclic phosphinic acid **309**[397]. The dibenzophosphole **310** suffers exclusive ring opening to **313** when fused with NaOH, but the benzyl analogue (**311**) preferentially ring opens to **314** (55%) but also affords 23% of the cyclic phosphinic acid **312**[398].



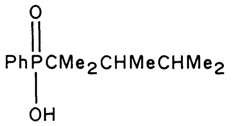
(**310**) R = Ph
(**311**) R = $PhCH_2$
(**312**) R = OH



(**313**) R = Ph
(**314**) R = $PhCH_2$



(**315**) R = $PhCH_2$
(**316**) R = OH
(**317**) R = Ph

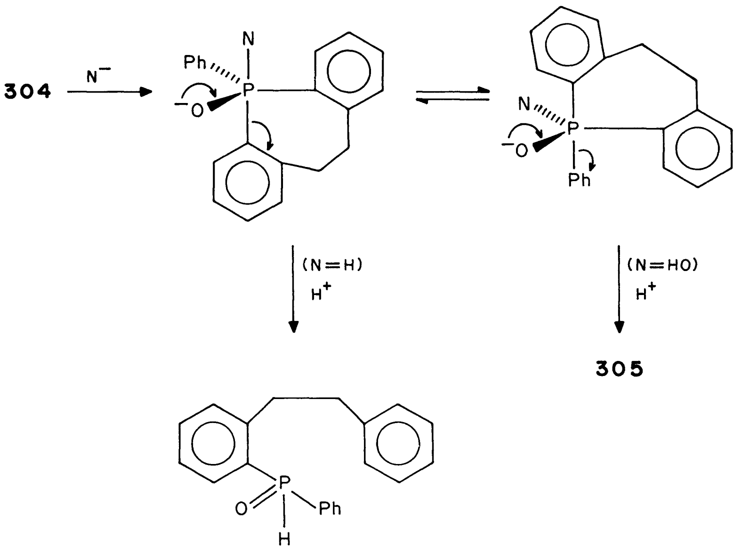


$\mathrm{Ph}\underset{\mathrm{OH}}{\overset{\mathrm{O}}{\mathrm{P}}}\mathrm{CMe_2CHMeCHMe_2}$

(**318**)

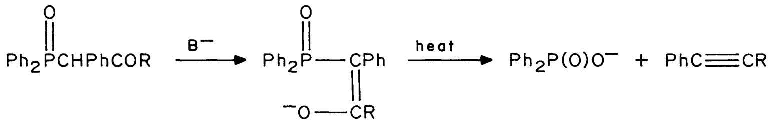
1-Benzyl-2,2,3,4,4-pentamethylphosphetane 1-oxide (**315**) is transformed exclusively into the phosphinic acid **316** with NaOH at 250 °C; the analogous 1-phenyl compound **317** yields both the cyclic phosphinic acid **316** and, preferentially, the acyclic phosphinic acid **318**, in the ratio 1:4[399]; the oxide **317** is stable towards aqueous sodium hydroxide[400].

It is apparent that the cleavage of acyclic phosphine oxides can generally occur when electronegative groups are attached directly to phosphorus, and the preferential site for fission can be predicted if there is a choice of leaving groups—that group forming the more stable anion will be expelled. Attempts have been made to explain the observed results in terms of pentacoordinate intermediates; the preferred choice between trigonal bipyramidal or square-planar intermediates seemed to be tbp[389]. The role that phosphorus(V) intermediates or transition states play in the chemistry of acyclic phosphine oxides is far from clearly understood, unlike their role for phosphate esters. The position is also unclear for cyclic phosphine oxides. The role of phosphorus(V) intermediates is well established in the chemistry of esters of cyclic phosphoric and phosphinic acids, and of cyclic phosphonium salts. In an attempt to discern a role for pentacoordinate intermediates in the chemistry of cyclic phosphine oxides, Gorenstein[401] examined the pH–rate profile for the epimerization and ^{18}O incorporation for 1-phenyl-2,2,3-trimethylphosphetane 1-oxide, but was unable to provide conclusive positive evidence. On the other hand, other workers have explained the behaviour of **304** towards nucleophiles in terms of phosphorus(V) intermediates (Scheme 75)[396,397], employing the concept of relative apicophilicities. The latter concept, in conjunction with the feature(s) of the cyclic phosphine oxide which controls the siting of the ring in the phosphorus(V) intermediate, i.e. ring size (a four-membered ring is likely to be restricted to an apical–equatorial position), together with the question of stability of the leaving group as an anion, will all contribute to the final outcome of the reaction of a phosphine oxide with a nucleophile.



SCHEME 75

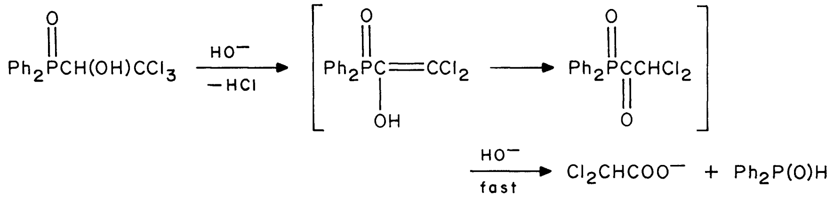
The Horner reaction is yet another example of a reaction in which the P—C (ligand) bond is cleaved, probably at some stage through the breakdown of a tbp intermediate formed by nucleophilic attack of O⁻ at electrophilic phosphorus. A similar breakdown accounts for the formation of acetylenes from the thermolysis of (2-ketoalkyl)phosphine oxides under basic conditions (Scheme 76)[402].



$$Ph_2\overset{O}{\overset{\|}{P}}CHPhCOR \xrightarrow{B^-} Ph_2\overset{O}{\overset{\|}{P}}\text{—}\underset{^-O\text{—}CR}{\underset{\|}{C}}Ph \xrightarrow{heat} Ph_2P(O)O^- + PhC{\equiv}CR$$

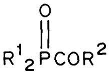
SCHEME 76

α-Hydroxyalkylphosphine oxides are particularly susceptible to degradation under alkaline conditions (Scheme 77)[403]. (1-Oxoalkyl)phosphine oxides (**319**) hydrolyse under even milder conditions to the secondary phosphine oxides $R^1{}_2P(O)H$, which then react with the starting material to give (hydroxyalkyl)bis(phosphine oxides) (**320**)[404].



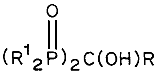
$$Ph_2\overset{O}{\overset{\|}{P}}CH(OH)CCl_3 \xrightarrow[-HCl]{HO^-} \left[Ph_2\overset{O}{\overset{\|}{P}}\underset{OH}{\underset{|}{C}}{=}CCl_2 \longrightarrow Ph_2\overset{O}{\overset{\|}{P}}\underset{O}{\underset{\|}{C}}CHCl_2 \right] \xrightarrow[fast]{HO^-} Cl_2CHCOO^- + Ph_2P(O)H$$

SCHEME 77



$R^{1}_{2}\overset{\overset{O}{\|}}{P}COR^{2}$

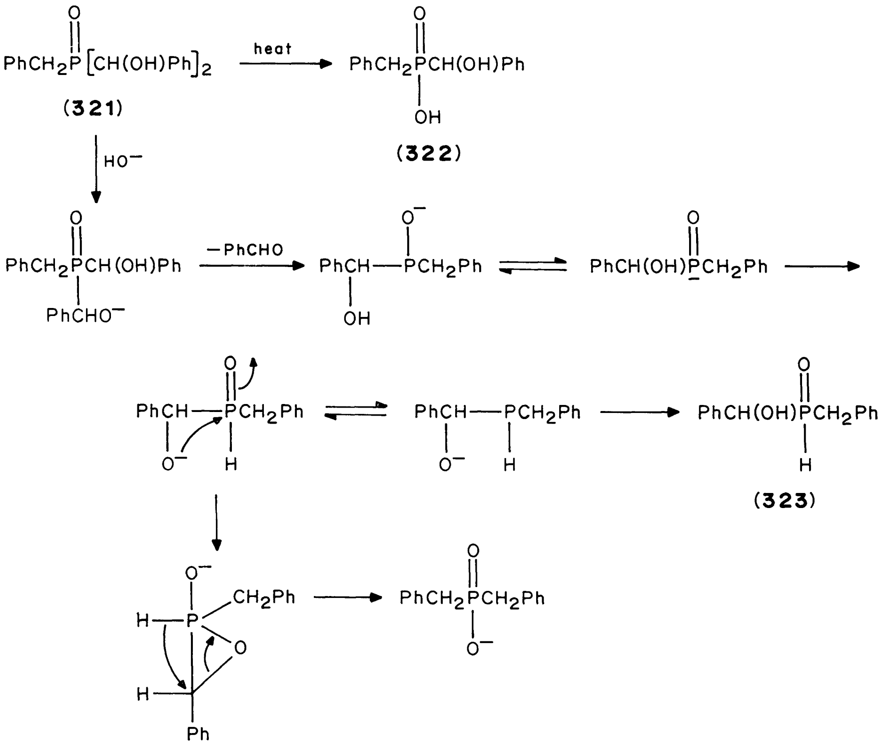
(319)



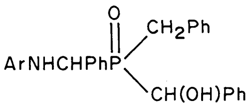
$(R^{1}_{2}\overset{\overset{O}{\|}}{P})_{2}C(OH)R^{2}$

(320)

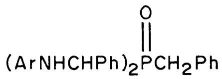
The phosphine oxide **321** decomposes in boiling benzene and benzyl(α-hydroxylbenzyl)phosphinic acid (**322**) can be isolated. In the presence of 1 M NaOH solution, the oxide **321** yields dibenzylphosphinic acid; a mechanism for this reaction has been postulated (Scheme 78)[405].



SCHEME 78



(324)

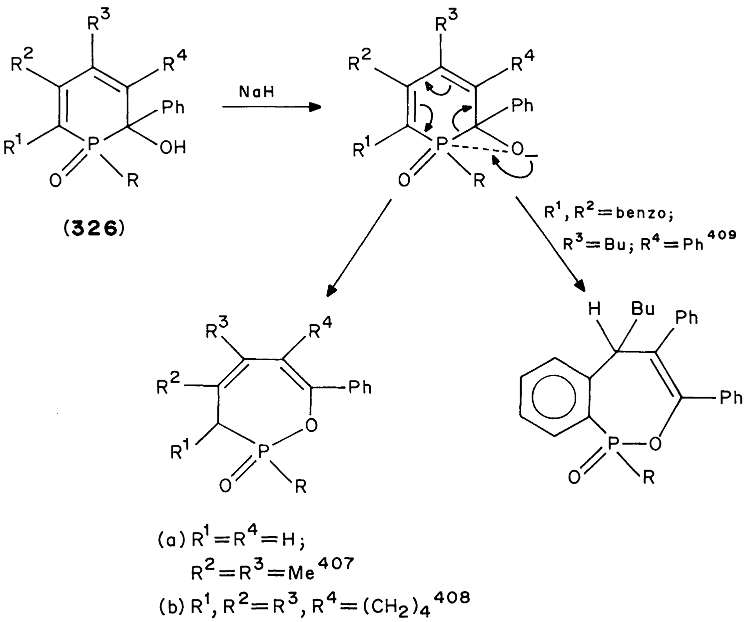


$(ArNHCHPh)_{2}\overset{\overset{O}{\|}}{P}CH_{2}Ph$

(325)

The same oxide (**321**), when heated with aromatic amines, yields first the monoamino compounds **324**, probably via the secondary phosphine oxide **323**; the final products are bis(α-aminobenzyl)benzylphosphine oxides (**325**). No such reaction occurs with branched-chain aliphatic amines[406].

In another rearrangement proceeding through nucleophilic intramolecular attack and of high synthetic potential, 2-hydroxy-2-aryl-1,2-dihydrophosphorins (**326**) are treated with NaH; the intermediate anion can furnish tautomeric-like products depending on the nature of the original substituents (Scheme 79)[407–409].



(326)

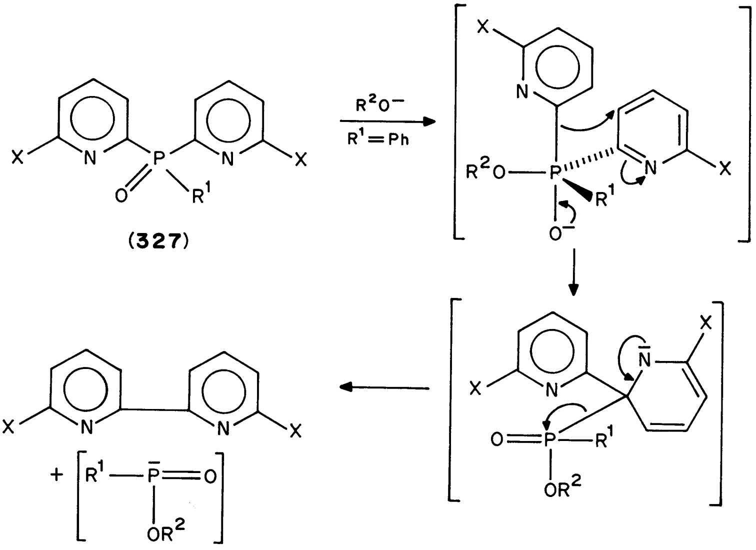
(a) $R^1 = R^4 = H$;
$R^2 = R^3 = Me$[407]
(b) $R^1, R^2 = R^3, R^4 = (CH_2)_4$[408]

SCHEME 79

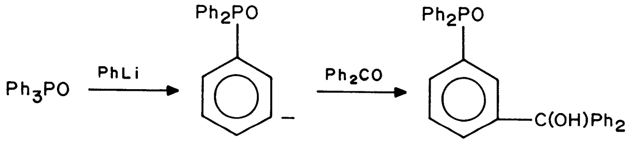
One of the more unusual examples of the fission of the P—C(ligand) bond is that depicted in Scheme 80, in which di-2-pyridinylphosphine oxides (**327**; X = H or Br, or XX = a polyether chain) are treated with NaOEt in toluene at 100 °C when the main reaction products are the 2,2′-bipyridinyl[410]. Carbon nucleophiles (MeMgI, PhMgBr, $PhCH_2MgCl$, PhLi, 2-pyrLi, etc.) yield additionally simple 2-substituted pyridines, and pyridine itself[411], also produced by the action of acidic reagents[412]. The phosphorus—carbon bond in tri-*tert*-butylphosphirane 1-oxide is cleaved by nitrogen nucleophiles, in particular the bases $LiNR_2$; fission also occurs to some extent at the C—C bond, and the relative extents of these reactions depend on R and the solvent[202].

Wittig and Cristau[413] were unable to corroborate earlier observations (Wittig and Rieber, 1949)[6–9] of the formation of tetraphenylphosphonium salts from Ph_3PO and PhLi, and instead showed that carbanions were formed which could be trapped in a reaction with benzophenone (Scheme 81). According to Schaub *et al.*[414], metallation of Ph_3PO with PhLi or Bu^tLi occurs at the (mono)*ortho* positions[414]. Exchange of organic groups when Ph_3PO was treated with RCH_2Li (R = H or Me) had already been demonstrated by Seyferth *et al.*[415].

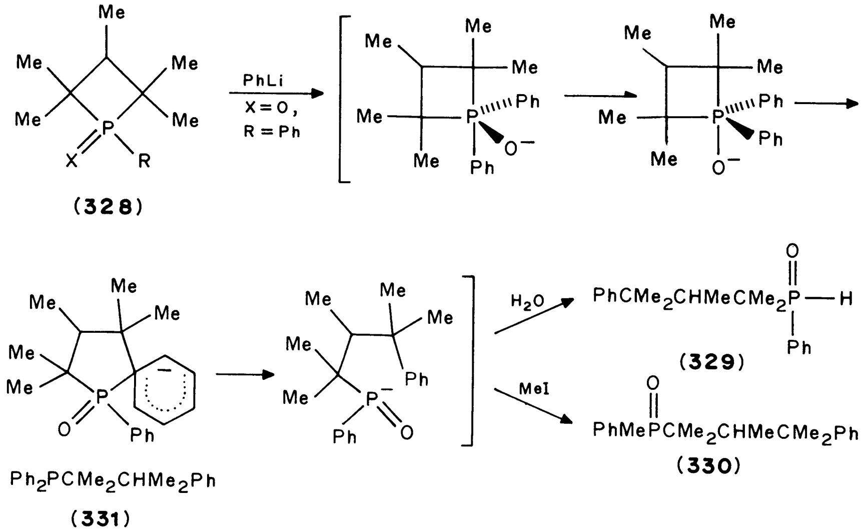
The fission of the P—C(sp) bond in diphenyl(phenylethynyl)phosphine oxide under the influence of PhLi to give Ph_3PO and the lithium salt of phenylacetylene has been formulated as occurring via a pentacoordinate intermediate[416].



SCHEME 80

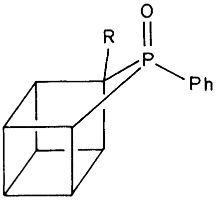


SCHEME 81

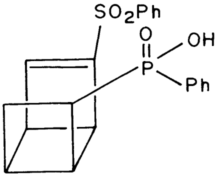


SCHEME 82

Ring cleavage occurs when the phosphetane 1-oxide **328** (X = O; R = Ph) is acted upon by PhLi (Scheme 82), as evidenced by subsequent methylation of the intermediate(s) to give the phosphine oxide **330**, and treatment with water when the secondary phosphine oxide **329** was obtained[417,418].



(332)



(333)

The phosphahomocubane **332** (R = H) is lithiated with PhLi in thf without ring opening; deuteriation or methylation gives **332** (R = D or Me), and PhSSPh gives *inter alia* the sulphide **332** (R = SPh). Oxidation of the latter with mCPBA and treatment of the sulphone with $NaN(SiMe_3)_2$ resulted in ring opening to the phosphinic acid **333**[419].

As in the case of the oxide, Seyferth and Welch[420] demonstrated exchange between Ph_3PS and RCH_2Li to give $Ph_2P(S)CHRLi$, and with PhLi, triphenylphosphine sulphide gives Ph_3P and PhSH (Wittig, 1969, unpublished results). In the latter example, the loss of sulphur and valence contraction are also to be found in reactions 82 and 83, and also occur when the sulphide **328** (X = S, R = Ph) is treated with one equivalent of PhLi when half the starting amount of starting sulphide is recovered and the phosphine (**331**) is obtained concurrently.

$$p\text{-}Tol_3PS + PhLi \longrightarrow p\text{-}Tol_3P + PhP(Tol\text{-}p)_2 \qquad (82)$$

$$Ph_3PS + p\text{-}TolLi \longrightarrow Ph_3P + Ph_2PTol\text{-}p \qquad (83)$$

It appears that, to some extent at least, attack occurs at sulphur in addition to phosphorus[417].

VII. REACTIONS OF PRIMARY AND SECONDARY PHOSPHINE CHALCOGENIDES

As indicated at the beginning of this chapter, the chalcogenide derivatives of primary and secondary phosphines are tautomeric substances with the phosphorus capable of existence in both the tricoordinate tervalent (**2.2**) and tetracoordinate quinquevalent (**2.1**) states. In practice the phosphorus adopts, almost exclusively (with two known exceptions), the latter state. Secondary phosphine oxides are not particularly stable substances with regard to heat. Thus, dimethylphosphine oxide begins to disproportionate to Me_2PH and $Me_2P(O)OH$ at ca 100 °C; the diethyl compound decomposes at 180–200 °C[421].

Chiral secondary phosphine oxides have been prepared in optically active forms; $Ph(PhCH_2)P(O)H$ is configurationally stable in MeOH at room temperature, but rapidly racemizes in the presence of a trace of mineral acid; it also undergoes rapid deuterium exchange at ambient temperature[422]. On the other hand, Ph(PhCHMe)P(O)H does not undergo stereomutation in MeOH containing NaOMe or 0.05 M HCl, but does epimerize in the presence of $LiAlH_4$[423].

The chalcogenides of primary phosphines, $RP(X)H_2$, are also tautomeric, and are relatively inaccessible substances and have been studied only poorly (see, e.g., ref. 424). The derivatives of secondary phosphines have now been well characterized and their reactions studied to a much greater extent. Their nucleophilic character in the presence of a base, reacting at either the chalcogen or phosphorus to give tervalent or quinquevalent phosphorus derivatives, has been recognized for some time. Their duality of behaviour is also to be noted, since not only can they react as nucleophiles in the absence of a base, as in the conversion of diarylphosphine oxides into diarylphosphinous chlorides (diarylchlorophosphines) by the action of PCl_3[425], but they can also behave as electrophiles towards bases. Thus, a rapid evolution of hydrogen occurs when secondary phosphine oxides are treated with an excess of NaOEt or NaOH in EtOH; the main phosphorus-containing product is a phosphinic acid. Thiophenoxide behaves in a similar fashion, e.g. with $Ph_2P(O)H$, when the phosphorus-containing product is *S*-phenyl diphenylphosphinothioate. This observation explains the formation of hydrogen when (α-hydroxyalkyl)phosphine oxides are in contact with alkaline reagents[426].

The reactions considered in this section are those in which the quinquecovalency of the phosphorus is maintained.

A. Oxidation and Reduction Reactions

The oxidation (addition of chalcogen) of secondary phosphine chalcogenides may be represented simply by the general equation 84. Secondary phosphine oxides are readily oxidized to phosphinic acids by means of hydrogen peroxide[427,428]; diarylphosphine oxides have also been oxidized with *tert*-butyl hydroperoxide or *p*-nitroperoxybenzoic acid and the kinetics of the reactions studied[427].

$$R_2P(X)H + \tfrac{1}{2}Y_2 \longrightarrow R_2P(X)YH \rightleftharpoons R_2P(Y)XH \qquad (84)$$

The analogous conversion of secondary phosphine sulphides into phosphinodithioic acids by the addition of elemental sulphur is also known. The addition of oxygen to a phosphine sulphide appears to be less satisfactory for those very few examples reported[429]; on the other hand, the successful addition of sulphur to *tert*-butylphenylphosphine oxide to give the corresponding phosphinothioic acid has been recorded, whilst the treatment of diarylphosphine oxides with diphenyl disulphide leads to *S*-phenyl esters of diarylphosphinothioic acids[430].

Iron powder has been used successfully in the desulphurization of secondary phosphine sulphides (diisobutyl, diphenyl) to the parent phosphines (Maier, 1964)[6–9].

B. Replacement Reactions

The simplest of these is that of the phosphine hydrogen by a metal when the chalcogenide is treated with the metal itself, or with a metal alkoxide or organometallic reagent such as an organolithium or Grignard reagent.

The replacement of hydrogen by a halogen, although well established, is not a reaction which always lends itself to synthetic utility since there are easier ways to prepare the products. $Ph_2P(O)H$ with $SOCl_2$ yields diphenylphosphinic chloride, $Ph_2P(O)Cl$. The interaction of $Et_2P(O)H$ and $SOCl_2$ initially affords $Et_2P(O)Cl$, but this reacts further with the starting oxide, and a sequence of steps leads eventually to Et_2PCl, Et_2PH and ultimately to Et_2PCl_3[431]. The direct thiocyanation of *tert*-butylphenylphosphine oxide yields the relatively stable $Bu^tPhP(O)SCN$ [compounds possessing the P(O)SCN grouping tend to be unstable], which then rearranges to $Bu^tPhP(O)NCS$[432].

Secondary phosphine oxides have been alkylated with reactive, e.g. benzylic, halides to give tertiary phosphine oxides[428,433], and a recently reported procedure for this same conversion involves the treatment of a secondary phosphine oxide with an alcohol (secondary and tertiary alcohols react more slowly than do primary alcohols) in the presence of 5–10 mol% of an alkyl chloride, bromide or iodide (equation 85)[434]. Benzylic halides, α-bromo ketones and methylolamines[435] have been used to alkylate secondary phosphine sulphides, either in the free state or as a metal derivative[429] (see also Section VII.C.3).

$$R^1R^2P(O)H + R^3OH \xrightarrow{R^3X} R^1R^2P(O)R^3 + H_2O \qquad (85)$$

C. Addition Reactions

Additions to systems possessing sp^2 or sp carbon form by far the most widely investigated and synthetically important group of reactions of secondary phosphine chalcogenides[436].

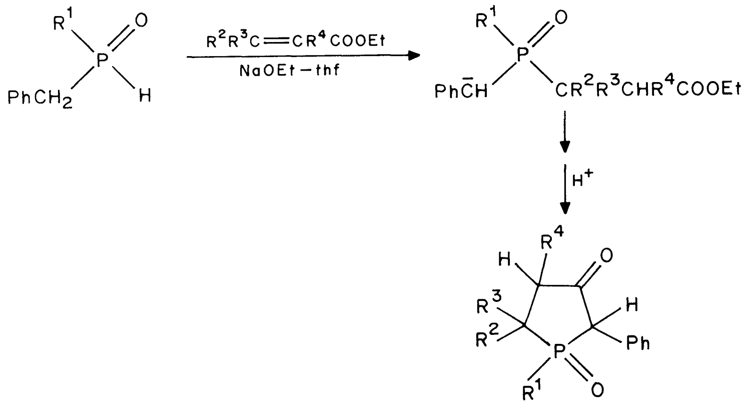
1. Additions to C=C and C≡C bonds

The general mode of addition of secondary phosphine chalcogenides to activated olefinic compounds is illustrated in equation 86.

$$R^1{}_2P(X)H + \underset{\textbf{(334)}}{R^2HC{=}CR^3Y} \xrightarrow{B} R^1{}_2P(X)CHR^2CHR^3Y \qquad (86)$$

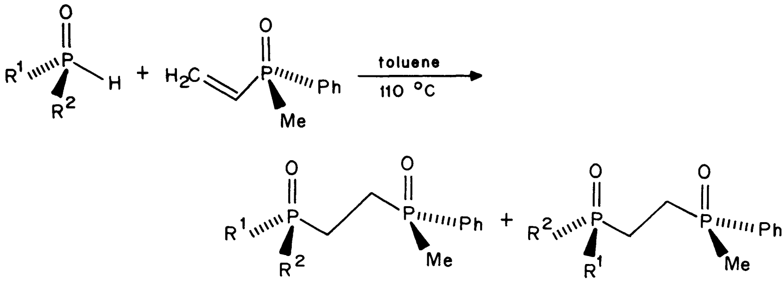
Additions of secondary phosphine oxides to derivatives of propenoic acid and those of homologous acids and other carbonyl compounds are well known, and including additions to **334** (R^2 = H, Me, Ph or COOEt; R^3 = H or Me; Y = CN, COOEt, $CONH_2$, COMe or COPh) for $R^1 = PhCH_2$ or Oct[437] and $R^1{}_2 = Ph(PhCH_2)$[438]. A series of similar additions have been reported for the phenophosphazine system[428] and for vinylsilanes[439].

The initial addition of secondary phosphine oxides to unsaturated carboxylic esters provides a route to phospholane oxides (Scheme 83). The yields of initial adducts are generally low for derivatives of propenoic acid but are greater (45–75%) for those of homologues and for cinnamic acid esters[440] (see also Scheme 90). Although addition reactions of secondary phosphine sulphides have been recorded[429,435,441], the general outcome is less successful than for the phosphine oxides.



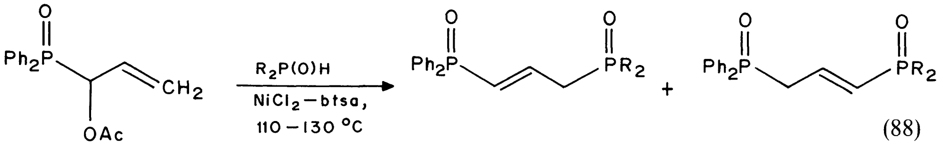
SCHEME 83

Recently studied examples of the addition of secondary phosphine oxides to tertiary vinylphosphine oxides include those of RPhP(O)H (R = Me or Bu^t) to (*S*)-methylphenylvinylphosphine oxide in boiling toluene, from which a mixture of diastereoisomeric products was obtained (equation 87)[298,442]. Assignment of configurations to separated compounds was sometimes made on the basis of optical rotation measurements (R^1 or $R^2 = Me$ or Ph) or X-ray crystallography ($R^1 = Bu^t$, $R^2 = Ph$) but was not always possible, e.g. when R^1 or R^2 is benzyl. The same compounds are obtainable in an addition–elimination sequence when chiral α-bromo- or α-chloro-vinylmethylphenylphosphine oxides are treated with secondary phosphine oxides in the presence of Et_3N[443].



(87)

In the presence of nickel(II) and bis(trimethylsilyl)acetamide secondary phosphine oxides do not add to (1-acetyloxyallyl)diphenylphosphine oxide, but rather displace the acetyloxy group with the formation of a mixture of isomeric [hydrogenolysed to the same 1,3-bis(diphenylphosphinoyl)propane] 1,3-bis(diphenylphosphinoyl)propenes (equation 88)[444].



(88)

2. *Additions to C═N and C≡N bonds*

The addition of diphenylphosphine oxide to the imino bond of the hydrazones of aldehydes or ketones, was reported in 1960 by Kreutzkamp[6–9]; it is a reaction which is easily reversible, particularly in the presence of traces of acid or base. Thermolytic cleavage of the products of addition leads to branched-chain tertiary phosphine oxides (Scheme 84), but the scope of this preparative process appears not to have been examined to any great extent[445].

$$\begin{tikzcd} \mathrm{Ph_2P(O)H + R^1R^2C{=}NNHTos\text{-}}p \arrow[r, shift left, "25\,^\circ\mathrm{C}"] & \mathrm{Ph_2P(O)CR^1R^2NHNHTos\text{-}}p \arrow[l, shift left] \arrow[d, "\text{heat, thf}"] \\ & \mathrm{Ph_2P(O)CHR^1R^2} \end{tikzcd}$$

SCHEME 84

Diphenylphosphine oxide adds to the nitriles RCN ($R = Ph$, $PhCH_2$ or CN) when heated in the presence of EtO^- to give the phosphinoylaldimines $Ph_2P(O)CR{=}NH$, and the kinetics of the reaction have been studied[446]. For α-ketonitriles, the initial reaction to give a 1:1 adduct occurs at the carbonyl group, but further reaction to give the 2:1 adduct involves the nitrile group (Scheme 85)[447].

$$Bu_2P(O)H + MeCOCN \longrightarrow Bu_2P(O)OCHMeCN \longrightarrow Bu_2P(O)OCHMe\overset{\overset{NH}{\|}}{C}\underset{\underset{O}{\|}}{P}Bu_2$$

SCHEME 85

3. *Additions to C=O and C=S bonds*

Numerous examples exist of the interaction of aldehydes or ketones with secondary phosphine chalcogenides. Until fairly recently, these consisted only of the intermolecular type (equation 89). More recently, however, examples of intramolecular reaction have been forthcoming, leading usefully to the synthesis of phosphorus-containing ring systems.

$$R^1{}_2P(X)H + R^2R^3C{=}O \rightleftharpoons R^1{}_2P(X)CH(OH)R^2R^3 \qquad (89)$$

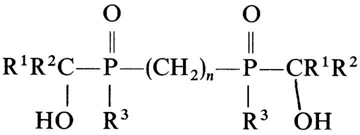
Within the grouping of intermolecular reactions, additions occur to saturated carbonyl compounds (1,2-additions), and also to conjugated systems, in which both 1,4- and 1,6-additions have been observed.

In contrast to the similar interactions between dialkyl hydrogen phosphonates and aldehydes or ketones which require a basic catalyst, those involving secondary phosphine oxides may not require such a catalyst. Reactions between dibutyl- or dioctyl-phosphine oxide and activated carbonyl compounds, e.g. $R^2 = H$, Me, Et or Ph, $R^3 = COMe$, COOalkyl or $P(O)(OEt)_2$ (equation 89) occur exothermically and are complete within a few days[448–450]. Mixtures of diastereoisomeric products (**335**) have been obtained from unsymmetric diarylphosphine oxides and chloral[451] and from ethylphenylphosphine oxide and acetophenone. The latter, at 25 °C, yielded a 70:30 mixture of the *erythro* and *threo* forms of the 1:1 adduct **336**, a result explained in terms of the preferred mutual transoidal approach of C=O and P=O[452]. Alkanebis(phosphine oxide)s react in the expected manner to give the adduct **337**[453]. Steric interference in reaction 89 has been observed; thus, di-*tert*-butylphosphine oxide fails to add to simple aldehydes or ketones even in the presence of a basic catalyst[454].

$Ar^1Ar^2P(O)CH(OH)CCl_3$ **(335)**

$EtPhP(O)C(OH)MePh$ **(336)**

The reaction between acetone and the magnesium salt of diphenylphosphine oxide yields a mixture of the expected 1:1 adduct **338** ($X = O$) together with **339** ($X = O$) and **340** ($X = O$), the latter adducts being derived from mesityl oxide and phorone, the source

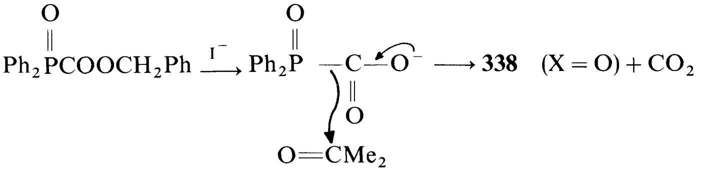


$$R^1R^2\underset{\underset{HO}{|}}{C}-\overset{\overset{O}{\|}}{\underset{\underset{R^3}{|}}{P}}-(CH_2)_n-\overset{\overset{O}{\|}}{\underset{\underset{R^3}{|}}{P}}-\underset{\underset{OH}{\backslash}}{C}R^1R^2$$

(337)

of which was the acetone and base[485]. The adduct **338** ($X = O$) has also been obtained, in an interesting manner, following the debenzylation of benzyl diphenylphosphinoylformate by NaI in acetone; evidently, under the experimental conditions, the diphenylphosphinoylcarboxyl anion decarboxylates very readily (Scheme 86)[456].

$Ph_2P(X)CMe_2OH$ **(338)** $Ph_2P(X)CMe_2CH_2COMe$ **(339)** $[Ph_2P(X)CMe_2CH_2]_2CO$ **(340)**



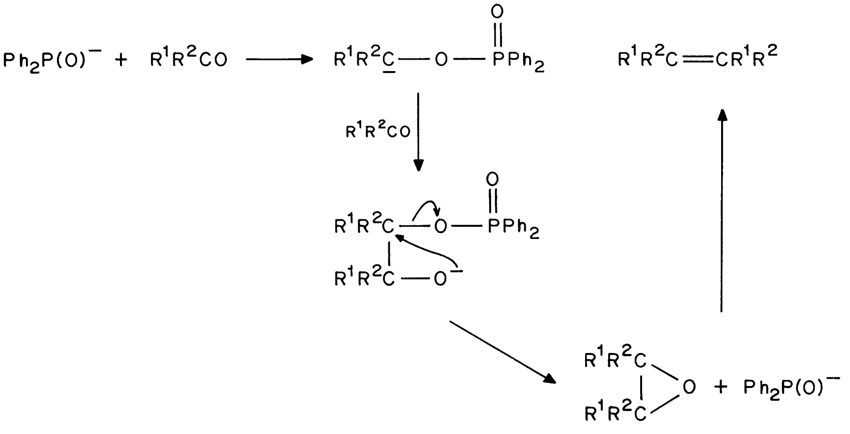
SCHEME 86

Additions to secondary phosphine sulphides are much slower and need to be base catalysed, but they are also reversible so as to make satisfactory characterization of the products impossible, or at least very difficult[429]. Combinations of the adducts **338**–**340** ($X = S$) are obtainable from diphenylphosphine sulphide and acetone under neutral to basic conditions[454].

The possible role of the carbonyl–phosphine oxide condensation in the aminomethylation of secondary phosphine oxides using mixtures of carbonyl reactant and amines has been discussed by Petrov *et al.*[457]. In the case of the $(PhCH_2)_2P(O)H$–$HCHO$–Et_2NH system, the two main constituents in the product are $(PhCH_2)_2P(O)CH_2NEt_2$ and $(PhCH_2)_2P(O)CH_2OH$; both are produced at 60–110 °C, but at 140–150 °C only the former is present, and the former is not obtained from the phosphinoylmethanol and amine at the lower temperatures. The reaction is therefore considered to proceed through an initial hydroxymethylation of the amine. The formation of the aminomethylphosphine oxide at higher temperatures may well proceed through dissociation of the hydroxymethylphosphine oxide into secondary phosphine oxide and HCHO followed by hydroxymethylation of the amine to Et_2NCH_2OH and its subsequent reaction; it is worth noting that the oxide $(PhCH_2)_2P(O)CH_2OMe$ does not dissociate when heated, nor does it exchange MeO for NEt_2 even at 180–190 °C[457]. Some comparison may be made between these results and those embodied in Scheme 78.

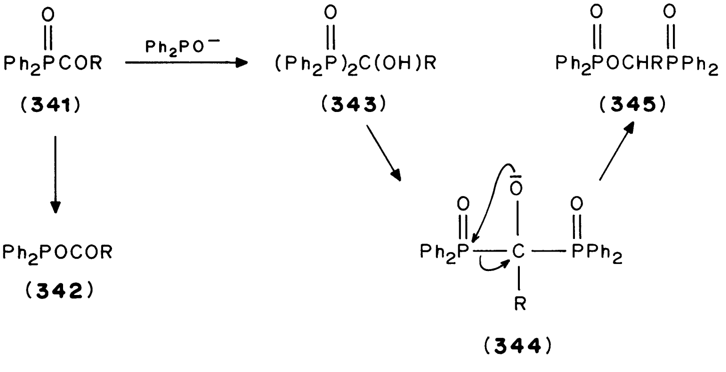
Following his original (1961) observations on the formation of *trans*-stilbene when benzaldehyde and diphenylphosphine oxide anion were heated together at 200 °C, Horner[6–9] suggested that the reaction might proceed via (α-hydroxybenzyl)diphenylphosphine oxide. However, it is now known that the latter is unstable to base, and even at 100 °C reverts to PhCHO and the secondary phosphine oxide anion in the presence of NaH. Moreover, it has now been demonstrated that $Ph_2P(O)^-$ with two equivalents of PhCHO at 180 °C yields *trans*-stilbene together with a mixture of *trans*- (45%) and *cis*- (40%) stilbene epoxides, a result similar to that produced when (α-hydroxybenzyl)-diphenylphosphine oxide is heated with one equivalent of PhCHO and NaH at 180 °C. Further, when heated with $Ph_2P(O)^-$ at 180 °C, *trans*-stilbene epoxide gives a quantitative yield of *trans*-stilbene. The formation of symmetrical alkenes from phosphine oxide anions and (aromatic) aldehydes or ketones is formulated as in Scheme 87[458].

The acylation of secondary phosphine oxides yields (1-oxoalkyl)phosphine oxides; thus, di-*tert*-butylphosphine oxide, as its lithium salt, affords $Bu^t_2P(O)COPh$ in 27% yield when treated with benzoyl chloride[452]. The acetylation of diphenylphosphine oxide at 55 °C with acetic anhydride leads to acetyldiphenylphosphine oxide (**341**; $R = Me$), which slowly isomerizes into diphenylphosphinous acetic anhydride (**342**; $R = Me$)



SCHEME 87

(Scheme 88). With more diphenylphosphine oxide anion, acetyldiphenylphosphine oxide yields the bis(diphenylphosphinoyl) compound **343**, rearrangement of which through the three-centre process indicated in **344** results in the formation of the phosphinic ester **345** (R = Me)[456,459]. The phosphine oxides PhRP(O)COMe (R = $PhCH_2$, Cy, Bu^t or Ar), when heated with the oxides PhRP(O)H also furnish compounds of types **343** and **345**[460,461]. The reported formation of tetraphenyldiphosphine monoxide from diphenylphosphine oxide and acetic anhydride in the presence of pyridine has been attributed to reaction between the anhydride **342** (R = Me) and the $Ph_2P(O)H$[462].

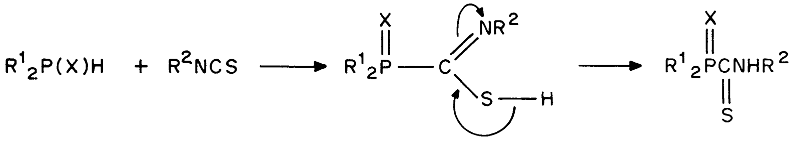


SCHEME 88

Benzoyldiphenylphosphine oxide (**341**; R = Ph), obtained from tetraphenyldiphosphine and benzoic acid, is rapidly converted into **345** (R = Ph); following a similar reaction with certain aliphatic acids, e.g. phenylacetic acid, phenoxyacetic acid and 3-phenylpropanoic acid, compounds of type **343** were isolable because of the slowness of the rearrangement steps. Other acids, e.g. di- and tri-phenylacetic acids, were converted into hydrocarbons[463]. The same products (Scheme 88; R = Me) have been observed following an Arbuzov reaction between the appropriate RCOCl and methyl diphenylphosphinite Ph_2POMe[464].

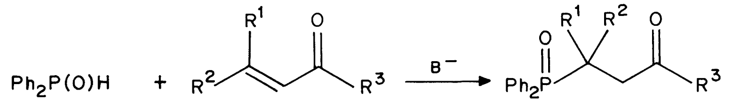
The nucleophilic activity of secondary phosphine oxides, already referred to, accounts for the formation of chlorodiphenylphosphine and acetic acid from a reaction between diphenylphosphine oxide and MeCOCl[465]; $Ph_2P(O)H$ and Ph_2PCl then react further in a stepwise sequence involving tetraphenyldiphosphine and its monoxide, diphenylphosphinic chloride and, ultimately, diphenylphosphinic acid and chlorodiphenylphosphine[466].

The addition of MeMgI to benzoylethylphenylphosphine oxide affords a mixture of *erythro* and *threo* diastereoisomers of (1-hydroxy-1-phenylethyl)ethylphenylphosphine oxide (**336**), the proportions of which (7:3) are essentially independent of reaction temperature, and are explicable in terms of a Cram model[452]. The additions of secondary phosphine oxides or sulphides to isothiocyanates requires basic catalysis and probably proceeds through an addition across the C=S bond followed by a prototropic shift (Scheme 89)[453,467].



SCHEME 89

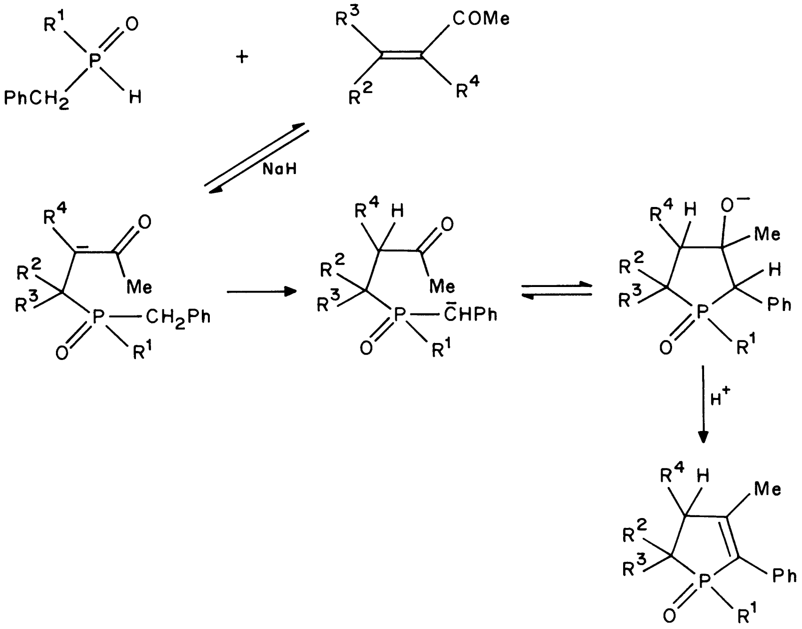
The conjugate (Michael) addition of, e.g., diphenylphosphine oxide anion to an unsaturated carbonyl compound is generalized in equation 90, and several examples of these and similar additions have been reported[181,433,456]. The failure of diphenylphosphine oxide to add in this manner to but-2-enal is rather unexpected; the product is, instead, 2-(diphenylphosphinoyl)pent-3-en-2-ol, formed by normal 1,2-addition[456]. An earlier recorded example of a 1,4-addition to a conjugated carbonyl system is to be found in the ready addition, in the absence of a catalyst, of diphenylphosphine oxide to *p*-benzoquinone; the phenolic product was thought to be diphenyl(2,5-dihydroxyphenyl)phosphine oxide[426,468,469]. A sequence potentially useful for the synthesis of phospholes or dihydrophospholes (Scheme 90) is initiated by the Michael addition of a secondary benzylphosphine oxide to an unsaturated methyl ketone (compare Scheme 83)[470].



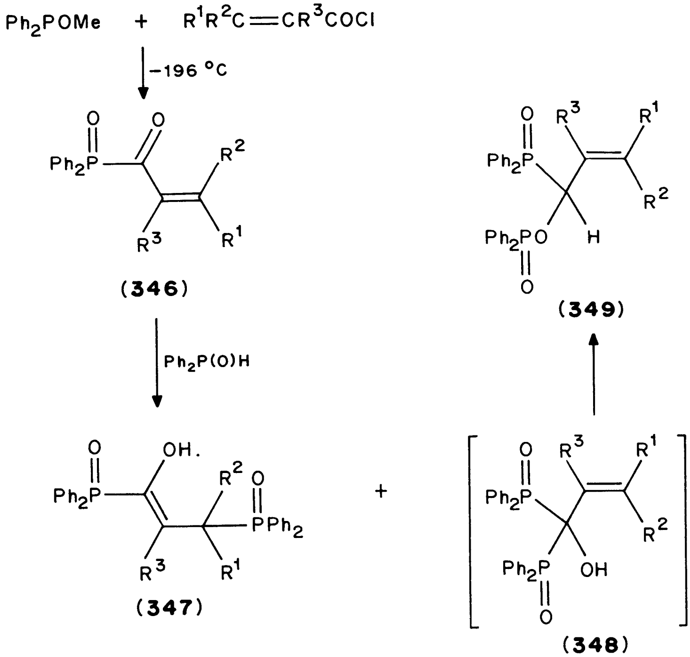
(90)

Diphenylphosphine oxide adds conjugatively to the unsaturated ketophosphine oxide **346** to give the enol **347**, and also non-conjugatively to give the adduct **348**; the latter compounds evidently rearrange to the isolable phosphinic esters **349** (Scheme 91)[471]. When the depicted synthesis of the oxides **346** is carried out using diethyl ether as solvent, the products also contain the appropriately *O*-acylated derivatives of **347**[472]. The structure of the compounds (*E*)-**347** ($R^1 = R^2 = Me$; $R^3 = H$) and **349** ($R^1 = R^2 = Me$; $R^3 = H$) were confirmed by X-ray crystallographic analysis.

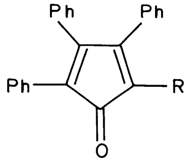
A particularly interesting case of conjugate addition is that of secondary phosphine oxides to cyclopentadienones leading to 1:1 adducts. The mixing of solutions of diphenylphosphine oxide and the cyclopentadienones **350** (R = Me or Ph) in the presence of dimethylamine results in a series of colour changes suggestive of reversibility of addition[473]. The adducts are thought to be formed by nucleophilic attack of phosphorus(III) on the carbon sited adjacent to the carbonyl group, the final site of protonation being dependent on the experimental conditions. The main product from **350** (R = Ph) was **351**. This compound is unstable to heat and to strong bases, being



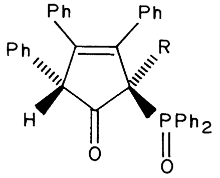
SCHEME 90



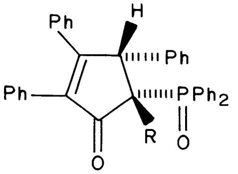
SCHEME 91



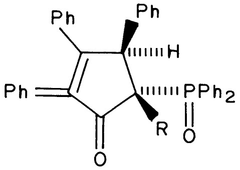
(350)



(351)

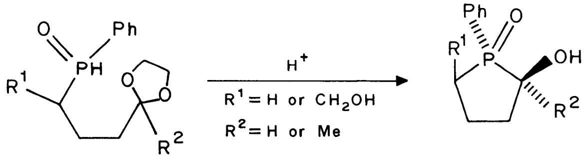


(352)



(353)

rapidly decomposed on alumina and silica; **351** was also the main product when $Ph_2P(O)Na$ reacted with tetraphenylcyclone, or when the addition was carried out in the presence of a very weak base[474]. When the addition was carried out in the presence of HCl, the products included tetraphenyldiphosphine dioxide, the three adducts **352**–**354** and the *trans*-2,3-dihydro derivative of the starting material. Of the diastereoisomers **352** and **353** (R = Me or Ph), the additions proceed with a bias towards **352**. This system thus presents evidence for conjugate 1:4 and 1:6 additions.



(354) **(355)**

The addition reactions thus far considered have all been of the intermolecular type. As an example of an intramolecular 1:2 addition, the conversion of **354** into the 2-hydroxyphospholane 1-oxide **355** following liberation of the δ-carbonyl group (by acidolytic removal of the protecting group) may be cited[475].

VIII. REFERENCES

1. G. Aksnes and K. Bergesen, *Acta Chem. Scand.* **18**, 1586 (1964).
2. H.-G. Henning, *Z. Chem.*, **14**, 209 (1974).
3. O. I. Kolodyazhnyi, *J. Gen. Chem. USSR*, **46**, 2285 (1976).
4. O. I. Kolodyazhnyi, *Tetrahedron Lett.*, **23**, 499 (1982).
5. I. Granoth, R. Alkabets, and E. Shirin, *J. Chem. Soc., Chem. Commun.*, 981 (1981).
6. K. D. Berlin and G. B. Butler, *Chem. Rev.*, **60**, 243 (1960).
7. H. R. Hays and D. J. Peterson, in *Organic Phosphorus Compounds* (Eds G. M. Kosolapoff and L. Maier), Vol. 3, Wiley, New York, 1972, Chapter 6, p. 341.
8. L. Maier, *Top. Phosphorus Chem.*, **2**, 43 (1965).
9. L. Maier, in *Organic Phosphorus Compounds* (Eds G. M. Kosolapoff and L. Maier), Vol. 4, Wiley, New York, 1972, Chapter 7, p. 1.
10. H. Fritzsche, U. Hasserodt and F. Korte, *Chem. Ber.*, **97**, 1988 (1964).

11. R. L. Wife, A. B. Van Oort, J. A. Van Doorn and P. W. N. M. Van Leeuwen, *Synthesis*, 71 (1983).
12. R. Koester and Y. Morita, *Angew. Chem.*, **77**, 589 (1965).
13. Y. Hanada, J. Inanaga and M. Yamaguchi, *J. Chem. Soc., Chem. Commun.*, 298 (1989).
14. F. Mathey and R. Maillet, *Tetrahedron Lett.*, 2525 (1980).
15. L. Horner, H. Hoffmann and P. Beck, *Chem. Ber.*, **91**, 1953 (1958).
16. V. N. Zemlyanoi, A. M. Aleksandrov and V. P. Kukhar', *J. Gen. Chem. USSR*, **55**, 2371 (1985).
17. L. D. Quin, N. S. Rao, R. J. Topping and A. T. McPhail, *J. Am. Chem. Soc.*, **108**, 4519 (1986).
18. J. K. Stille, J. L. Eichelberger, J. Higgins and M. E. Freeburger, *J. Am. Chem. Soc.*, **94**, 4761 (1972).
19. R. Luchenbach, *Phosphorus*, **3**, 77 (1973).
20. P. D. Henson, K. Naumann and K. Mislow, *J. Am. Chem. Soc.*, **91**, 5645 (1969).
21. T. Imamoto, T. Takeyama and T. Kusumoto, *Chem. Lett.*, 1491 (1985).
22. T. Imamoto, T. Kusumoto, N. Suzuki and K. Sato, *J. Am. Chem. Soc.*, **107**, 5301 (1985).
23. E. Cernia, G. M. Giongo, F. Marcati, W. Marconi and N. Pallaclino, *Inorg. Chim. Acta*, **11**, 195 (1974).
24. G. Déléris, J. Dunoguès and R. Calais, *Bull. Soc. Chim. Fr.*, 672 (1974).
25. B. Kim, M. Kodomari and S. L. Regen, *J. Org. Chem.*, **49**, 3233 (1984).
26. L. Horner and G. Simons, *Phosphorus Sulfur*, **19**, 77 (1984).
27. K. M. Pietrusiewicz and M. Zabłocka, *Phosphorus Sulfur*, **40**, 47 (1988).
28. K. L. Marsi, *J. Org. Chem.*, **39**, 265 (1974).
29. O. Dahl and F. K. Jensen, *Acta Chem. Scand., Ser. B*, **29**, 863 (1975).
30. N. S. Rao and L. D. Quin, *J. Am. Chem. Soc.*, **105**, 5960 (1983).
31. G. Maerkl and R. Potthast, *Tetrahedron Lett.*, 1755 (1968).
32. W. Egan, G. Chauviere, K. Mislow, R. T. Clarke and K. L. Marsi, *J. Chem. Soc., Chem. Commun.*, 733 (1970).
33. L. D. Quin, C. Symmes, E. D. Middlemass and H. F. Lawson, *J. Org. Chem.*, **45**, 4688 (1980).
34. Mazhur-ul Haque, W. Horne, S. E. Cremer, P. W. Kremer and J. T. Mort, *J. Chem. Soc., Perkin Trans 2*, 1467 (1980).
35. M. Moriyama and W. C. Bentrude, *J. Am. Chem. Soc.*, **105**, 4727 (1983).
36. D. Valentine, J. F. Blount and K. Toth, *J. Org. Chem.*, **45**, 3691 (1980).
37. L. Horner and W. D. Balzer, *Tetrahedron Lett.*, 1157 (1965).
38. H. Fritzsche, U. Hasserodt and F. Korte, *Chem. Ber.*, **98**, 171 (1965).
39. C. C. Santini and F. Mathey, *Can. J. Chem.*, **61**, 21 (1983).
40. I. G. Malakhova, E. N. Tsvetkov and M. I. Kabachnik, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **23**, 1761 (1974).
41. B. T. Smith and M. C. Baird, *Inorg. Chim. Acta*, **62**, 135 (1982).
42. W. E. Hill, M. Q. Islam, T. R. Webb and C. A. McAuliffe, *Inorg. Chim. Acta*, **146**, 111 (1988).
43. G. P. Schiemenz, M. Finzenhagen, and P. Nielsen, *Phosphorus Sulfur*, **21**, 253 (1985); G. P. Schiemenz and P. Nielsen, *Phosphorus Sulfur*, **21**, 259 (1985).
44. K. Tani, T. Ise, Y. Tatsuno and T. Saito, *J. Chem. Soc., Chem. Commun.*, 1641 (1984).
45. K. Yamamoto and Saeed-Ur-Rehman, *Chem. Lett.*, 1603 (1984).
46. S. Juge and J. P. Genet, *Tetrahedron Lett.*, **30**, 2783 (1989).
47. B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman and D. J. Weinkauff, *J. Am. Chem. Soc.*, **99**, 5346 (1977).
48. J. M. Brown and A. R. Lucy, *J. Organomet. Chem.*, **314**, 241 (1986).
49. T. Minami, Y. Okada, R. Nomura, S. Hirota, Y. Nagahara and K. Fukuyama, *Chem. Lett.*, 613 (1986).
50. H. Brunner and M. Proebster, *Inorg. Chim. Acta*, **61**, 129 (1982).
51. J. Minami, T. Hanamoto and I. Hirao, *J. Org. Chem.*, **50**, 1278 (1985).
52. Y. Okada, T. Minami, Y. Sasaki, Y. Umezu and M. Yamaguchi, *Tetrahedron Lett.*, **31**, 3905 (1990).
53. L. Horner and G. Simons, *Phosphorus Sulfur*, **19**, 65 (1984).
54. H. Takaya, K. Mashima and K. Koyano, *J. Org. Chem.*, **51**, 629 (1986).
55. C. R. Johnson and T. Imamoto, *J. Org. Chem.*, **52**, 2170 (1987).
56. T. H. Chan and L. T. L. Wong, *Can. J. Chem.*, **49**, 530 (1971).
57. C. H. Chen, K. E. Brighty and F. M. Michaels, *J. Org. Chem.*, **46**, 361 (1981).
58. W. L. Orton, K. A. Mesch and L. D. Quin, *Phosphorus Sulfur*, **5**, 349 (1979).

59. L. D. Quin and N. S. Rao, *J. Org. Chem.*, **48**, 3754 (1983).
60. Md. Amin, D. G. Holah, A. N. Hughes and T. Rukachaisirikul, *J. Heterocycl. Chem.*, **22**, 513 (1985).
61. C. Symmes and L. D. Quin, *J. Org. Chem.*, **41**, 238 (1976).
62. S. G. Borleske and L. D. Quin, *Phosphorus*, **5**, 173 (1975).
63. Y. Segall, I. Granoth, and A. Kalier, *J. Chem Soc., Chem. Commun.*, 501 (1974).
64. C. H. Chen, J. J. Doney, J. L. Fox and H. R. Luss, *J. Org. Chem.*, **50**, 2914 (1985).
65. K. A. Petrov, V. A. Chauzov, L. P. Chernobrovkina and N. Yu. Lebedeva, *J. Gen. Chem. USSR*, **49**, 2325 (1979).
66. S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, **32**, 4066 (1967).
67. K. L. Marsi, *J. Am. Chem. Soc.*, **91** 4724 (1969).
68. P. Coggon, J. F. Engel, A. T. McPhail and L. D. Quin, *J. Am. Chem. Soc.*, **92**, 5779 (1970).
69. H. Yamamoto, T. Hanaya, N. Shigetoh, H. Kawamoto and S. Inokawa, *Chem. Lett.*, 349 (1989).
70. H. J. Meeuwissen, G. Sirks, F. Bickelhaupt, C. H. Stam and A. L. Spek, *J. R. Neth. Chem. Soc.*, **101**, 443 (1982).
71. H. J. Meeuwissen, Th. A. van der Knaap and F. Bickelhaupt, *Tetrahedron*, **39**, 4225 (1983).
72. T. H. Chan and B. S. Ong, *J. Org. Chem.*, **39**, 1748 (1974).
73. C. Bolm and K. B. Sharpless, *Tetrahedron Lett.*, **29**, 5101 (1988).
74. L. D. Quin, A. N. Hughes, H. F. Lawson and A. L. Good, *Tetrahedron*, **39**, 401 (1983).
75. K. Naumann, G. Zon and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7012 (1969).
76. R. A. Lewis, K. Naumann, K. E. DeBruin and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 1010 (1969).
77. D. L. Morris and K. D. Berlin, *Phosphorus*, **4**, 69 (1974).
78. K. E. DeBruin, G. Zon, K. Naumann and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7027 (1969).
79. L. D. Quin, K. C. Caster, J. C. Kisalus and K. A. Mesch, *J. Am. Chem. Soc.*, **106**, 7021 (1984).
80. G. A. Gray, S. E. Cremer and K. L. Marsi, *J. Am. Chem. Soc.*, **98**, 2109 (1976).
81. J. R. Corfield, M. J. P. Harger, J. R. Shutt and S. Trippett, *J. Chem. Soc. C*, 1855 (1970).
82. R. K. Oram and S. Trippett, *J. Chem. Soc., Perkin Trans. 1*, 1300 (1973).
83. S. E. Cremer, F. R. Farr. P. W. Kremer, H. Hwang, G. A. Gray and M. G. Newton, *J. Chem. Soc., Chem. Commun.*, 374 (1975).
84. L. D. Quin and F. C. Bernhardt, *J. Org. Chem.*, **51**, 3235 (1986).
85. G. A. Olah and D. Hehemann, *J. Org. Chem.*, **42**, 2190 (1977).
86. O. Samuel, R. Couffignal, M. Lauer, S. Y. Zhang and H. B. Kagan, *Nouv. J. Chim.*, **5**, 15 (1981).
87. P. Maeding, *Z. Chem.*, **26**, 408 (1986).
88. R. Luchenbach, *Tetrahedron Lett.*, 2177 (1971).
89. F. Mathey, *Tetrahedron Lett.*, 1753 (1979).
90. R. B. King, J. C. Cloyd and P. K. Hendrick, *J. Am. Chem. Soc.*, **95**, 5083 (1973).
91. R. B. King and J. C. Cloyd, *J. Am. Chem. Soc.*, **97**, 46, 53 (1975).
92. F. Mathey, *J. Organomet. Chem.*, **87**, 371 (1975).
93. F. Mathey and G. Sennyey, *J. Organomet. Chem.*, **105**, 73 (1976).
94. F. Mathey and F. Mercier, *Tetrahedron Lett.*, **22**, 319 (1981).
95. F. Mathey and F. Mercier, *Tetrahedron Lett.*, 3081 (1979).
96. F. Mercier, F. Mathey, J. Angelault, J.-C. Couturier and Y. Mary, *J. Organomet. Chem.*, **231**, 237 (1982).
97. F. Mathey, F. Mercier and C. Santini, *Inorg. Chem.*, **19**, 1813 (1980).
98. G. A. Olah, A. Berrier and L. Ohannesian, *Nouv. J. Chim.* **10**, 253 (1986).
99. F. Mathey, *Tetrahedron*, **32**, 2395 (1976).
100. E. Deschamps and F. Mathey, *J. Org. Chem.*, **55**, 2494 (1990).
101. J.-M. Alcaraz and F. Mathey, *Tetrahedron Lett.*, **25**, 4659 (1984).
102. R. A. Zingaro, B. H. Steeves and K. Irgilic, *J. Organomet. Chem.*, **4**, 320 (1965).
103. S. O. Grim and J. D. Mitchell, *J. Chem. Soc., Chem. Commun.*, 634 (1975).
104. S. O. Grim, P. H. Smith, I. J. Colquhoun and W. McFarlane, *Inorg. Chem.*, **19**, 3195 (1980).
105. D. H. Brown, R. J. Cross and R. Keat, *J. Chem. Soc., Dalton Trans.*, 871 (1980).
106. W.-W. duMont and H.-J. Kroth, *J. Organomet. Chem.*, **113**, C35 (1976); W.-W. duMont, *Angew. Chem., Int. Ed. Engl.*, **19**, 554 (1980).
107. G. Zon, K. E. DeBruin, K. Naumann and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7023 (1969).
108. J. Omelańczuk and M. Mikołajczyk, *J. Am. Chem. Soc.*, **101**, 7992 (1979).
109. M. Wada, M. Kanzaki, M. Fujiwara, K. Kajihara and T. Erabi, *Chem. Lett.*, 867 (1990).

110. L. Horner and M. Jordan, *Phosphorus Sulfur*, **8**, 215 (1980).
111. J.-L. Lecat and M. Devaud, *Tetrahedron Lett.*, **28**, 5821 (1987).
112. J. Omelańczuk and M. Mikołajczyk, *Tetrahedron*, **27**, 5587 (1971).
113. F. Mathey, *Tetrahedron Lett.*, 133 (1978).
114. C. C. Santini, J. Fischer, F. Mathey and A. Mitschler, *J. Am. Chem. Soc.*, **102**, 5809 (1980).
115. B. E. Maryanoff, R. Tang and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 273 (1973).
116. I. G. M. Campbell, R. C. Cookson and M. B. Hocking, *Chem. Ind. (London)*, 359 (1962).
117. T. W. Campbell, J. J. Monagle and V. S. Foldi, *J. Am. Chem. Soc.*, **84**, 3673 (1962); J. J. Monagle, T. W. Campbell and H. F. McShane, *J. Am. Chem. Soc.*, **84**, 4288 (1962).
118. G. Aksnes and P. Frøyer, *Acta Chem. Scand.*, **23**, 2697 (1969).
119. H. Hoffman, H. Foerster and G. Tor-Poghossian, *Monatsh. Chem.*, **100**, 311 (1969).
120. J. J. Monagle and J. V. Mengenhauser, *J. Org. Chem.*, **31**, 2321 (1966).
121. C. R. Hall and D. J. H. Smith, *J. Chem. Soc., Perkin Trans. 2*, 1373 (1977).
122. C. R. Hall, D. J. H. Smith and P. Watts, *J. Chem. Soc., Perkin Trans. 2*, 1379 (1977).
123. E. Ciganek, *J. Org. Chem.*, **35**, 1725 (1970).
124. V. V. Kormachev, T. V. Vasil'eva, B. I. Ionin and V. A. Kukhtin, *J. Gen. Chem. USSR*, **45**, 293 (1975).
125. J. Michalski, A. Okruszek and W. Stec, *J. Chem. Soc., Chem. Commun.*, 1495 (1970).
126. W. J. Stec, A. Okruszek and J. Michalski, *J. Org. Chem.*, **41**, 233 (1976).
127. R. Luchenbach, *Synthesis*, 307 (1973).
128. R. Luchenbach and M. Kern, *Chem. Ber.*, **108**, 3533 (1975).
129. M. Mikołajczyk and J. Łuczak, *Synthesis*, 114 (1975).
130. M. Mikołajczyk and J. Łuczak, *J. Org. Chem.*, **43**, 2132 (1978).
131. R. S. Davidson, M. D. Walker and R. K. Bhardwaj, *Tetrahedron Lett.*, **28**, 2981 (1987).
132. K. Sakaki and S. Oae, *Chem. Lett.*, 1003 (1977).
133. M. Mikołajczyk and J. Łuczak, *J. Gen. Chem. USSR*, **58**, 1804 (1988).
134. F. Sánchez-Baeza, G. Durand, D. Barceló and A. Messeguer, *Tetrahedron Lett.*, **31**, 3359 (1990).
135. L. Woźniak, J. Kowalski and J. Chojnowski, *Tetrahedron Lett.*, **26**, 4965 (1985).
136. S. Tamagaki and R. Akatsuka, *Bull. Chem. Soc. Jpn.*, **55**, 3037 (1982).
137. R. K. Bhardwaj and R. S. Davidson, *Tetrahedron*, **43**, 4473 (1987).
138. L. Horner and H. W. Flemming, *Phosphorus Sulfur*, **14**, 245 (1983).
139. A. Skowronska and E. Krawczyk, *Synthesis*, 509 (1983).
140. T. H. Chan and J. R. Frinkebine, *Tetrahedron Lett.*, 2091 (1974); T. H. Chan and J. R. Frinkebine, *J. Am. Chem. Soc.*, **94**, 2880 (1972).
141. J. Heliński, Z. Skrzypczyński, J. Wasiak and J. Michalski, *Tetrahedron Lett.*, **31**, 4081 (1990).
142. K. S. Brusik and W. J. Stec, *J. Org. Chem.*, **55**, 6131 (1990).
143. D. Hellwinkel, in *Organic Phosphorus Compounds* (Eds. G. M. Kosolapoff and L. Maier), Vol. 3, Wiley, New York. 1972, Chapter 5B, p. 185.
144. F. G. Mann and J. Watson, *J. Org. Chem.*, **13**, 502 (1948).
145. V. D. Romanenko, V. I. Torstenko and L. N. Markovski, *Synthesis*, 823 (1980).
146. K. L. Marsi, *J. Org. Chem.*, **40**, 1779 (1975).
147. A. Schmidpeter and H. Brecht, *Z. Naturforsch., Teil B*, **24**, 179 (1969).
148. K. L. Marsi and J. L. Jasperse, *J. Org. Chem.*, **43**, 760 (1978).
149. D. Crich and H. Dyker, *Tetrahedron Lett.*, **30**, 475 (1989).
150. C. Glidewell and E. J. Leslie, *J. Chem. Soc., Dalton Trans.*, 527 (1977).
151. S. Holand and F. Mathey, *J. Org. Chem.*, **46**, 4386 (1981).
152. R. L. Blankespoor, M. P. Doyle, D. J. Smith, D. A. Van Dyke and M. J. Waldyke, *J. Org. Chem.*, **48**, 1176 (1983).
153. N. Kuhn and H. Schumann, *Phosphorus Sulfur*, **26**, 199 (1986).
154. H. Binder and E. Fluck, *Z. Anorg. Allg. Chem.*, **365**, 170 (1969).
155. M. Masaki and K. Fukui, *Chem. Lett.*, 151 (1977).
156. G. Wunsch, K. Wintersberger and H. Geierhaas, *Z. Anorg. Allg. Chem.*, **369**, 33 (1969).
157. G. Maerkl, D. E. Fischer and H. Olbrich, *Tetrahedron Lett.*, 645 (1970).
158. A. J. Downs and R. Schmutzler, *Spectrochim. Acta, Part A*, **23**, 681 (1967).
159. M. Fild and R. Schmutzler, *J. Chem. Soc. A*, 840 (1969).
160. A. Łopusiński and J. Michalski, *J. Am. Chem. Soc.*, **104**, 290 (1982).
161. V. G. Kostina and N. G. Feshchenko, *J. Gen. Chem. USSR*, **49**, 2165 (1979).
162. R. G. Cavell and R. D. Leary, *J. Chem. Soc., Chem. Commun.*, 1520 (1970).

163. D. Hellwinkel and W. Krapp, *Chem. Ber.*, **111**, 13, (1978).
164. Y. Segall and I. Granoth, *J. Am. Chem. Soc.*, **100**, 5130 (1978).
165. K. A. Petrov, V. A. Chauzov, N. Yu. Mal'kevich and S. M. Kostrova, *J. Gen. Chem. USSR*, **48**, 74 (1978).
166. D. Hellwinkel, *Chem. Ber.* **102**, 548 (1969).
167. K. Akiba, K. Okada and K. Ohkata, *Tetrahedron Lett.*, **27**, 5221 (1986).
168. J. L. Eichelberger and J. K. Stille, *J. Org. Chem.*, **36**, 1840 (1971).
169. L. D. Quin and E. Middlemass, *J. Am. Chem. Soc.*, **99**, 8370 (1977).
170. G. P. Schiemenz, *Chem. Ber.*, **99**, 504 (1966).
171. B. A. Arbuzov, A. P. Rakov, A. O. Vizel', L. A. Shapshinskaya and N. P. Kulikova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1237 (1968).
172. R. Bodalski, T. Janecki, Z. Gałdecki and M. Głowka, *Phosphorus Sulfur*, **14**, 15 (1983).
173. H. Imoto and M. Yamashita, *Synthesis*, 323 (1988).
174. A. Bell, A. H. Davidson, C. Earnshaw, H. K. Norrish, R. S. Torr, D. B. Trowbridge and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 2879 (1983).
175. A. B. McElroy and S. Warren, *Tetrahedron Lett.*, **26**, 2119 (1985).
176. A. B. McElroy and S. Warren, *Tetrahedron Lett.*, **26**, 5709 (1985).
177. O. Awerbouch and Y. Kashman, *Tetrahedron*, **31**, 33 (1975).
178. Y. Kashman and O. Awerbouch, *Tetrahedron*, **31**, 45 (1975).
179. L. D. Quin, J. C. Kisalus and K. A. Mesch, *J. Org. Chem.*, **48**, 4466 (1983); J. Szewczyk, E. Y. Yao, and L. D. Quin, *Phosphorus, Sulphur, Silicon, Relat. Elem.*, **54**, 135 (1990).
180. D. Levin and S. Warren, *Tetrahedron Lett.*, **27**, 2265 (1986).
181. P. E. Cann, D. Howells and S. Warren, *J. Chem. Soc., Perkin Trans. 2*, 304 (1972).
182. C. Symmes and L. D. Quin, *J. Org. Chem.*, **44**, 1048 (1979).
183. L. P. Zhuravleva, M. G. Sulermanova, A. P. Marchenko, M. I. Z'ola, N. N. Kovalyukh and A. V. Kirsanov, *J. Gen. Chem. USSR*, **41**, 1960 (1971).
184. L. D. Quin, E. Middlemass and N. S. Rao, *J. Org. Chem.*, **47**, 905 (1982).
185. A. J. Macpherson and D. J. H. Smith, *J. Chem. Res.* (*S*), 32 (1984); (*M*) 0315.
186. A. M. Aguiar, J. R. Smiley-Irelan and N. S. Bhacca, *J. Org. Chem.*, **34**, 3349 (1969).
187. S. Kh. Nurtdinov, R. A. Fakhrutdinova, T. V. Zykova, F. Sh. Shagvaleev, R. Z. Musin, Yu. Ya. Efremov and V. S. Tsivunin, *J. Gen. Chem. USSR*, **57**, 2036 (1987).
188. S. Warren, *Acc. Chem. Res.*, **11**, 401 (1978).
189. D. Howells and S. Warren, *J. Chem. Soc., Perkin Trans. 2*, 992 (1974).
190. F. Allen, O. Kennard, L. Nassimbeni, R. Shepherd and S. Warren, *J. Chem. Soc., Perkin Trans. 2*, 1530 (1974).
191. A. H. Davidson, I. Fleming, J. I. Grayson, A. Pearce, R. L. Snowden and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 550 (1977).
192. A. H. Davidson, C. Earnshaw, J. I. Grayson and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1452 (1977).
193. D. Howells and S. Warren, *J. Chem. Soc., Perkin Trans. 2*, 1645 (1973).
194. C. Earnshaw, J. I. Grayson and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1506 (1979).
195. D. Howells and S. Warren, *J. Chem. Soc., Perkin Trans. 2*, 1472 (1973).
196. R. S. Torr and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1169 (1983).
197. K. Ikai, A. Iida and M. Yamashita, *Synthesis*, 595 (1989).
198. G. Maerkle and A. Merz, *Tetrahedron Lett.*, 1269 (1971).
199. T. Chan and K. T. Nwe, *Tetrahedron*, **31**, 2537 (1975).
200. M. Heuschmann and H. Quast, *Chem. Ber.*, **115**, 3384 (1982).
201. T. Oshikawa and M. Yamashita, *Bull. Chem. Soc. Jpn.*, **59**, 3293 (1986).
202. H. Quast and M. Heuschmann, *Liebigs Ann. Chem.*, 977 (1981).
203. L. D. Quin and R. C. Stocks, *J. Org. Chem.*, **39**, 686 (1974).
204. L. Maier, *Phosphorus*, **1**, 245, 249 (1972).
205. E. Malinski, A. Piekos and T. A. Modro, *Can. J. Chem.*, **53**, 1468 (1975).
206. A. Stachlewska-Wróblowa and K. Okón, *Bull. Acad. Pol. Sci., Ser. Chim.*, **9**, 289 (1961).
207. V. V. Kormachev, Yu. N. Mitrasov and V. A. Kukhtin, *J. Gen. Chem. USSR*, **48**, 1079 (1978).
208. K. B. Dillon, M. P. Nisbet and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 465 (1982).
209. L. D. Quin and A. N. Hughes, in *The Chemistry of Organophosphorus Compounds* (Ed. F. R. Hartley), Vol. 1, Wiley, Chichester, 1990, Chapter 10, p. 295.
210. M. El-Deck, G. D. Macdonell, S. D. Venkataramu and K. D. Berlin, *J. Org. Chem.*, **41**, 1403 (1976).

211. J. I. Grayson, H. K. Norrish and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 2556 (1976).
212. C. H. Chen and K. E. Brighty, *Tetrahedron Lett.*, **21**, 4421 (1980).
213. E. I. Matrosov, K. Zh. Kulumbetova, L. I. Arkhipova, T. Ya. Medved' and M. I. Kabachnik, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 193 (1972).
214. E. N. Tsvetkov, R. A. Malevannaya, L. I. Petrovskaya and M. I. Kabachnik, *J. Gen. Chem. USSR*, **44**, 1203 (1974).
215. E. N. Tsvetkov, R. A. Malevannaya and M. I. Kabachnik, *J. Gen. Chem. USSR*, **45**, 706 (1975).
216. E. N. Tsvetkov, I. G. Malakhova and M. I. Kabachnik, *J. Gen. Chem. USSR*, **48**, 1125 (1978).
217. J. E. MacDiarmid and L. D. Quin, *J. Org. Chem.*, **46**, 1451 (1981).
218. K. A. Petrov, V. A. Chauzov, T. S. Erokhina and I. V. Pastukhova, *J. Gen. Chem. USSR*, **46**, 2387 (1976).
219. L. Maier and G. Rist, *Phosphorus Sulfur*, **32**, 65 (1987).
220. D. Seyferth and P. Hilbert, *Org. Prep. Proced. Int.*, **3**, 51 (1971).
221. Yu. I. Baranov, S. V. Gorelenko and S. P. Kochkol'da, *J. Gen. Chem. USSR.*, **39**, 803 (1969).
222. B. Klabuhn, H. Goetz, P. Steirl and D. Alscher, *Tetrahedron*, **32**, 603 (1976).
223. S. Varbanov, V. Vasileva, V. Zlateva, T. Radeva and G. Borisov, *Phosphorus Sulfur*, **21**, 17 (1984).
224. G. Borisov, V. Vasileva, E. N. Tsvetkov, T. E. Kron and M. I. Kabachnik, *Phosphorus Sulfur.*, **21**, 59 (1984).
225. V. D. Romanenko, V. I. Tovstenko, L. A. Robenko and L. N. Markovskii, *J. Gen. Chem. USSR*, **49**, 208 (1979).
226. G. A. Kutyrev, R. A. Cherkasov and A. N. Pudovik, *J. Gen. Chem. USSR*, **44**, 979 (1974).
227. W. Wegener and P. Scholz, *Z. Chem.*, **12**, 103 (1972).
228. A. W. Frank, *Phosphorus Sulfur*, **22**, 265 (1985).
229. I. V. Martynov, A. Yu. Aksinenko, A. N. Chekhlov and V. B. Sokolov, *J. Gen. Chem. USSR*, **59**, 713 (1989).
230. J. B. Rampal, K. D. Berlin and N. Satyamurthy, *Phosphorus Sulfur*, **13**, 179 (1982).
231. A. Stachlewska-Wróblowa and K. Okón, *Bull. Acad. Pol. Sci., Ser. Chim.*, **9**, 297 (1961).
232. V. V. Kormachev, T. V. Vasil'eva, K. V. Solodova, O. T. Alekseeva, and V. A. Kukhtin, *J. Gen. Chem. USSR*, **49**, 525 (1979).
233. J. Burden, I. N. Rozhkov and G. M. Perry, *J. Chem. Soc. C*, 2615 (1969).
234. D. G. Naae and T.-W. Lin, *J. Fluorine Chem.*, **13**, 473 (1979).
235. V. A. Shokol, V. V. Doroshenko and G. I. Derkach, *J. Gen. Chem. USSR*, **45**, 1680 (1975).
236. K. Moedritzer, *Z. Anorg. Allg. Chem.*, **458**, 183 (1979).
237. C. M. Angelov, *Phosphorus Sulfur*, **15**, 177 (1983).
238. S. R. Postle and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 2084 (1977).
239. W. Hagens, H. J. T. Bos, W. Veskuil and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **88**, 71 (1969).
240. W. Hagens, H. J. T. Bos and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **92**, 762 (1973).
241. K. M. Pietrusiewicz, M. Zabłocka and L. Monkiewicz, *J. Org. Chem.*, **49**, 1522 (1984).
242. J. Berlan, J.-P. Battioni and K. Koosha, *Tetrahedron Lett.*, 3351 (1976).
243. K. M. Pietrusiewicz and M. Zablocka, *Tetrahedron Lett.*, **29**, 937 (1988).
244. A. M. Aguiar and J. R. Smiley Irelan, *J. Org. Chem.*, **34**, 4030 (1969).
245. M. I. Kabachnik, E. N. Tsvetkov and C.-Y Chang, *J. Gen. Chem. USSR*, **32**, 3279 (1962).
246. G. Maerkl and B. Merkl, *Tetrahedron Lett.*, **22**, 4459 (1981).
247. D. J. Collins, S. Mollard, N. Rose and J. M. Swan, *Aust. J. Chem.*, **27**, 2365 (1974).
248. D. Cavalla, W. B. Cruse and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1883 (1987).
249. K. M. Pietrusiewicz and M. Zabłocka, *Tetrahedron Lett.*, **29**, 1991 (1988).
250. N. A. Portnoy, C. J. Morrow, M. S. Chattha, J. C. Williams and A. M. Aguiar, *Tetrahedron Lett.*, 1397 (1971).
251. G. Maerkl and B. Merkl, *Tetrahedron Lett.*, **24**, 5865 (1983).
252. J. C. Williams, J. A. Kuczkowski, N. A. Portnoy, K. S. Yong, J. D. Wander and A. M. Aguiar, *Tetrahedron Lett.*, 4749 (1971); M. Maumy, *Bull. Soc. Chim. Fr.*, 1600 (1972); J. Skolimowski and M. Simalty, *Synthesis*, 109 (1979).
253. A. Naaktgeboren, J. Meijer, P. Vermeer and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **94**, 92 (1975).
254. T. Ya. Medved', S. A. Pisareva, Yu. M. Polikarpov and M. I. Kabachnik, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2706 (1971).
255. M. A. Weiner and G. Pasternack, *J. Org. Chem.* **34**, 1130 (1969).
256. G. Maerkl and B. Merkl, *Tetrahedron Lett.*, **22**, 4463 (1981)

257. L. Horner and H. Lindel, *Phosphorus Sulfur* , **20**, 161 (1984).
258. S. D. Darling and S. J. Brandes, *J. Org. Chem.*, **47**, 1413 (1982).
259. E. P. Kyba, S. P. Rines, P. W. Owens and S.-S. P. Chou, *Tetrahedron Lett.*, **22**, 1875 (1981).
260. Y. Kashman and O. Awerbouch, *Tetrahedron Lett.*, 3217 (1973).
261. T. Minami, H. Sako, T. Ikehira, T. Hanamoto and I. Hirao, *J. Org. Chem.*, **48**, 2569 (1983).
262. T. H. Chan and K. T. Nwe, *Tetrahedron Lett.*, 4815 (1973).
263. L. D. Quin and F. C. Bernhardt, *Magn. Reson. Chem.*, **23**, 929 (1985).
264. M. B. Hocking and G. W. Bushnell, *Can. J. Chem.*, **68**, 1020 (1990).
265. Y. Kashman, and O. Awerbouch, *Tetrahedron*, **31**, 53 (1975); Y. Kashman, I. Wagenstein and A. Rudi, *Tetrahedron*, **32**, 2427 (1976).
266. W. Roesch and M. Regitz, *Z. Naturforsch., Teil B*, **41**, 931 (1986).
267. L. D. Quin, A. N. Hughes, J. C. Kisalus and B. Pete, *J. Org. Chem.*, **53**, 1722 (1988).
268. E. Deschamps and F. Mathey, *J. Chem. Soc., Chem. Commun.*, 1214 (1984).
269. H. Tomioka, S. Miura and Y. Izowa, *Tetrahedron Lett.*, **24**, 3353 (1983).
270. Y. Kashman and O. Awerbouch, *Tetrahedron*, **29**, 191 (1973).
271. M. Maffei and G. Buono, *New J. Chem.*, **12**, 923 (1988).
272. M. L. Curtin and W. H. Okamura, *J. Org. Chem.*, **55**, 5278 (1990).
273. T. Kauffman, H. Ahlers, K.-J. Echsler, H. Schulz, and H.-J. Tihard, *Chem. Ber.*, **118**, 4496 (1985).
274. I. G. Kolokol'tseva, V. N. Chistokletev, B. I. Ionin and A. A. Petrov, *J. Gen. Chem. USSR*, **38**, 1203 (1968).
275. A. Sedqui, J. Vebrel and B. Laude, *Chem. Lett.*, 965 (1984).
276. A. Brandi, P. Cannavo, K. M. Pietrusiewicz, M. Zabłocka, and M. Wieczorek, *J. Org. Chem.*, **54**, 3073 (1989).
277. K. M. Pietrusiewicz and A. Brandi, *Phosphorus Sulfur Silicon Relat. Elem.*, **42**, 135 (1989).
278. K. M. Pietrusiewicz, M. W. Wieczorek, G. Bujacz and A. Brandi, *Phosphorus Sulfur Silicon Relat. Elem.*, **48**, 11 (1990).
279. G. Maerkl and H. Baier, *Tetrahedron Lett.*, 4439 (1972).
280. A. Brandi, S. Cicchi, A. Goti, K. M., Pietrusiewicz and W. Wisniewski, *Tetrahedron*, **46**, 7093 (1990).
281. A. N. Pudovik, N. G. Khusainova, E. A. Berdnikov and Z. A. Nasybullina, *J. Gen. Cem. USSR*, **44**, 213 (1974).
282. N. G. Khusainova, Z. A. Berdikhina, E. A. Berdnikov, A. I Konovalov and A. N. Pudovik, *J. Gen. Chem. USSR*, **47**, 1339 (1977).
283. G. Himbert and M. Regitz, *Chem. Ber.*, **107**, 2513 (1974).
284. J. Gloede, K.-H. Schano and H. Gross, *Z. Chem.*, **18**, 18 (1978).
285. A. N. Pudovik, R. D. Gareev, A. V. Aganov, O. E. Raevskaya and L. A. Stabrovskaya, *J. Gen. Chem. USSR*, **41**, 1013 (1971).
286. H. Heydt and M. Regitz, *Liebigs Ann. Chem.*, 1766 (1977).
287. H. Heydt, K.-H. Busch, and M. Regitz, *Liebigs Ann. Chem.*, 590 (1980).
288. M. Regitz and W. Anschuetz, *Chem. Ber.*, **102**, 2216 (1969).
289. A. Hartmann and M. Regitz, *Phosphorus*, **5**, 21 (1974).
290. W. Disteldorf and M. Regitz, *Chem. Ber.*, **109**, 546 (1976).
291. W. Jugelt and D. Schmidt, *Tetrahedron*, **25**, 5569, 5585 (1969).
292. G. Keglevich, I. Petneházy, P. Miklós, A. Almásy, G. Tóth, L. Töke and L. D. Quin, *J. Org. Chem.*, **52**, 3983 (1987).
293. G. Keglevich, G. Tóth, I. Petneházy, P. Miklós and L. Töke, *J. Org. Chem.*, **52**, 5721 (1987).
294. S. P. Mesyats, E. N. Tsvetkov, É. S. Petrov, M. I. Terekhova, A. I. Shatenshtein and M. I. Kabachnik, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2399 (1974); S. P. Mesyats, E. N. Tsvetkov, E'. S. Petrov, N. N. Shelganova, T. M. Shcherbina, A. I. Shatenshtein and M. I. Kabachnik, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2406 (1974).
295. G. P. Schiemenz and M. Finzenhagen, *Liebigs Ann. Chem.*, 1476 (1981).
296. A. I. Razumov, P. A. Gurevich, S. A. Muslimov and V. G. Usacheva, *J. Gen. Chem. USSR*, **46**, 2279 (1976).
297. R. S. Torr and S. Warren, *J. Chem. Soc., Perkin Trans 1*, 1173 (1983).
298. K. M. Pietrusiewicz and M. Zabłocka, *Tetrahedron Lett.*, **29**, 1987 (1988).
299. C. Santelli-Rouvier, *Synthesis*, 64 (1988).
300. H. H. Karsch, *Chem. Ber.*, **115**, 818 (1982).
301. F. Mathey, *Tetrahedron*, **30**, 3127 (1974).

302. K. M. Pietrusiewicz and M. Zabłocka, *Tetrahedron Lett.*, **30**, 477 (1989).
303. C. A. Maryanoff, B. E. Maryanoff, R. Tang and K. Mislow, *J. Am. Chem. Soc.*, **95**, 5839 (1973).
304. Yu. M. Polikarpov, K. Zh. Kulumbetova, T. Ya. Medved' and M. I. Kabachnik, *Bull. Acad. Sci. USSR., Div. Chem. Sci.*, 1253 (1970).
305. J. J. Richard and C. V. Banks, *J. Org. Chem.*, **28**, 123 (1963).
306. C. A. Cornish and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 2585 (1985).
307. A. D. Buss, N. Greeves, R. Mason and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 2569 (1987).
308. P. Wallace and S. Warren, *Tetrahedron Lett.*, **26**, 5713 (1985).
309. S. O. Grim, L. C. Satek and J. D. Mitchell, *Z. Naturforsch., Teil B*, **35**, 832 (1980).
310. I. Yamamoto, S. Tanaka, T. Fujimoto and K. Ohta, *J. Org. Chem.*, **54**, 747 (1989).
311. J. I. Grayson, S. Warren and A. T. Zaslona, *J. Chem. Soc., Perkin Trans. 1*, 967 (1987).
312. R. K. Haynes and S. C. Vonwiller, *J. Chem. Soc., Chem. Commun.*, 92 (1987); R. K. Haynes, S. C. Vonwiller, and T. W. Hambley, *Aust. J. Chem.*, **42**, 1671 (1989).
313. R. K. Haynes and A. G. Katsifis, *Aust. J. Chem.*, **42**, 1473 (1989).
314. L. Horner, *Fortschr. Chem. Forsch.*, **7**, 1 (1966).
315. U. Lachmann, H.-G. Henning and D. Gloyna, *J. Prakt. Chem.*, **318**, 489 (1976).
316. B. E. Maryanoff and A. B. Reitz, *Chem. Rev.*, **89**, 863 (1989).
317. C. Earnshaw, C. J. Wallis and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 3099 (1979).
318. D. K. Derchand, A. W. Murray and E. Smeaton, *Tetrahedron Lett.*, **27**, 4635 (1986).
319. A. D. Buss, W. B. Cruse, O. Kennard and S. Warren, *J. Chem. Soc., Perkin Trans 1*, 243 (1984).
320. A. D. Buss and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 2307 (1985).
321. A. D. Buss, N. Greeves, D. Levin, P. Wallace and S. Warren, *Tetrahedron Lett.*, **25**, 357 (1984).
322. D. Cavalla and S. Warren, *Tetrahedron Lett.*, **23**, 4505 (1982).
323. A. D. Buss, S. Warren, J. S. Leake and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 2215 (1983).
324. D. Levin and S. Warren, *Tetrahedron Lett.*, **26**, 505 (1985).
325. J. H. Davies and P. Kirby, *J. Chem. Soc.*, 3425 (1964).
326. L. Horner, I. Ertel, H.-D. Ruprecht and O. Bělovsky, *Chem. Ber.*, **103**, 1582 (1970).
327. A. H. Davidson and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 639 (1976).
328. B. Lythogo, T. A. Moran, M. E. N. Nambudiry and S. Ruston, *J. Chem. Soc., Perkin Trans. 1*, 2386 (1976).
329. M. Maleki, J. A. Miller and O. W. Lever, *Tetrahedron Lett.*, **22**, 3789 (1981).
330. L. D. Bergel'son, V. A. Vaver, L. I. Borsukov and M. M. Shemyakin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 474 (1966).
331. M. I. Kabachnik and T. A. Mastryukova, *J. Gen. Chem. USSR.*, **54**, 1931 (1984).
332. E. F. Birse, A. McKenzie and A. W. Murray, *J. Chem. Soc., Perkin Trans. 1*, 1039 (1988).
333. Y. Ikeda, J. Ukai, N. Ikeda and H. Yamamoto, *Tetrahedron*, **43**, 723 (1987).
334. T. Kauffman and P. Schwartze, *Chem. Ber.*, **119**, 2150 (1986).
335. B. Deschamps, J. P. Lampin, F. Mathey and J. Seyden-Penne, *Tetrahedron Lett.*, 1137 (1977).
336. T. G. Roberts and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 1953 (1985).
337. E. Juaristi, B. Gordillo and L. Valle, *Tetrahedron*, **42**, 1963 (1986).
338. A. J. Bridges and G. H. Whitham, *J. Chem. Soc., Chem. Commun.*, 142 (1974).
339. P. F. Newton and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 3067 (1979).
340. D. Boeckh, R. Huisgen and H. Noeth, *J. Am. Chem. Soc.*, **109**, 1248 (1987).
341. N. A. Bondarenko and E. N. Tsvetkov, *J. Gen. Chem. USSR*, **59**, 1361 (1989).
342. M. Cherest, H. Felkin and N. Prudent, *Tetrahedron Lett.*, 2199 (1968).
343. J. Elliott and S. Warren, *Tetrahedron Lett.*, **27**, 645 (1986).
344. J. Elliott, D. Hall and S. Warren, *Tetrahedron Lett.*, **30**, 601 (1989).
345. J. M. Clough and G. Pattenden, *Tetrahedron Lett.*, 5043 (1979); J. M. Clough and G. Pattenden, *Tetrahedron*, **37**, 3911 (1981).
346. K. C. Nicolau, R. Zipkin and D. Tanner, *J. Chem. Soc., Chem. Commun.*, 349 (1984).
347. E. G. Baggiolini, J. A. Iacobelli, B. M. Hennessy and M. R. Uskoković, *J. Am. Chem. Soc.*, **104**, 2945 (1982).
348. H. T. Toh and W. Okamura, *J. Org. Chem.*, **48**, 1414 (1983).
349. J. L. Mascaveňas, A. Mourino and L. Castedo, *J. Org. Chem.*, **51**, 1269 (1986).
350. B. Hagenbruch and S. Huenig, *Liebigs Ann. Chem.*, 340 (1984).
351. M. P. Savage and S. Trippett, *J. Chem. Soc. C*, 1842 (1966).
352. D. Levin and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1799 (1988).

353. P. Wallace and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 2971 (1988).
354. P. S. Brown, A. B. McElroy and S. Warren, *Tetrahedron Lett.*, **26**, 249 (1985).
355. A. B. McElroy and S. Warren, *Tetrahedron Lett.*, **26**, 1677 (1985).
356. D. Cavalla and S. Warren, *Tetrahedron Lett.*, **24**, 295 (1983).
357. C. A. Cornish and S. Warren, *Tetrahedron Lett.*, **24**, 2603 (1983).
358. J. A. M. van den Goorbergh and A. van der Gen, *Tetrahedron Lett.*, **21**, 3621 (1980).
359. M. P. Bosch, F. Camps, J. Coll, A. Guerrero, T. Tatsuoka and J. Meinwald, *J. Org. Chem.*, **51**, 773 (1986).
360. S. V. Ley and B. Lygo, *Tetrahedron Lett.*, **25**, 113 (1984).
361. M. D. Ironside and A. W. Murray, *Tetrahedron Lett.*, **30**, 1691 (1989).
362. J. I. Grayson and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 2263 (1977).
363. A. Loupy, K. Sogadii and J. Seyden-Penne, *Synthesis*, 126 (1977).
364. J. Rachoń and U. Schoellkopf, *Liebigs Ann. Chem.*, 99 (1981).
365. N. A. Portnoy, K. S. Yong and A. M. Aguiar, *Tetrahedron Lett.*, 2559 (1971).
366. B. H. Bakker, D. S. Tjin A-Lim, and A. van der Gen, *Tetrahedron Lett.*, **25**, 4259 (1984).
367. N. L. J. M. Broekof, F. L. Jonkers and A. van der Gen, *Tetrahedron Lett.*, **21**, 2671 (1980).
368. E. W. Collington, J. G. Knight, C. J. Wallis and S. Warren, *Tetrahedron Lett.*, **30**, 877 (1989).
369. S. Warren and A. T. Zaslona, *Tetrahedron Lett.*, **23**, 4167 (1982).
370. N. L. J. M. Broekhof and A. van der Gen, *Tetrahedron Lett.*, **22**, 2799 (1981).
371. C. Earnshaw, R. S. Torr and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 2893 (1983).
372. T. A. M. van Schaik, A. V. Henzen and A. van der Gen, *Tetrahedron Lett.*, **24**, 1303 (1983).
373. A. G. M. Barrett and T. A. Miller, *Tetrahedron Lett.*, **29**, 1873 (1988).
374. J. Kallmerten and M. D. Wittman, *Tetrahedron Lett.*, **27**, 2443 (1986).
375. M. L. Edwards, D. M. Stemerick, E. T. Jarvi, D. P. Matthews and J. R. McCarthy, *Tetrahedron Lett.*, **31**, 5571 (1990).
376. P. F. Newton and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 3072 (1979).
377. A. C. Connell and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 995 (1983).
378. G. F. Meijs and P. C. H. Eichinger, *Tetrahedron Lett.*, **28**, 5559 (1987).
379. D. J. Petersen, *J. Org. Chem.*, **33**, 780 (1968).
380. R. Nagata, M. Kawakami, T. Matsuura and I. Saito, *Tetrahedron Lett*, **30**, 2817 (1989).
381. S. Zbaida and E. Breuer, *Tetrahedron*, **34**, 1241 (1978).
382. H. Quast and M. Heuschmann, *Chem. Ber.*, **115**, 901 (1982).
383. L. D. Quin, E.-Y. Yao and J. Szewczyk, *Tetrahedron Lett.*, **28**, 1077 (1987).
384. R. Hussong, H. Heydt and M. Regitz, *Phosphorus Sulfur*, **25**, 201 (1985).
385. A. N. Hughes, S. Phisithkul and T. Rukachaisirikul, *J. Heterocycl. Chem.*, **16**, 1417 (1979).
386. A. G. Evans, J. C. Evans and D. Sheppard, *J. Chem. Soc., Perkin Trans. 2*, 1166 (1976).
387. L. P. Zhuravleva, M. I. Z'ola, M. G. Suleimanova and A. V. Kirsanov, *J. Gen. Chem. USSR*, **38**, 341 (1968).
388. R. Luchenbach, *Tetrahedron Lett.*, 2015 (1976).
389. P. Haake and G. W. Allen, *Tetrahedron Lett.*, 3113 (1970).
390. D. W. Allen, B. G. Hutley and M. T. J. Mellor, *J. Chem. Soc., Perkin Trans. 2*, 1705 (1977).
391. K. R. Martin and C. E. Griffin, *J. Heterocycl. Chem.*, **3**, 92 (1966).
392. C. E. Griffin, R. P. Peller and J. A. Peters, *J. Org. Chem.*, **30**, 91 (1965).
393. R. C. Paul, *J. Chem. Soc.*, 574 (1955); A. B. Burg and A. J. Sarkis, *J. Am. Chem. Soc.*, **87**, 238 (1965).
394. H. Hartmann, C. Beerman and H. Z. Czempik, *Z. Anorg. Allg. Chem.*, **287**, 261 (1956); H. Hartman and A. Meixner, *Naturwissenschaften*, **50**, 403 (1963).
395. J. L. Suggs and L. D. Freedman, *J. Org. Chem.*, **36**, 2566 (1971).
396. I. Granoth, Y. Segall and H. Leader, *J. Chem. Soc., Chem. Commun.*, 74 (1976).
397. B. R. Ezzell and L. D. Freedman, *J. Org. Chem.*, **35**, 241 (1970).
398. B. R. Ezzell and L. D. Freedman, *J. Org. Chem.*, **34**, 1777 (1969).
399. B. R. Ezzell, *J. Org. Chem.*, **35**, 2426 (1970).
400. S. E. Cremer and R. J. Chorvat, *Tetrahedron Lett.*, 413 (1968).
401. D. G. Gorenstein, *J. Am. Chem. Soc.*, **94**, 2808 (1972).
402. S. T. D. Gough and S. Trippett, *J. Chem. Soc.*, 2333 (1962).
403. G. Aksnes and R. O. Larsen, *Liebigs Ann. Chem.*, 1967 (1981).
404. E. Lindner and G. Frey, *Z. Naturforsch., Teil B*, **35**, 1150 (1980).
405. A. B. Pepperman and T. H. Siddall, *J. Org. Chem.*, **41**, 2931 (1976).

406. A. B. Pepperman and T. H. Siddall, *J. Org. Chem.*, **40**, 1373, 2053 (1975).
407. F. Mathey, D. Thavard and B. Bartet, *Can. J. Chem.*, **53**, 855 (1975).
408. F. Mathey and D. Thavard, *Can. J. Chem.*, **56**, 1952 (1978).
409. A. N. Hughes, K. Amornraksa, S. Phisithkul and V. Reutrakul, *J. Heterocycl. Chem.*, **13**, 937 (1976).
410. G. R. Newkome and D. C. Hager, *J. Am. Chem. Soc.*, **100**, 5567 (1978).
411. Y. Uchida, K. Onoue, N. Tada, F. Nagao and S. Oae, *Tetrahedron Lett.*, **30**, 567 (1989).
412. Y. Uchida and H. Kozawa, *Tetrahedron Lett.*, **30**, 6365 (1989).
413. G. Wittig and H.-J. Cristau, *Bull. Soc. Chim. Fr.*, 1293 (1969).
414. B. Schaub, T. Jenny and M. Schlosser, *Tetrahedron Lett.*, **25**, 4097 (1984).
415. D. Seyferth, D. E. Welch and J. K. Heeren, *J. Am. Chem. Soc.*, **85**, 642 (1963).
416. W. Smadja, M. Simalty-Siemiatycki and C. Prévost, *Bull. Soc. Chim. Fr.*, 971 (1966).
417. W. Hawes and S. Trippett, *J. Chem. Soc. C*, 1465 (1969).
418. J. R. Corfield, and S. Trippett, *J. Chem. Soc. C*, 334 (1971)
419. J. P. Albarella and T. J. Katz, *J. Org. Chem.*, **43**, 4338 (1978).
420. D. Seyferth and D. E. Welch, *J. Organomet. Chem.*, **2**, 1 (1964).
421. H. R. Hays, *J. Org. Chem.*, **33**, 3690 (1968).
422. T. L. Emmick and R. L. Letsinger, *J. Am. Chem. Soc.*, **90**, 3459 (1968).
423. W. B. Farnham, R. A. Lewis, R. K. Murray and K. Mislow, *J. Am. Chem. Soc.*, **92**, 5808 (1970).
424. S. A. Buckler and M. Epstein, *J. Am. Chem. Soc.*, **82**, 2076 (1960).
425. R. E. Montgomery and L. D. Quin, *J. Org. Chem.*, **30**, 2393 (1965).
426. I. G. M. Campbell and I. D. R. Stevens, *J. Chem. Commun.*, 505 (1966).
427. R. Curci and F. D. Furia, *Tetrahedron*, **28**, 3905 (1972).
428. L. D. Freedman and H. S. Freeman, *Chem. Rev.*, **87**, 289 (1987).
429. G. Peters, *J. Org. Chem.*, **27**, 2198 (1962).
430. M. Grayson, C. E. Farley and C. A. Streuli, *Tetrahedron*, **23**, 1065 (1967).
431. G. Aksnes and P. Majewski, *Phosphorus Sulfur*, **26**, 261 (1986).
432. A. Łopusinski, L. Łuczak and J. Michalski, *Tetrahedron*, **38**, 679 (1982).
433. H. Hoffmann and P. Schellenbeck, *Chem. Ber.*, **99**, 1134 (1966).
434. V. A. Chauzov, Yu. N. Studnev, L. P. Kostina and A. V. Fokin, *J. Gen. Chem. USSR*, **59**, 2211 (1989).
435. L. Maier, *Helv. Chim. Acta*, **49**, 1249 (1966).
436. A. N. Pudovik and I. V. Konovalova, *Synthesis*, 81 (1979).
437. R. C. Miller, J. S. Bradley and L. A. Hamilton, *J. Am. Chem. Soc.*, **78**, 5299 (1956).
438. Z. Gałdecki, M. L. Głowka and K. M. Pietrusiewicz, *J. Chem. Soc., Perkin Trans. 2*, 1720 (1979).
439. A. A. Zhadanov, N. A. Kurasheva, L. I. Kuteinikova and Le Ngog Khan, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 172 (1985).
440. R. Bodalski and K. M. Pietrusiewicz, *Tetrahedron Lett.*, 4209 (1972).
441. H. Niebergall, *Macromol. Chem.*, **52**, 218 (1962).
442. K. M. Pietrusiewicz, M. Zabłocka, and W. Wieczorek, *Phosphorus Sulfur Silicon Relat. Elem.*, **42**, 183 (1989).
443. K. M. Pietrusiewicz, W. Wiśniewski and M. Zabłocka, *Tetrahedron*, **45**, 337 (1989).
444. X. Lu, X. Tao, J. Zhu, X. Sun and J. Xu, *Synthesis*, 848 (1989).
445. S. H. Bertz and G. Dabbagh, *J. Am. Chem. Soc.*, **103**, 5932 (1981).
446. A. N. Pudovik, T. M. Sudakova and G. I. Evstaf'ev, *J. Gen. Chem. USSR*, **44**, 2371 (1974).
447. T. M. Sudakova, É. Kh. Ofitserova and A. N. Pudovik, *J. Gen. Chem. USSR*, **45**, 2512 (1975).
448. A. N. Pudovik, I. V. Gur'yanova, M. G. Zimin and A. V. Durneva, *J. Gen. Chem. USSR*, **39**, 989 (1969).
449. V. S. Abramov, N. I. D'yakonova and V. D. Efimova, *J. Gen. Chem. USSR*, **39**, 1932 (1969).
450. J. A. Mikroyannidis, *Phosphorus Sulfur*, **25**, 39 (1985).
451. L. D. Quin and R. E. Montgomery, *J. Org. Chem.*, **28**, 3315 (1963).
452. S. Musierowicz and W. T. Waszkuć, *Phosphorus Sulfur*, **3**, 345 (1977).
453. B. Walther, R. Schoeps, W. Kolbe and D. Scheller, *Z. Chem.*, **19**, 417 (1979).
454. A. P. Stewart and S. Trippett, *J. Chem. Soc. C*, 1263 (1970).
455. M. Yoshifugi, H. Gomi and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **47**, 2905 (1974).
456. P.E. Cann, S. Warren and M. R. Williams, *J. Chem. Soc., Perkin Trans. 1*, 2377 (1972).
457. K. A. Petrov, V. A. Chauzov and T. S. Erokhina, *J. Gen. Chem. USSR*, **45**, 727 (1975).

458. W. M. Horspool, S. T. McNeilly, J. A. Miller and I. M. Young, *J. Chem. Soc., Perkin Trans. 1*, 1113 (1972).
459. J. A. Miller and D. Stewart, *J. Chem. Soc., Perkin Trans. 1*, 1898 (1977).
460. E. Lindner and G. Frey, *Chem. Ber.*, **113**, 3268 (1980).
461. E. Lindner and D. Huebner, *Chem. Ber.*, **116**, 2574 (1983).
462. S. Inokawa, Y. Tanaka, H. Yoshida and T. Ogata, *Chem. Lett.*, 469 (1972).
463. R. S. Davidson, R. A. Sheldon and S. Trippett, *J. Chem. Soc. C*, 1700 (1968).
464. N. J. De'ath, S. T. McNeilly and J. A. Miller, *J. Chem. Soc., Perkin Trans. 1*, 741 (1976).
465. J. A. Miller and D. Stewart, *J. Chem. Soc., Perkin Trans. 1*, 1340 (1977).
466. D. Hunter, J. K. Michie, J. A. Miller and W. Stewart, *Phosphorus Sulfur*, **10**, 267 (1981).
467. I. Ijima, K. Akiba and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **42**, 2975 (1969).
468. I. M. Magdeev, Ya. A. Levin and B. E. Ivanov, *J. Gen. Chem. USSR*, **42**, 2409 (1972).
469. A. A. Kutyrev, O. I. Lebedeva and V. V. Moskva, *J. Gen. Chem. USSR*, **60**, 705 (1990).
470. R. Bodalski, K. M. Pietrusiewicz and J. Koszuk, *Tetrahedron*, **31**, 1907 (1975).
471. E. Lindner, E. Tamoutsidis, W. Hiller and R. Fawzi, *Chem. Ber.*, **116**, 3151 (1983).
472. E. Lindner and E. Tamoutsidis, *Chem. Ber.*, **116**, 3141 (1983).
473. M. J. Gallagher and I. D. Jenkins, *J. Chem. Soc. C*, 210 (1971).
474. J. A. Miller, *Tetrahedron Lett.*, 4335 (1969); J. A. Miller, G. M. Stevenson and B. C. Williams, *J. Chem. Soc. C*, 2714 (1971).
475. S. Musierowicz, W. T. Waszkuć and H. W. Krawczyk, *Phosphorus Sulfur*, **5**, 377 (1979).
476. M. Regitz and Otto J. Scherer (Eds.), *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Georg Thieme Verlag, Stuttgart, 1990.
477. S. L. Brock and J. M. Mayer, *Inorg. Chem.*, **30**, 2138 (1991).
478. L. D. Quin, J. C. Kisalius, J. J. Skolimowski and N. S. Rao, *Phosphorus, Sulphur, Silicon Relat. Elem.*, **54**, 1 (1990).
479. G. Keglevich, F. Janke, V. Fülöp, A. Kálmán, G. Tóth and L. Töke, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **54**, 73 (1990).
480. J. Park and S. F. Pedersen, *J. Org. Chem.*, **55**, 5924 (1990).
481. R. K. Haynes, J. P. Stokes and T. W. Hambley, *J. Chem. Soc., Chem. Commun.*, 58 (1991).

IX. ADDENDA

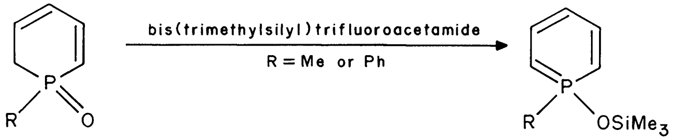
Some aspects of the chemistry of phosphine chalcogenides have been considered, of necessity, in a recent volume on phosphorus chemistry[476].

Section II.A.1.

The transfer of phosphoryl oxygen from a phosphine oxide to a metal centre represents a unique approach to the deoxygenation of a phosphine oxide. The transfer occurs when the initial adduct from a tungsten(II) complex, $WCl_2(PMeR_2)_4$ (R = Me or Ph), and the phosphine oxide, e.g. $Ph_2P(O)CH_2CH_2PPh_2$, is heated. The products of the reaction include the complexes $W(O)Cl_2(diphos)(PMeR_2)_2$ and $W(O)Cl_2(PMeR_2)_3$. One serious limitation to the scope of the procedure is the lack of reactivity shown by non-chelating phosphine oxides[477].

Section II.D.

The treatment of 1,2-dihydrophosphorin 1-oxides with bis(trimethylsilyl)trifluoroacetamide at room temperature results in their rapid and quantitative conversion into cyclic silyoxylphosphoranes, as indicated in equation (91). The reaction proceeds in a like manner with 1,4-dihydro-,4-azaphosphorine 1-oxides. More forcing conditions are required with 2,5-dihydrophosphole 1-oxide, and a quaternary phosphonium structure has been tentatively assigned to the product[478]. The high reactivity in the case of the six-membered ring compounds is connected, ultimately, with the generation of the relatively stabilized phosphabenzene ring[477], either by rapid initial prototropy and nucleophilic attack on the silylating reagent by OH, or nucleophilic attack on the latter by the phosphoryl group and subsequent rapid loss of H from the adjacent ring CH_2 group.



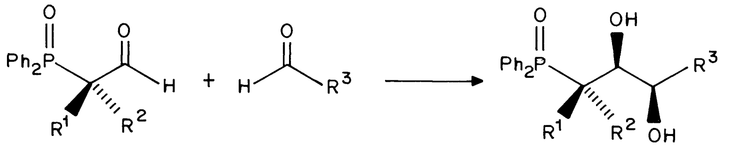
(91)

Section II.H.4.

The adduct 217 ($R^1 = H$, $R^2 = Me$, $R^3 = Ph$, $X = O$), obtained by the addition of dichlorocarbene to 2,5-dihydro-3-methyl-1-phenylphosphole, has been shown by X-ray analysis to have the cyclopropane ring *trans* to the phosphoryl bond[479].

Section IV.B.6.

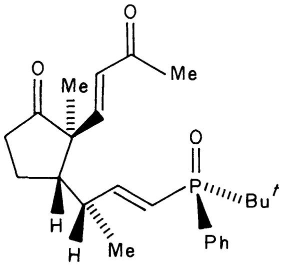
A cross-coupling reaction between α,α-disubstituted α-diphenylphosphinoyl acetaldehydes and saturated aldehydes occurs in the presence of a vanadium-containing catalyst formulated as $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$, to give the *threo* diols (**356**) with excellent diastereospecificity within the range 7.5:1 to >99:1 depending on R^1 and R^2[480].



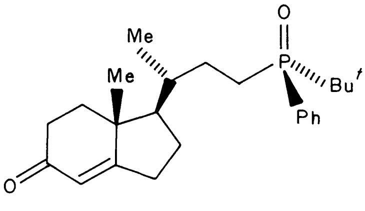
(356)

Section V.E.6.

In an application of some of the chemistry indicated in Scheme 59, lithiated (±)-(*E*)-but-2-enyl (*tert*-butyl)phenylphosphine oxide has been treated with 2-methylcyclopent-2-enone, and the product acted upon by 4-chlorobut-3-en-2-one, to give the (±)-phosphine oxide (**357**); the Ph and Bu^t groups are sufficiently dissimilar sterically to ensure that the product is obtained an only one diastereoisomeric form. Hydrogenolysis of **357** in the presence of Pd/C gives a tetrahydro derivative which, when acted upon by 2% aqueous KOH solution cyclizes to the (±)-phosphine oxide (358), useful in the synthesis of analogues of vitamin D[481].



(357)



(358)

CHAPTER **8**

Coordination chemistry of phosphine chalcogenides and their analytical and catalytic applications

T. S. LOBANA[a]

Department of Chemistry, Guru Nanak Dev University, Amritsar 143005, India

---

[a] This chapter is dedicated to my mother, the late Mrs. Vidya Kaur, wife of S. Harnam Singh of Village Gado Majra, Rajpura (Patiala).

The chemistry of organophosphorus compounds, Volume 2, Phosphine oxides, sulphides, selenides and tellurides
Edited by Frank R. Hartley. © 1992 John Wiley & Sons, Ltd. ISBN: 0-471-93056-3

I. INTRODUCTION

A. History, Previous Reviews and Scope

Tertiary phosphine oxides, sulphides, selenides and tellurides constitute an important class of ligands after tertiary phosphines[1-15]. The former ligands contain pentavalent phosphorus with O, S, Se or Te as the donor atoms, while the latter type have P as the donor atom.

The first tertiary phosphine oxide complexes, namely $[MX_2L_2]$ (M = Zn, Cd, Hg; X = Cl, I; L = Ph_3PO), were reported in 1906[16], but the first significant studies on the coordination chemistry of tertiary phosphine oxides were carried out only during the late 1950s and 1960s. Similarly, the first complex of a phosphine sulphide. $[(HgCl_2)_2Et_3PS]$, was reported in 1947 by Malatesta[17], but 1960 is often considered as the first year of the coordination chemistry of phosphine chalcogenides when Bannister and Cotton[18] reported a few metal complexes, $[PdCl_2L_2]$ and $[SnCl_4L_2]$ (L = Ph_3PS or Ph_3PSe). The first stable complexes of any phosphine telluride, $[M(CO)_5(TePR_3)]$ (M = Cr, Mo, W; R = Me_3C), were reported only recently[19].

The coordination chemistry of monotertiary phosphine oxides, sulphides, selenides or tellurides has been extensively studied, particularly of first three types of ligands; corresponding studes with di- or poly-tertiary phosphine oxides and chalcogenides are much fewer. However, multidentate tertiary phosphine derivatives have attracted considerable interest, particularly recently for several reasons. For instance, the anionic derivatives of $\{Ph_2PE\}_2CH_2$ and $\{Ph_2PE\}_3CH$ namely, $\{Ph_2PE\}_2CH^-$ and $\{Ph_2PE\}_3C^-$ (E = O, S, Se), and unsymmetrical phosphorus ligands such as $R_2P(E)CH_2PR_2$ and $R_2P(S)(CH_2)_nP(Se)Ph_2$ ($n = 1, 2$) provide an interesting set of ligands whose coordination chemistry is rich from the structural bonding and spectroscopic points of view. The anionic ligands, e.g. $\{Ph_2P(E)\}_2CH^-$, can bind to a metal via (a) methine carbon, (b) C and one E donor atom with a second E donor atom being uncoordinated or (c) E donor atoms. The free E donor atom [case (b)] can be made to coordinate to another metal ion, forming homo- or hetero-polymetallic complexes. Also, the coordinated and free E donor atoms show exchange behaviour with one another. Similarly, $\{Ph_2P(E)\}_3C^-$-type ligands form interesting cage compounds such as [HgClL] (L = $\{Ph_2PE)\}_3C^-$)[20]. The unsymmetrical ligands mentioned above and also the anionic ligands provide very interesting systems for ^{31}P NMR study.

Tertiary phosphine oxides have been applied in a number of areas. The most notable

TABLE 1. Previous reviews on metal–phosphine oxide, chalcogenide and telluride chemistry

	Topic	Year of publication	Ref.
	Phosphine oxides		
1	Properties and applications of uranium(IV) and uranium(VI) complexes with phosphines, phosphonium salts, tertiary phosphine oxides and tetracoordinated phosphorus compounds	1968	22
2	Bibliographic revision of the coordination chemistry of phosphine oxides	1976	23
3	Some considerations on coordination compounds of phosphine oxides with lanthanide perchlorates	1976	24
4	Actinide nitrate complexes	1981	25
5	Fluoro complexes of silicon(IV) with oxygen-containing donor ligands	1983	26
6	Transition metal chemistry review, 1981, Part B	1984	27
7	Preparation and stereochemistry of rare earth phosphine oxide complexes	1984	28
8	Coordination compounds of phosphine oxides	1975	29
9	Coordination chemistry of metal ions with bidentate di-tertiary phosphine and arsine dioxides	1979	30
	Phosphine sulphides, selenides or tellurides		
10	Interaction of organophosphine oxides, sulphides selenides and tellurides with metal salts and formation of complexes	1971	31
11	Preparation, chemistry and physical properties of phosphine sulphides, selenides and tellurides	1972	32
12	Oxidation and other products from the reaction of thiones and phosphine sulphides with metal salts and halogens	1976	33
13	Phosphine sulphides and their complexes with metals: carbon-13 NMR spectroscopy	1977	34
14	Coordination compounds of metal ions with tertiary phosphine and arsine sulphides or selenides	1978	35
15	Structure and bonding of metal complexes of tertiary phosphine and arsine chalcogenides including analytical, catalytic and other applications of the complexes	1989	21
	Extraction area		
16	Solvent extraction properties of di-tertiary phosphine dioxides	1982	36
17	Extraction of mineral acids, actinides and lanthanides by diphosphine dioxides	1986	37
18	Recovery of uranium using di(2-ethylhexyl)phosphoric acid–trioctylphosphine oxide	1987	38
19	Solvent extraction with organophosphines—Commercial and potential applications	1988	39

are liquid–liquid extraction chemistry of metals, reversed-phase chromatography, ion-selective electrodes, extractive metal determinations and catalysis. Analogous studies on phosphine chalcogenides are limited[21].

Table 1 gives a list of previous reviews on phosphine oxides or chalcogenides. Although the area of phosphine chalcogenides has been well reviewed[21], a similar recent or authoritative coverage of phosphine oxides could not be found in any commonly available international journals or series. A similar situation prevails for the extraction chemistry, particularly of mono-tertiary phosphine oxides. The work on phosphine tellurides is very limited however.

The coverage of the literature in this review is up to November 5, 1990, based on *Chemical Abstracts* and on leading and available international journals. Efforts have been made to cover almost every significant investigation, although the possibility of a few omissions cannot be ruled out. This review incorporates the complexes formed by the common metal salts, and also by all other metal compounds with anions derived from carboxylic acids, β-diketones, pyrazolones, Schiff bases, thio ligands, etc. Complexes formed by the organometallic moieties including metal carbonyls are also discussed. In brief, the review provides detailed coverage of the coordination chemistry of tertiary phosphine oxides, sulphides, selenides and tellurides, with the incorporation of significant applications of the ligands.

B. Types of Ligands

The ligands whose coordination chemistry is described in this review are essentially tetriary phosphine derivatives. The primary or secondary phosphine oxides or chalcogenides are not included and may form the basis for a future review, although not much work on the coordination chemistry of primary or secondary phosphine oxides has been reported. However, Walther[40] reviewed the coordination chemistry of secondary phosphine chalcogenides in 1984.

Among the tertiary phosphine oxides and chalcogenides, the ligands having the formula R_3PE ($R =$ alkyl or aryl group with or without one or more substituent; $E = O$, S, Se, Te) are discussed. Thus ligands of the type $(Me_2N)_3PE$ with P—N and not P—C bonds and those of the type $(R'O)R_2PE$, $(R'O)_2RPE$ and $(R'O)_3PE$ having P—R bonds replaced with P—OR′ bonds (where R and R′ may be the same or different) are mentioned in the review, particularly in the section on extraction chemistry, but their coordination chemistry is again excluded. Otherwise, the review would have become unmanageable. However, future reviews may cover the coordination chemistry of $(R'O)R_2PE$-type ligands, etc., which has been significantly studied. The same applied to di- and poly-tertiary phosphine oxides and chalcogenides.

Some of the important types of ligands whose coordination chemistry is discussed in this review are as follows:

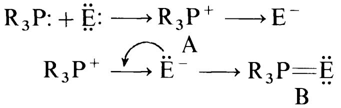
(a) $R_3PE[R = Ph, Bu^n$ etc.; $E = O, S, Se$ or Te);
(b) $Ph_2P(E)(CH_2)_nP(E)Ph_2$ [$n = 1,2$, etc.; $E = O, S, Se$];
(c) $\{Ph_2P(O)CH_2\}_2P(O)Ph, \{Ph_2P(O)CH_2CH_2\}_2P(O)Ph$;
(d) *cis*-$Ph_2P(O)CH{=}CHP(O)Ph_2$;
(e) $\{Ph_2P(E)\}_2CH^-, \{Ph_2P(E)\}_3C^-$;
(f) $Ph_2P(E)CH_2PR^1R^2[R^1, R^2 = Ph, Ph$, etc.];
(g) $Ph_2P(S)(CH_2)_nP(Se)Ph_2(n = 1,2)$;
(h) $\{Ph_2P(E)\}_3CH$.

Ligands having PO substituents in the *ortho* position of the benzene ring and a few macrocyclic ligands containing PO and ethereal oxygen and some related ligands are also covered.

C. Nature of Bonding

The nature of metal—phosphine bonds has been well studied using various techniques such as photoelectron spectroscopy and pK_a values, and also theoretical models[42–45]; the corresponding studies on metal phosphine oxides, sulphides, etc., are limited. However, an attempt is made in this section to review briefly the bonding considerations involved.

The ligands of the type R_3PE (E = O, S, Se, Te) bind to a metal centre via E donor atoms. The formation of bonds between R_3P and E atoms is believed to involve a σ bond, $R_3P \rightarrow E$, and a π bond, $p(\pi)(E) \rightarrow d(\pi)(P)$[19,21,46] leading to multiple bonding in the chromophore $>P{=}E$ (A and B):

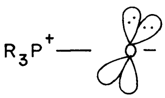


$$R_3P\!: + \ddot{\underset{..}{E}}\!: \longrightarrow \underset{A}{R_3P^+ \longrightarrow E^-}$$

$$R_3P^+ \longrightarrow \ddot{E}^- \longrightarrow \underset{B}{R_3P{=}\ddot{\underset{..}{E}}}$$

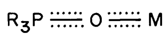
X-ray data show that metal—O bonds[41] have multiple bond character, whereas metal—E (E = S, Se, Te)[19,21] bonds are simple single bonds involving the donation of a pair of electrons from the E atom to the metal.

The angles at oxygen, viz. M—O—P, vary[41] from 113 to 180°, whereas the angles M—E—P (E = S, Se, Te)[19,21] lie in the range 96–120°, most being below 116°[21]. The bonding in P—E bonds (E = S, Se, Te) can be readily rationalized in terms of structures A and B. Structure A (sp^3) suggests M—S—P angles of 109°28′ whereas B suggests angles of 120° (sp^2). The fact that the angles are generally below 120° shows that the P—E bond is a resonance hybrid of structures A and B. The metal—O bonding cannot be explained in terms of structure A or B. M—O—P angles of 180° have been obtained in the case of aluminium(III) and gallium(III) complexes[41]. This can be explained by depicting the P—E bond as a hybrid of two structures, C and D[41]:



C

D



E

Model D is isolobal with CO, NO^+ and CN^-. Thus the $>P^-{\equiv}O\!:^+$ moiety will form a σ bond to a metal centre followed by the electron density distribution over the entire P—E—M framework (E), which explains the multiple bond character in M—O bonds[41].

The second possible explanation appears to be equally good. The linearity of the M—O—P bonds can be explained using mode B also. Here a σ bond from O to M is followed by a π bond from O to M. Depending on the extent of O to M π bonding, the M—O—P angles will vary from 109°28′ to 180°. The fact that the angles at S or Se fall below 109°28′ can be attributed to the higher angular flexibility at the bulkier S or Se atoms compared with the smaller O atom.

Finally, the X-ray data have shown that the $>P{=}S$ group shows unidentate and bridging behaviour[21] and probably there is no example[41] where X-ray measurements have established bridging by a $>PO$ group or $>PSe$ group, although other data have suggested bridging by PO groups in some cases as cited in the text.

II. TERTIARY PHOSPHINE OXIDES

A. Mono-tertiary Phosphine Oxides

For simplicity, the work reported is divided into sections devoted to transition elements, Main Group elements and alkali and alkaline earth elements.

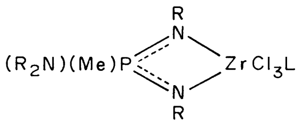
1. Transition elements

Both d- and f-block elements are discussed here.

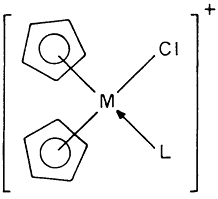
a. Complexes of the scandium Group (IIIB). Scandium(III) and yttrium(III) form several complexes with R$_3$PO ligands of the type (A) [ScCl$_3$L$_3$] and [ScCl$_{6-n}$L$_n$]$^{n-3}$ (^{45}Sc NMR study)[47], (B) [Sc(NCS)$_3$L$_3$][48](L = Ph$_3$PO), (C) [Sc[TTA)$_3$L$_2$] (L = topo, Ph$_3$PO)[49–51], (D)[MA$_3$L] [HA = 2,2,6,6-tetramethylheptane-3,5-dione (HPVA)[52,53], (E) [M(OR)$_3$L] (R = 2,6-di-*tert*-butyl-4-methylphenoxo, L = Ph$_3$PO)[54], (F) [ScL$_4$(EtOH)$_2$](ClO$_4$)$_3$ (L = Me$_3$PO, Ph$_3$PO)[55,56], (G) [YCl$_3$L$_n$] (n = 3,4) and [YCl$_3$L$_3$]. Me$_2$CO (L = Ph$_3$PO)[57]. Whereas the formation of complexes A was revealed by ^{45}Sc NMR, the other complexes were formed from direct reaction of a metal salt with ligand. The coordination number of the complexes A–D and G varied from 4, 6 to 8. Finally, the phenoxo complexes [M(OR)$_3$L (E)[54] represent unique examples of four-coordinated compounds with high solubility in hydrocarbons [see Section II.A.1.i for more complexes of yttrium (III)].

b. Complexes of the titanium Group (IVB). Various titanium and zirconium complexes are listed in Table 2. Titanium(IV) formed adducts with 1:1 or 1:2 M:L ratios whereas zirconium(IV) adducts have 1:1, 1:2, 1:4 or 1:6 M:L ratios. Alkoxytitanium(IV) complexes were hygroscopic. Peroxyzirconium(IV) complexes (G) [ZrO$_2$Al$_n$] (n = 1,2) with chealating bi- or tri-dentate anions are very stable. ^{19}F NMR studies suggested a *cis*-octahedral structure for complexes [TiF$_4$L$_2$] (L = Ph$_3$PO, Bu$^n_3$PO)[65]. The 1:1 adducts [MCl$_4$(OPPh$_3$)] are likely to have halogen-bridged dimeric structures.

A 1:1 adduct of Ph$_3$PO with {*N,N'*-bis(trimethylsily)diamido-*N''*-bis(trimethylsilyl)-*P*-methylphosphonoimidato}-trichlorozirconium(IV) (**1**)[82]



(**1**)



(**2**)

Organozirconium and-hafnium dimers, [(η^5-cp)$_2$M(μ-Cl)]$_2$(BF$_4$)$_2$ formed complex **2** with Ph$_3$PO[83]. Similarly, [(η^5-cp)$_2$MClL]I$_3$ was obtained from [(η^5-cp)$_2$M(μ-Cl)]$_2$ and Ph$_3$PO followed by treatment with excess of iodine.

c. Complexes of the vanadium Group (VB). Reaction of [V(CO)$_6$] with Ph$_3$PO did not give a substituted product, but rather an ionic complex, viz. [VL$_4$][V(CO)$_6$]$_2$[84], was obtained. Numerous other vanadium complexes have been reported, although an X-ray analysis has only been reported for one complex. The complexes are of the formulations [VCl$_3$L$_2$] (L-R$_3$PO; R = Et, Pr, Cy, Ph)[85]; [VCl$_4$(OPPh$_3$)][58]; [VOX$_2$(OPPh$_3$)$_2$] (X = Cl,

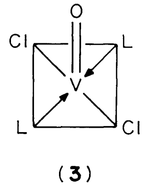
TABLE 2. Complexes of the titanium Group (IVB)

	Complex	X	L	Ref.
A	$[TiX_4L_n]$	Cl	$Ph_3PO(n = 1)$	58–61
		F, Cl, Br	$R_3PO(n = 2)$ (R = Ph, Bu^n, etc.)	62–65
		Cl	$Ph_2P(O)CH{=}CH_2$	66
B	(i) $[TiX_mA_{4-m}L_2]$[a] ($m = 2,3$)	Cl	Ph_3PO	67
	(ii) $[TiA_4L]$[a]	—	Ph_3PO	67
C	(i) $[Ti(OR)X_3L]$[b] (R = Me, Et, ClC_2H_4, $F_3C_2H_2O$)	Cl	Ph_3PO	68, 69
	(ii) $[Ti(OR)X_3L_2]$ (R = Me, Et)	NCS	Ph_3PO	70
D	$[ZrX_4L_n]$	(i) Cl	$Ph_3PO(n = 1)$	60
		(ii) Cl, NO_3	R_3PO(R = Me, Bu, Bz, Ph) ($n = 2$)	71–75
E	$[ZrOX_2L_2]$	Cl, Br, NCS, SeCN, NO_3	Ph_3PO	76, 77
F	(i) $[ZrOL_4L_2]$	—	Ph_3PO	76
	(ii) $[ZrOL_4](BPh_4)_2$	—	Ph_3PO	78
	(iii) $[ZrOL_6](ClO_4)_2$	—	Ph_3PO	76
G	(i) $[ZrO_2AL_2]$[c]	—	Ph_3PO	79
	(ii) $[ZrO_2AL]$[d]	—	Ph_3PO	80
H	$[Zr(OAc)_m(SO_3F)_{4-m}L_n]$ ($m = 0,2,3$)	—	Ph_3PO	81
I	$[ZrO(SO_3F)_2L_n]$	—	Ph_3PO	81

[a] HA = 1-naphthol.
[b] ClC_2H_4O = 2-chloroethoxy; $F_3C_2H_2O$ = 2,2,2-trifluoroethoxy.
[c] H_2A = succinic acid.
[d] H_2A = pyridine-2,6-dicarboxylic acid and salicylideneaminobenzoic acid.

Br)$^{86-94}$; $[VOCl(OH)(topo)_2]^{95}$; $[VOL_nX_2]$ ($n = 2$ for $X = BPh_4$, $n = 4$ for $X = ClO_4$, $L = Ph_3PO)^{90,96}$; $[VO(acac)_2(OPBu)_3)]^{97}$; $[V(NO)Cl_2(OPPh_3)_4$ ^{93}; $[V(NO)_2L_4]Br$ ($L = R_3PO$; R = Me, Ph)^{98}; $[V(OR)_3L]$ ($R = ClC_2H_4$; $L = Ph_3PO)^{99}$; $[V(SO_3CF_3)_3L]$, $[VO(SO_3CF_3)_nL]$ ($n = 2, 3$; $L = Ph_3PO)^{100}$; and $[V(SO_3F)_3(OPPh_3)$ ^{101}. The hydroxy complex $[VOCl(OH)$ $(topo)_2]^{95}$ was obtained by an extractive method, whereas the other complexes were obtained by normal direct reactions.

Monomeric vanadyl halide complexes, $[VOX_2L_2]^{86-94}$, have been well studied. An X-ray study of $[VOCl_2(OPPh_3)_2]$ showed a square-pyramidal structure with *trans*-Ph_3PO ligand (**3**)^{89}. For the other complexes, namely $[VOL_4]$ $(ClO_4)_2$ and $VOL_2(BPh_4)_2$, square-pyramidal structures are suggested, but need to be confirmed from X-ray analysis, particularly the latter, which would shed light on possible coordination



(**3**)

by BPh$_4$ anion[90,96]. Similarly, in vanadium–alkoxide complexes, [V(OR)$_3$L], bridging by OR groups is suggested[99]. Finally, the SO$_3$CF$_3$ groups in [V(SO$_3$CF$_3$)$_3$L], [VO(SO$_3$CF$_3$)$_n$L] and [V(SO$_3$F)$_3$L] act as chelating agents[100,101].

Niobium(V) and tantalum(V) form complexes of the type [MX$_5$L] (X = Cl, Br; L = Ph$_3$PO[60,102–104] Ta, Cl, BzPh$_2$PO[102]); [NbOX$_3$L$_2$] (X = F, Cl, Br; L = Ph$_3$PO)[102,105–108]; [NbCl$_4$(NO)(MeCN)(OPPh$_3$)][109]; [M(OR)$_2$X$_3$L] (X = Cl, Br; R = Me, Et; L = Ph$_3$PO)[110,111]; [M(OMe)$_5$(OPMe$_3$)][112]; [(Nb$_6$Cl$_{12}$)Cl$_2$L$_4$] (L = Ph$_3$PO)[113]; M[NbO(C$_2$O$_4$)$_2$L$_2$] (M = NH$_4$, K, Rb, Cs; L = Me$_3$PO, Ph$_3$PO)[114,115]; [Me$_2$MCl$_3$L][116,117], [Me$_3$MCl$_2$L] (L = Ph$_3$PO)[118]; [MeMOCl$_2$L$_2$] (L = Me$_3$PO, Ph$_3$PO); and [MeNbOBr$_2$L] (L = Ph$_3$PO)[119]. Similarly, a few niobium(III) and niobium(IV) complexes, [(η^5-cp)$_2$Nb(PMe$_3$)L] (BF$_4$) and [(η^5-cp)$_2$NbClL] (BF$_4$) (L = Ph$_3$PO)[120], are known.

The complexes [MX$_5$L] and [NbOX$_3$L$_2$] were obtained from reaction of [MX$_5$] or [NbOX$_3$] with L. In the reaction of [NbX$_5$] with L, the abstraction of oxygen from the ligand takes place, forming [NbOX$_3$L$_2$]-type complexes. Similarly, the oxygen abstraction phenomenon was also observed when [MeNbX$_4$] was reacted with R$_3$PO[119]. Metal–alkoxide complexes, e.g. [M(OR)$_2$X$_3$L][110,111], were obtained by the reaction of [MX$_5$] with ROH in the presence of the ligand L. The formation of [M(OMe)$_5$L] was detected in solution by ^{1}H NMR spectrometry and was in equilibrium:

$$2[\mathrm{M(OMe)_5L}] \rightleftharpoons [\mathrm{M_2(OMe)_{10}L}] + \mathrm{L}$$

^{19}F NMR studies revealed the formation of a number of unusual species. For instance, reaction of [MF$_5$] with Ph$_3$PO in CH$_2$Cl$_2$ or PhMe gave *cis*- amd *trans*-[MF$_4$L$_2$]$^+$F$^-$ and small amounts of the dimers [M$_2$F$_{10}$L][121–123]. When acetonitrile was the solvent, only [MF$_5$L] complexes were formed. Similarly, the formation of [MF$_5$L] and also *cis*- and *trans*-[MF$_4$L$_2$]F (L = Bu$_3$PO) was observed when the solvent was toluene[124,125]. Ageing of a solution of *trans*-[TaF$_4$(PBu$_3$)$_2$]F[124] gave the same products. The addition of BF$_3$ led to the disappearance of the above-mentioned species and instead BF$_3$L, B$_2$F$_6$L, BF$_4^-$, etc., were formed[126]. This demonstrates the greater affinity of BF$_3$ for Bu$_3$PO than that of [MF$_5$] (M = Nb, Ta). Mixed halide complex species, namely, two *trans* forms of [TaF$_3$Cl$_2$L], *trans*-[TaE$_2$Cl$_3$L] and two *cis*-forms of [TaF$_2$Cl$_3$L] were detected by ^{19}F NMR in a 1:1:1 solution of TaF$_5$, PCl$_5$ and R$_3$PO(R = Bu^n, Ph) in PhMe[127]. An increase in the basicity of the ligand shifted the ^{19}F NMR signal to high field when MF$_5$ was reacted with (RC$_6$H$_4$)$_3$PO and Me$_2$P(O)(RC$_6$H$_4$) (R = H, *p*-Me, MeO, Cl, Me$_2$N, *m*-Cl, NO$_2$, Me)[128–130].

d. Complexes of the chromium Group (VIB). Various complexes of this group are given in Tables 3–5. Reaction of chromium(II) halides with the ligand L in organic solvents gave moisture- and air-sensitive complexes, [CrX$_2$L$_2$][131,132], which on reaction with NO gave the nitrosyl complexes [Cr(NO)$_2$X$_2$L$_2$][135]. The bromo complexes [CrBr$_2$L$_2$] exist in two forms. The green forms of [CrBr$_2$L$_2$] and [CrCl$_2$L$_2$] possess halogen-bridged dimeric structures. Formation of [CrI$_2$L$_2$(thf)$_2$][131] was detected by electronic absorption spectroscopy (Table 3).

The dimeric chromium(II) trifluoroacetate complex [Cr$_2$(O$_2$CCF$_3$)$_4$L$_2$] (L = Me$_3$PO), obtained from [Cr$_2$(O$_2$CCF$_3$)$_4$(ether)$_2$] and Me$_3$PO, showed a normal μ value of 3.06 BM[136] compared with a value of 0.89 BM for the ether solvate. X-ray analysis showed a dimeric structure (**4**) with a weak Cr—Cr bond.

The chromium(III) complexes, [CrX$_3$L$_3$] [Cr(O$_2$NO)$_2$L$_2$](NO$_3$), [CrX$_3$L(bipy)] and [CrL$_4$(OClO$_3$)$_2$](ClO$_4$)[132–134,136,137] are assigned octahedral structures having bidentate NO$_3$ and unidentate ClO$_4$ groups. Thiosemicarbazone in [CrAA′L] complexes is tridentate[139] (O, N, S), whereas salen in [(C$_6$F$_5$)Cr(salen)L] is tetradentate[140] (O$_2$N$_2$); both of these complexes are octahedral (Table 3).

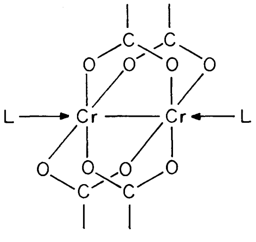
Reaction of CrO$_3$ with glycol and R$_3$PO (R = Et, Ph) gave the chromium(V) complexes

TABLE 3. Complexes of chromium

	Complex	X	L	Ref.
A	(i) $[CrX_2L_2]$	Cl, Br, I	Ph_3PO	131
			R_3PO(R = Et, Pr, Cy, Ph)	132
	(ii) $[CrX_2(NO)_2L_2]$	Cl, Br, I	Ph_3PO	135
	(iii) $[Cr_2X_4L_2]$	CF_3COO	Me_3PO	136a
B	(i) $[CrX_3L_3]$	Cl, NCS, ClO_4	Ph_3PO	133, 134
		NCS	R_3PO(R = Et, Bu, Cy)	132
	(ii) $[CrX_2L_2]X$	NO_3	Ph_3PO	133
	(iii) $[CrX_3L(bipy)]$	Cl	Ph_3PO	136b
	(iv) $[CrL_4X_2]X$	ClO_4	Bu_3PO	137
C	$(L_nH)[CrX_4(NH_3)_2]$	NCS	R_3PO(R = Et, Pr, Bu, Cy; n = 1,2)	138
D	(i) $[CrAA'L]^a$	—	Ph_3PO	139
	(ii) $[(C_6F_5)Cr(salen)L]^b$	—	Ph_3PO	140
	(iii) $[CrOAL](SO_3CF_3)^c$	—	Ph_3PO	141

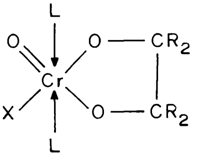
[a] H_2A = salicylaldehyde thiosemicarbazone; HA′ = quinolin-8-ol.
[b] salen = *N*,*N*′-ethylenebis(salicylaldiminate).
[c] H_2A = 5,5′-dichloro-8,8,8′,8′-tetramethylbis(salicylidene)ethylenediamine.

$[Cr(O)XL_2(O_2C_2R_4)]$ (R = H, Me, X = Cl)[142] with the proposed structure **5**. X-ray study of another chromium(V) complex, [CrOAL] (SO_3CF_3)[141] (Table 3), showed octahedral geometry with *trans* L and O groups with the Schiff base occupying the equatorial plane. The $(L_nH)[CrX_4(NH_3)_2]$ complexes have hydrogen-bonded L_nH^+ cations with no Cr–ligand interaction. Finally, reaction of the unsymmetrical phosphine ligand $Ph_2P(O)CH(R)PPh_2$ (R = Pr) with $[Cr(CO)_6]$ gave $[Cr(CO)_4L]$ with *cis*-octahedral geometry[143].



CF_3 groups omitted

(**4**)



(**5**)

A wide variety of molybdenum and tungsten complexes have been reported (Tables 4 and 5). $[MoOX_3L_2]$ complexes[150] were obtained from MoX_3 or $K_3[MoCl_6]$ and molten Ph_3PO involving oxidation of Mo^{III} to Mo^V. Reaction of $MoCl_5$ with Ph_3PO gave $[MoOCl_3L_2]$ and $[MoO_2Cl_2L_2]$[157] and when dioxane $(C_4H_8O_2)$ was the solvent, $[MoOCl_3L(C_4H_8O_2)]$[151] was obtained. Oxidation of $[M(CO)_4L_2]$ and $[M(CO)_3L_3]$ (L = Ph_3PO) by Cl_2 or Br_2 gave $[MoX_3L_2]$ and $[MO_2X_2L_2]$ complexes[146]. Interestingly, reaction of $[MoSCl_3]$ with Ph_3PO in MeCN gave three products: $[MoOCl_3L_2]$ $[MoO_2Cl_2L_2]$ and $[MoO(S)Cl_2L_2]$[147]. The complex $(HPPh_3)$ $[WOCl_4L]$ (L = Ph_3PO)[167] was obtained by the partial hydrolysis of $[WCl_4(PhC{\equiv}CPh)]_2$ in the presence of Ph_3PO

TABLE 4. Complexes of molybdenum and tungsten

		Complex	L	Ref.
A	(i)	$[MoI_3L(PMe_2Ph)]$	Me_2PhPO	168
	(ii)	$[Mo_2Cl_6L_3]$	Ph_3PO	169
	(iii)	$[MoCl_4L_2]$	Ph_3PO	170
	(iv)	$[MoCl_5L]$	Ph_3PO	64
	(v)	$[WCl_4(PPh_3)L]$	Ph_3PO	171
B	(i)	$[MoOX_3L_2]$ $(X = Cl, Br)$	Ph_3PO	144–150
	(ii)	$[MoOX_3L(C_4H_8O_2)_2]^a$ $(X = Cl, Br)$	Ph_3PO	151, 152
	(iii)	$[MoOCl_3L]$	Ph_3PO	153
			$Et_2P(O)CH_2CH_2PEt_2$	154
	(iv)	$[WOCl_3L_2]$	Ph_3PO	155, 156
C	(i)	$[MO_2X_2L_2]$ $(X = Cl, Br)$	Ph_3PO	144, 146, 147, 152 155, 157–161
		$[MoO_2F_2L_2]$	Ph_3PO	158, 162
	(ii)	$[MoO_2(ONO_2)_2L_2]$	Ph_3PO	160, 161
	(iii)	$[MoO_2Cl_2L(C_4H_8O_2)]^a$	Ph_3PO	152
	(iv)	$[MoO(S)Cl_2L_2]$	Ph_3PO	147
	(v)	$(Et_4N)[WO_2F_3L]$	Me_3PO	163
D	(i)	$MoOF_4L]$	Ph_3PO	164a
	(ii)	$[WOX_4L_n]$ $(X = F, Cl)$	$R_3PO (n = 1,2)$	106, 164a
			$(R = Ph, Bu^n$, etc.)	165, 166
	(iii)	$(HPPh_3)[WOCl_4L]$	Ph_3PO	167
E	(i)	$[(Mo_6Cl_8)Cl_4L_2]$	Ph_3PO	172
	(ii)	$(L_nH)_2[(Mo_6Cl_8)Cl_6]$	Ph_3PO	172
F	(i)	$[Mo(O_2)_2L_2]$ $(M = Mo, W)$	Ph_3PO, Pr^n_3PO, Bu^n_3PO	173–175
	(ii)	$[W(O_2)_2A_2L]^b$	Ph_3PO	176
G	(i)	$[MoCl_4(NO)L]$	Ph_3PO	177
	(ii)	$(Et_4N)[MoCl_4(NO)L]$	Ph_2MePO, Ph_2EtPO	178
	(iii)	$[MCl_3(NO)L_2]$ $(M = Mo, W)$	Ph_2MePO, Ph_2EtPO, Ph_3PO	161, 178–179
	(iv)	$[MoCl_3(NO)L'_2L]$ $(L' = PhMe_2P, Ph_2Pr^nP)$	$MePh_2PO$, Ph_2Pr^nPO	178
	(v)	$[M(NO)_2Cl_2L_2]$	Ph_3PO, $EtPh_2PO$, Et_2PhPO, Cy_3PO, $Ph_2(R)PO$ (R = neomenthyl)	182–184
	(vi)	$[Mo(NO)_2Cl_2L_2]\cdot C_6H_6$	Ph_3PO	183
	(vii)	$[Mo(NO)_2(OEt)_2L]_2$	Ph_3PO	185
	(viii)	$[Mo(NO)(S_2CNR_2)_2L]$ $(R = Me, Et)$	Ph_3PO	186
H	(i)	$[MoCl_4(NPR_3)(OPR_3)]$	L^c	178, 187, 188
	(ii)	$[MoCl_2(=NH)OL_2]$	R_3PO $(R_3 = Ph_3, Ph_2Et, PhEt_2)$	189
	(iii)	$[WCl_3(=NPh)L_2]$	Me_3PO	190
	(iv)	$[WCl_4(=NC_2Cl_5)]L$	Ph_3PO	151
	(v)	$[MoCl_3(=N)L_n]$	Ph_3PO $(n = 1,2)$	191–193
	(vi)	$[MoCl_3(NH_2)L_2]Cl$	Ph_2MePO, Ph_2EtPO	178

[a] $C_4H_8O_2$ = dioxane.

[b] HA = *S*-benzyldithiocarbazate.

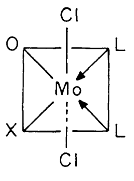
[c] $PR_3 = Ph_2PrP, Ph_3P, Ph_2EtP, PhMe_2P, Et_3P, \frac{1}{2}Ph_2PCH_2CH_2PPh_2$.

TABLE 5. Complexes of organo-molybdenum and tungsten

Complex	L	Ref.
A. (i) *cis*-$[\mathrm{M(CO)_4L_n}]$	$\mathrm{Ph_3PO}$($n = 2$)	194,195
($\mathrm{M = Mo, W}$)	$\mathrm{Ph_2P(O)CH(R)PPh_2}$ ($\mathrm{R = Pr}$)	143
(ii) $[\mathrm{W(CO)_5L}]$	$\mathrm{Ph_2P(O)CH_2CH_2PPh_2}$	196
	$\mathrm{R_3PO}$($\mathrm{R = Me, Ph}$)	197
	$\mathrm{Ph_2P(O)NPPh_3}$	197
	$\mathrm{Ph_2P(O)(CHPPh_3)}$	198
(iii) $[\mathrm{M(CO)_3L_3}]$	$\mathrm{Ph_3PO}$, $\mathrm{Bu_3PO}$, $\mathrm{EtPh_2PO}$, $\mathrm{Et_2PhPO}$, $\mathrm{Et_3PO}$	195,199–201
(iv) $[\mathrm{M(CO)_nCl_2L_2}]$ ($\mathrm{M = Mo, W}$; $n = 2, 3$).	$\mathrm{Ph_3PO}$	202,203
(v) $[\mathrm{M(CO)_3I_2L_2}]$	$\mathrm{Ph_3PO}$	204
B. (i) $[\mathrm{M(CO)_3L(OH)}]_2$	$\mathrm{Ph_3PO}$, $\mathrm{Ph_2EtPO}$, $\mathrm{PhEt_2PO}$, $\mathrm{Et_3PO}$	205
(ii) $[\mathrm{M(CO)_2(NO)L(OH)}]_2$	$\mathrm{Ph_3PO}$, $\mathrm{Et_3PO}$	205
C. $[\mathrm{M(S_2CNEt_2)_2(CO)_2L}]$	$\mathrm{Ph_3PO}$	206
D. (i) $[\mathrm{Mo(Me)(cp)(NO)XL}]$ ($\mathrm{X = Cl, Br}$)	$\mathrm{Ph_3PO}$	207
(ii) $[\mathrm{MeWCl_3EL}]$($\mathrm{E = O, S, Se}$)	$\mathrm{Ph_3PO}$	208
(iii) $[\mathrm{Me_3CC{\equiv}WCl_3L}]$ $[\mathrm{Me_3CC{\equiv}WCl_3LL'}]$ ($\mathrm{L' = Et_3P}$)	$\mathrm{Et_3PO}$	209
(iv) $[\mathrm{MeWOCl_3L}]$	$\mathrm{R_3PO}$	210
(iv) $[\mathrm{MeWO_2ClL}]$	$\mathrm{R_3PO}$	210
$[\mathrm{MeWO_2ClL_2}]$	$\mathrm{Ph_3PO}$	211

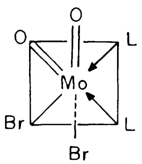
and $\mathrm{CH_2Cl_2}$. From solution-phase ^{19}F NMR studies, several type of species such as *trans*-$[\mathrm{WOF_4L}]$, $[\mathrm{MO_2F_2L_2}]$, $[\mathrm{M_2O_2F_8L}]$ and $[\mathrm{W_2O_2F_9L_2}]^-$ ($\mathrm{M = Mo, W}$; $\mathrm{L = Ph_3PO}$)[164b] were detected, depending on the ligand concentration. The complex species $[\mathrm{MoOCl_3L}]$and $[\mathrm{MoOCl_4^-}]^-$ also reacted with $\mathrm{Ph_3PO}$ to form $[\mathrm{MoOCl_3L_2}]$ and $[\mathrm{MoOCl_4L}]^-$ and it was found that the ability to form the complexes varied in the order $\mathrm{C_5H_5N > Ph_3PO \approx H_2O >}$ thf.

X-ray studies of $[\mathrm{MoOCl_3L_2}]$[147], $[\mathrm{MoO(S)Cl_2L_2}]$[147], *cis*-$[\mathrm{MoCl_2BrL_2}]$[158], $\mathrm{(HPPh_3)}$-$[\mathrm{WOCl_4L}]$[167], $[\mathrm{WOCl_3L_2}]$[156] ($\mathrm{L = Ph_3PO}$) and $[\mathrm{MoOCl_3L}]$ [$\mathrm{L = Et_2P(O)CH_2CH_2PEt_2}$][154] have shown them all to involve octahedral structures (**6**–**10**). The moiety $\mathrm{MO_2^{2+}}$ is non-linear[158,160–163], unlike $\mathrm{UO_2^{2+}}$, which is linear (cf. Section II.A.1.j)

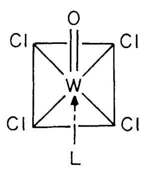


X = Cl, S

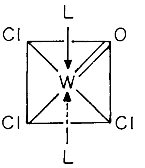
(**6**)



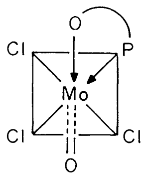
(**7**)



(**8**)

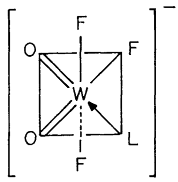


(**9**)



(**10**)

NMR studies (^1H, ^{19}F and ^{31}P) of $(Et_4N)[WO_2F_3L]$ ($L = Me_3PO$)[163] reveal a *trans*-labilizing affect of the oxo ligand as the fluoride liquid in the *trans* position is readily dissociated. Structure **11** is suggested as the basis of NMR data. Further, the *trans* influence of the ligand L on the W=O bond ($L = R_3PO$) in WOF_4L varies as R = amyl > *n*-butyl > *n*-octyl > phenyl[166].

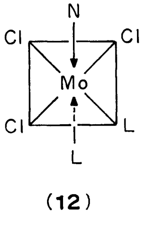


(**11**)

Only a few diperoxo complexes $[MO(O_2)_2L_2]$ are known (Table 4). The activation energies for the loss of dioxygen from the dry or the dissolved complexes are independent of whether the ligand is a phosphine oxide or an arsine oxide. In the tungsten thiocarbazate complex $[W(O_2)_2A_2L]$[176], the *S*-benzyldithiocarbazate $H_2NN{=}C(SH)SCH_2Ph$ acts as a uni-negative bidentate ligand. Further X-ray analyses of peroxo complexes would be very valuable.

The nitrosyl complexes G (Table 4) have been obtained by a number of different routes: (a) $[MoCl_3(NO)L_2]$ from $[MoCl_3(NO)]$ and Ph_3PO[181] or from $[MoO_2(OAc)_4]$ and NOCl in the presence of Ph_3PO[161]; (b) $[Mo(NO)_2Cl_2L_2]$ ($L = Ph_3PO$)[171] by reductive nitrosation of $[MoCl_5]$ with NO in the presence of Ph_3P in CH_2Cl_2; (c) $[Mo(NO)_2(OEt)_2L]$ from $[Mo(NO)_2(MeNO_2)_4](BF_4)_2$, Ph_3PO and MOEt (M = Li, Na) in $MeNO_2$[185]; and (d) $[W(NO)_2Cl_2L_2]$ from $[W(NO)_2Cl_2]$ and L[184]. Reaction of $[Mo(CO)_2(S_2CNR_2)_2L]$ with NOBr gave $[Mo(NO)_2Br_2L_2]$ ($L = Ph_3PO$)[186].

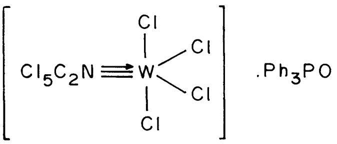
It was noted that the coordinated NO in these complexes[178] showed no sign of reactivity with nucleophiles or electrophiles. Further, on heating $[M(NO)_2Cl_2L_2]$ ($L = Ph_3PO$)[183] at 300 °C, $[MOCl_2L_2]$ and N_2O were formed, implying an intramolecular redox reaction in the halonitrosyl complexes. Nitric oxide oxidizes M^{II} to the M^{IV} state. In the complex $[Mo(NO)_2Cl_2L_2]$. C_6H_6 [183], benzene was lost at 100 °C. No X-ray study has been reported for any nitrosyl complex. However,, for $[MCl_3(NO)L_2]$, structure **12** was suggested[161,178,180,181].

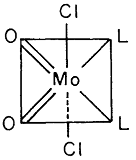


(**12**)

Complexes H(i–vi) (Table 4) represent respectively phosphineiminato, imido, phenylimido pentachloroethylimido, nitrido and amido complexes of molybedenum and tungsten. Phosphineimine derivatives H(i) were formed by the oxidation of $[MoCl_4L_2]$ $(L = Ph_2PrP)$ by sulphonylazide, p-$MeC_6H_4SO_2N_3$[178,188]. Similarly, the reaction of $[MoOCl_3]$ with Me_3SiN_3 in thf and R_3PO gave the imido complexes $[MoCl_2(NH)O(OPR_3)_2]$[189]. The nitrido complexes $[MoCl_3(\vdots N)L_n]$ were obtained by the addition of Ph_3PO to a molybdenum(II) nitrido species formed from $[MoCl_4L_2]$ (L = thf, MeCN) and trimethylsilylazide[192]. An interesting observation is that reductive hydrolysis of $[MoCl_3(\vdots N)L]$ $(L = Ph_3PO)$[193] gave 11–13% NH_3 under mild conditions whereas only a trace of NH_3 was formed from hydrolysis of $(Et_4N)[Mo(N)Cl_4]$[193].

ESR and magnetic moment studies suggest that the phosphineiminato complexes are mononuclear[187]. Complex H(iv) showed no ligand coordination (**13**). For complexes H(i, iii, v, vi), octahedral structures have been suggested. The X-ray analysis of $[MoCl_2({=}NH)O{=}(OPEtPh_2)_2]$[189] has shown a distorted octahedral structure, **14**.

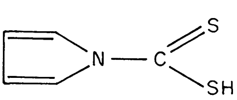




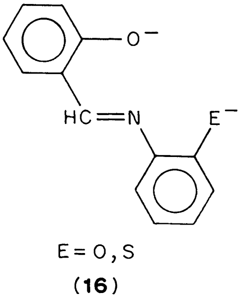
(13) **(14)**

Dimeric molybdenum(II) acetate, $[MO_2(O_2CCF_3)_4]$, forms a 1:2 adduct with Me_3PO[212]. NMR studies (^{19}F, ^{31}P) reveal extensive dissociation of the adduct $[Mo_2(O_2CCF_3)_4L_2]$. Other analogous molybdenum(II) derivatives, $[Mo_2A_2(OAc)_2L]$ $\{L = Ph_3PO$, HA = pyrrolyldithiocarboxylate (**15**)$\}$[213] and $[Mo_2(S_2PEt_2)(OAc)_3L](BF_4)$ $(L = Et_3PO)$[213], are also known.

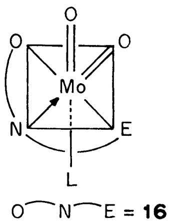
A tridentate dianionic Schiff base **16** gave a complex $[MoO_2AL]$ $(L = Ph_3PO;$ $H_2A = $ **16**)[214] with a *cis*-MoO_2 moiety (**17**). An oxotungsten(V) dimer with unusual stereochemistry, namely, *anti*-bis (μ-isobutylthiolato)bis{oxodichloro(triphenylphosphine oxide)}tungsten(V), *anti*-$[Cl_2(O)LW(\mu\text{-}SBu^i)_2W(O)Cl_2L]$ $(L = Ph_3PO)$ has been reported[215]. The molecule has a a crystallographically imposed centre of symmetry and therefore possesses the very unusual feature of terminal oxo ligands lying in an *anti* disposition to one another. Similarly, an adduct of Ph_3PO with the arylazomolybdenum cluster is also known[216].



(15)



(16)



(17)

Table 5 contains a number of organo-molybdenum and-tungsten complexes obtained by different methods of preparation. $[M(CO)_4L_4]$ complexes were obtained by the reaction of $[M(CO)_6]$ with Ph_3PO in toluene[194]. The monosubstituted complex, $[W(CO)_5L]$ $[L = Ph_2P(O)CH_2CH_2PPh_2]$ was obtained from the filtrate of the reaction of $[W(CO)_5(Ph_2PCH_2CH_2PPh_2)]$ with $K_2[PtCl_4]$[196]. However, this complex has no W—O bond; the ligand binds through the Ph_2P group. Trisubstituted $[M(CO)_3L_3]$ complexes were obtained either from the reaction of $[(C_7H_8)Mo(CO)_3]$ with Ph_3PO under a nitrogen atmosphere or from $[M(CO)_6]$ and L in a light petroleum–benzene mixture[201]. The reaction of $[Mo_2(CO)_6(OH)_3H_3]$ with Ph_3PO gave $[Mo(CO)_3L_3]$[200]. These trisubstituted derivatives, being unstable to air, must be kept under a nitrogen atmosphere[195,199].

The X-ray analysis of octahedral $[W(CO)_5L]$ $\{L = Ph_2P(O)(CHPPh_3)\}$ showed that the W—C bond *trans* to W—O was shorter than the other W—C bonds (1.949 Å versus average 2.025 Å)[198]. Similarly, an X-ray study of $[W(CO)_5L]$ $\{L = Ph_2P(O)NPPh_3\}$ showed W—O rather than W—P bonding[197]. Kinetic studies of ligand substitution (L by CO) revealed the high *trans* effect of $Ph_2P(O)NPPh_3$, which was similar to an anionic oxygen donor atom.

Thermal studies of $[M(CO)_nCl_2L_2]$[202,203] have shown that the carbonyl groups are lost in one step, unlike the multiple steps required for the ligand L. Tungsten complexes showed higher thermal stability than molybdenum complexes. Further, the stability based on the nature of the ligand was found to decrease in the order $L = Ph_3P > Ph_3As > Ph_3PO$[202]. Methyltungsten(V) complexes were stable[210] and ^1H NMR revealed that the Me group was never *trans* to a W=E bond (E = O, S, Se)[208]. ^{95}Mo and ^{183}W NMR studies of $[M(S_2CNEt_2)_2(CO)_2L]$ ($L = Ph_3PO$) showed that the adduct participates in a dynamic equilibrium with $[Mo(S_2CNEt_2)(CO)_2]$[206].

e. Complexes of the manganese Group (VIIB). Several complexes of mangenese(II) are known, some of which are listed in Table 6. Although the complexes can be formed by direct reaction of a phosphine oxide with a manganese salt, the higher thermodynamic stability of the Mn—O bond results in phosphine complexes such as $[MnX_2(PR_3)]$ ($R_3 = Et_3$, Me_3, Ph_3) being converted into the corresponding phosphine oxide complexes in the presence of air[240,241]. The existence of a dioxygen complex, namely $[MnBr_2(O_2)L]$ ($L = Me_3P$), was detected in the solid state, but it undergoes irreversible transformation to $[MnBr_2(OPMe_3)]$[242]. Interestingly, the air oxidation of an ethanol

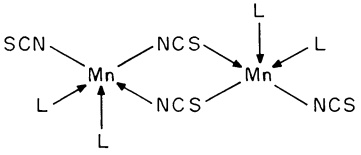
TABLE 6. Complexes of the manganese Group (VIIB)

	Complex	L	Ref.
A	(i) $[MnX_2L_2]$ ($X = Cl, Br, I, NO_3$)	Ph_3PO, p-Tol_3PO, Bz_2PhPO, Bz_3PO	217–226
	(ii) $[MnCl_2L_2]$	$RCH_2P(O)Me_2$ ($R = Cl, MeO, PhO$)	227
B	(i) $[MnL_4](ClO_4)_2$	Bu_3PO	137
	(ii) $[MnI_2L_4]$	Ph_3PO	228
	(iii) $[MnL_4(OClO_3)](ClO_4)$	Ph_3PO, Ph_2MePO, Me_3PO	228–232
	(iv) $[MnL_4(BF_4)_2]$	Ph_3PO	233
	(v) $[MnL_5](BF_4)_2$	Me_3PO	234
	(vi) $[MnL_n(NCS)_2]$	Ph_3PO, $PhMe_2PO$, Pr_3PO, Bu_3PO ($n = 1$–4)	228, 235–237
	(vii) $[MnA_2L_2]^a$	Bu_3PO	238
	(viii) $[Mn(NCSe)_2L_4]$	Ph_3PO	239

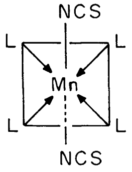
^{a}HA = Hhfa.

solution of $[Mn(CNR)_4L_2][MnBr]$ ($R = Bu^t$, $L = Me_2PhP$) gave a mixed phosphine–phosphine oxide complex, $[Mn(CNR)_4L_2][MnBr_3L']_2$ ($L' = Me_2PhPO$) with a *trans*-octahedral cation and a tetrahedral anion[243]. X-ray diffraction showed distorted tetrahedral structures for $[MnX_2(OPPh_3)_2]$ (X = Cl, I) complexes[217,223].

X-ray analyses of $[Mn(NCS)_2L_2]$ (**18**) and $[Mn(NCS)_2L_4]$ (**19**) ($L = Ph_3PO$) have been reported[235]. In complex **18** the geometry about manganese is square-pyramidal with Ph_3PO in the axial positions. Complex **19** has a *trans*-octahedral structure. The magnetic moments suggest polymeric structures for $[MnL_n(NCS)_2]$ ($n = 1, 3$) complexes with antiferromagnetic interactions. An interesting feature of thiocyanate complexes of manganese(II) is that when $n = 3$ or 4, the complexes react reversibly with SO_2 forming $[MnL_n(NCS)_2(SO_2)]$, whereas there is no similar reaction for $n = 1$ or 2. Dilute solutions of $[MnL_4(NCS)_2(SO_2)]$ effect the air oxidation of SO_2 to H_2SO_4, which was confirmed by X-ray analysis of the isolated product, $(Ph_3PO)(Ph_3POH)(HSO_4)$.



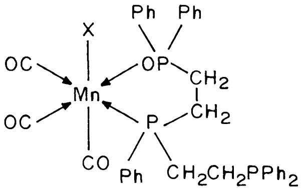
(18)



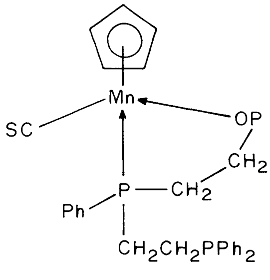
(19)

Like the thiocyanate complexes, manganese(II) iodide also formed an SO_2 complex, *trans*-$[MnL_4(SO_2)_2]I_2$ ($L = Ph_3PO$), with Mn—OSO bonding[244]. It displayed reversible loss of SO_2 to form $[MnL_4(SO_2)I_2]$.

Ultraviolet irradiation of an equimolar mixture of $[(cp)Mn(CO)_3]$ and $Ph_2P(CH_2)_2PPh_2$ in benzene or cyclohexane gave $[(cp)Mn(CO)_2L]$ $\{L = Ph_2PCH_2CH_2P(O)Ph_2\}$[245]. Similarly, oxidation of $[Mn(CO)_3LX]$ ($\{X = Br, I; L = PhP(CH_2CH_2PPh_2)_2\}$ with O_2 gave *fac*-$[Mn(CO)_3L'X]$ (**20**)[246]; photochemical reaction of $[(cp)Mn(CS)L]$ with ozone gave $[(cp)Mn(CS)L']$ (**21**)[247]. It may be noted that Mn—CS bonding is stronger than Mn—CO bonding since reaction of $[(cp)Mn(CO)_2(CS)]$ with L gave $[(cp)Mn(CS)L]$ and not $[(cp)Mn(CO)L]$.

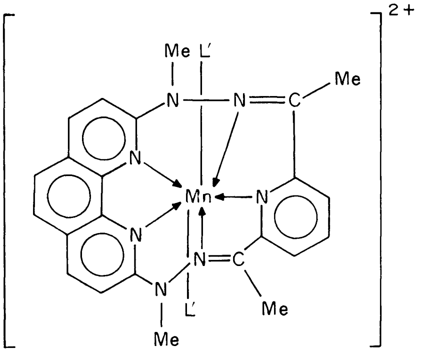


(20)



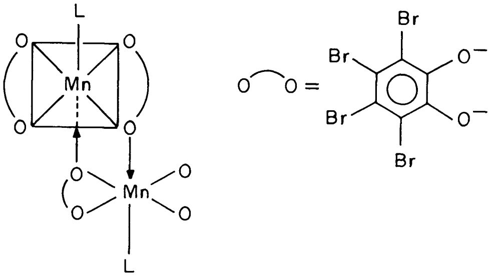
(21)

Salt-like mixed-valence complexes of manganese carbonyls of the type $[Mn^{II}LX]$[*cis*-$Mn^{I}(CO)_4X_2]$ ($X = Cl, Br, I$; $L = Ph_3PO$) have been reported[248,249]. X-ray study of the iodo complex showed a square-pyramidal cation and a *cis*-octahedral anion[248]. In $[Mn(CO)_5(CH_2P(O)Ph_2)]$ there was no coordination by the PO group[250a] but the possibility of intermolecular coordination by PO when a carbonyl group is replaced promises further activity in this type of complex. A seven-coordinate complex, $[MnLL'_2](BF_4)_2$ (**22**) (L′ = Ph_3PO; L = quinquedentate macrocycle), has been reported[250b].



(**22**)

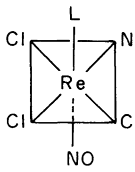
Manganese(III) chloride and nitrate form air-stable 1:2 and 1:3 complexes, MnX_3L_n (X = Cl, n = 2,3; X = NO_3, n = 2)[251-53]. Similarly, the manganese(III) tetrabromocatecholate complex $K[Mn(Br_4C_6O_2)_2L]H_2O \cdot Me_2CO$ (L = Ph_3PO) has been reported[254] and X-ray analysis showed that the dianion $Br_4C_6O_2^{2-}$ chelates to manganese in a planar arrangement with Ph_3PO bonded to the apical site. The sixth site of the octahedron is occupied by the catecholate oxygen of an adjacent complex, leading to the formation of a dimer (**23**).



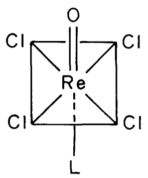
(**23**)

Rhenium(III) halides gave $[ReX_3L_n]$ (X = Cl, Br; n = 2,3; L = Ph_3PO) complexes[255-257]. The complexes with Re=O bonds, such as $[ReOX_3L_2]$ (X = Cl, Br; L = Ph_3PO, Et_2PhPO, Ph_2EtPO) and $[ReO(OEt)Cl_2L_2]$ (L = Ph_3PO)[258,259] were obtained via inner-sphere oxidation of the coordinated phosphine ligands on thermal heating. However, direct reaction of K_2ReOX_5 with Ph_3PO also gave the same products[259a]. Air oxidation of the monomers $[ReX_3(NCR)(PPh_3)_2]$ (R = alkyl; X = Cl, Br) gave $[ReOCl_3L(Ph_3P)]$ (L = Ph_3PO)[260]. Similarly, reaction of the dimer $[ReCl_3(NR)L]_2$ (L = Ph_3P; R = arylimido) with O_2 gave $[ReCl_3(ONR)(OPPh_3)]$ and $[ReCl_4(NR)(OPPh_3)]$ as a side-product. It required milder conditions than those needed for the reaction of $[ReCl_3(NR)(PPh_3)_2]$ with O_2 (R = p-MeC_6H_4)[261].

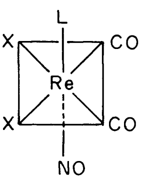
The complexes $(HPPh_3)_2$ $[ReX_6]$ (X = Cl, Br) lost HX on heating and formed $[ReCl_4L_2]$ and $(HPPh_3)$ $[ReLBr_5]$ (L = Ph_3PO)[262a]. Similarly, $[ReCl_4L_2]$ was formed on heating a solution of $(HPPh_3)_2[ReCl_6]$ in acetone in the presence of HCl[262b]. Further, the inner-sphere oxidation of $[Re(PPhEt_2)Cl_4]$ gave $[Re(OPPhEt_2)_2Cl_4]$[263]. Several other rhenium complexes reported are as follows: (a) $[ReCl_3(OPPh_3)_2(ONAr)]$ formed by the oxidation of $[ReCl_3(PPh_3)_2(ArN)]$ with O_2 in boiling toluene[264]; (b) $[ReCl_3(NO)(NPPh_3)(OPPh_3)]$ (**24**) prepared by the reaction of $[ReCl_3(NO)_2]$ and Ph_3PO in CH_2Cl_2(^{31}P, X-ray)[265]; (c) $[(cp)Re(NO)(PPh_3)(OPPh_3)]X$ ($X = BF_4$, PF_6) formed from $[(cp)Re(NO)(PPh_3)ClCH_2Cl]^+$ and Ph_3PO (here CH_2Cl_2 is coordinated)[266]; (d) $[ReOCl_4(OPPh_3)]$ (**25**) formed from $[ReOCl_4]$ and Ph_3PO[267]; (e) $[Re(CO)_3L_2X]$ (X = Cl, Br, I)[268]: (f) $[Re(CO)_2(NO)X_2(OPPh_3)]$ (X = Br, I) (**26**) prepared by the reaction of the halogen-bridged dimer, $[Re(CO)_2(NO)X_2]_2$ and Ph_3PO[269]; (g) $[Re_2X_4(OAc)_2L_2]$ (X = Cl, Br) (**27**) formed from $[ReX_2(OAc)]$. H_2O and Ph_3PO[270–272]; (h) deoxygenation of $[MeReO_3]$ with Ph_3P in the presence of Me_3SiCl gave a 70% yield of the oxygen bridged complex, $[MeCl_2L(O)Re—O—Re(O)Cl_2LMe]$ (**28**)[273a], and (i) $[ReCl_4(NO)(OPPh_3)(NO)(MeCN)]$ was prepared from $[ReCl_5(NO)]$ and Ph_3P in acetonitrile[273b]; Structures **24** and **28** were confirmed by X-ray analysis[265,273]. The Re—N and P—N bond distances suggested double bond character in the Re—$NPPh_3$ bond in **24**. The Re—Re bond in **27** is fairly strong and dissociates above 320 °C. No loss of ligand takes place below 300 °C.



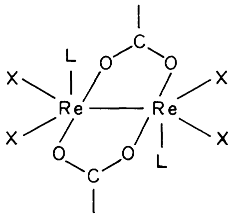
(24)



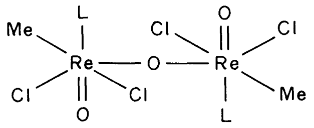
(25)



(26)



(27)



(28)

f. Complexes of the iron, cobalt and nickel Group (VIII)

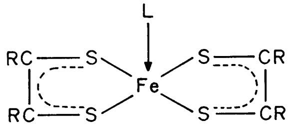
i. Iron sub-Group. Several iron(II) complexes have been reported; $[FeLX_2]$($X = Br$, SO_3F, $L = Ph_3PO$)[63,274]; $[FeL_2X_2]$ {X = Cl, Br; $L = Ph_3PO$, $Me_2P(O)CH_2R$ (R = Cl, OMe, OPh), HFA, Bu_3PO, SO_4, Ph_3PO}[227,238,275,276]; $[FeL_4X]X$ ($X = OClO_3$; $L = Me_3PO$, Ph_3PO, $MePh_2PO$)[231,232]; $[FeL_4X_2]$ ($X = OClO_3$; $L = Bu_3PO$, Ph_3PO, BF_4, I_3, Ph_3PO)[137,230,233,277–279]; $[FeL_n][Fe_2(CO)_8]$ ($n = 2,3$; $L = Ph_3PO$)[280]. A number of complexes have been obtained indirectly: $[Fe(OPPh_3)_4](ClO_4)_2$ was obtained from the reaction of iron(III) perchlorate with Ph_3P, which involved reduction of Fe^{III} to Fe^{II} and oxidation of Ph_3P to Ph_3PO[279]; similarly, $[Fe(OPPh_3)_4(I_3)_2]$ was obtained[278] from the reaction of either as iron(II) or an iron(III) salt with iodide ions and Ph_3P in the presence of O_2.

X-ray studies have not been reported for any of the above complexes. However, based on Mössbauer studies, distorted tetrahedral structures were suggested for the complexes

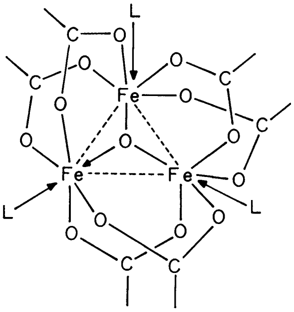
$[FeL_2X_2]^{275}$. For complexes $[FeL_4X]X$ square-pyramidal and for $[FeL_2(hfa)_2]$ $(L = Bu_3PO)^{238}$ and $[FeL_4X_2]^{137,230,233,277-279}$ octahedral structures have been suggested. A thermal study of $[FeL_2(hfa)_2]^{238}$ revealed that the chelate ring formed by the hfa^- anion is stable in the gas phase. However, hfa^- changes to the mononuclear mode and at higher temperatures loss of Bu_3PO takes place with rupture of the M—O bonds. From Mössbauer studies[275], an interesting observation is that Cl^- and Ph_3PO have a similar ligand field effect.

Two iron(II)-phthalocyanine(HPc) complexes, [Fe(Pc)(CO)L] and $[Fe(Pc)(L_2)]$ $(L = Ph_3PO)$, are known[281]. The replacement of Ph_3PO in $[Fe(Pc)(Ph_3PO)_2]$ by CO led to a decrease in the quadrupole splitting and isomer shift values, consistent with a decrease in the main axial bond distances on carbonylation and a concomitant increase in s-electron density along the z-axis. Similarly, a high-spin iron(III)–porphyrin complex, $[FeL_2(A)](ClO_4)(H_2A$ = tetraphenylporphyrin), has been reported; it exhibited certain properties similar to those of aquomethaemoglobin[282].

A few square-pyramidal iron–dithiolene complexes such as $(Bu_4N)[Fe(S_2C_2R_2)_2L]$-$(R = CN, CF_3; L = Ph_3PO$; **29**) have been reported[283–285]. Reaction of $(Bu_4N)_2[Fe_2$-$(S_2C_2R_2)_4]$ with Ph_3P in the presence of O_2 gave the same product. Here activation of molecular oxygen by the iron–dithiolene complex takes place. In contrast, cobalt–dithiolene complexes were not effective in activating the oxidation of Ph_3P.

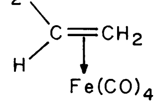


(29)



(30)

A trinuclear mixed-valence complex, $[Fe^{II}Fe^{III}_2(O)(O_2CCF_3)_6(OPPh_3)_3]$ (**30**) is known[286]; Mössbauer study revealed octahedral environments about each iron centre. An oxo complex, $[L_4FeOOFeL_4{\cdot}2H_2O]X_4$ $(X = ClO_4; L = Ph_3PO)$ was obtained when $[FeL_4](ClO_4)_2$ was reacted with H_2O_2, m-$C_6H_4C(O)OOH$ or other oxidants in acetonitrile[287]. The same material was obtained by the addition of H_2O_2 and two molar hydroxide ions to $[FeL_4](ClO_4)_3$ in acetonitrile. Reaction of vinyldiphenylphosphine oxide with $[Fe_3(CO)_{12}]$ did not give substituted products like those formed with Ph_3P; instead, a π-bonded complex (**31**) was obtained[315].



(31)

Several other complexes of iron(III) are known: $[FeCl_3L]$ $(L = Ph_3PO)^{60}$, $[FeX_3L_2]$ $\{X = Cl, Br, NO_3, NCS; L = Ph_3PO, Ph_2P(O)CH{=}CH_2, Bz_2PhPO, Bz_3PO\}^{66,289-292}$,

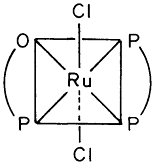
$[FeL_4](ClO_4)_3$ ($L = Ph_3PO$, Me_3PO, Bz_2PhPO, Bz_3PO)[229,232,292,293], $[Fe(NCS)_3L_3]$ ($L = Ph_3PO$, Cy_3PO, Bu_3PO)[294], $[Fe(NCS)_3(OPPh_3)_2]$[291], $[(FeCl_2L)_2O]$ ($L = Ph_3PO$)[295], $[Fe(OR)_3L]$ ($R = Me_3Si$, $ClCHCH_2$, Cl_3CCH_2; $L = Ph_3PO$)[296–299], $[Fe(NCS)_3L_2(HgCl_2)_3]$[300] and $[Fe(NO_3)_2XL_2]$ ($X = Cl$, I; $L = Ph_3PO$)[301].

In general, these complexes were obtained by the direct reaction of the metal salt with the ligand, but some complexes were obtained indirectly. For example, reaction of $FeBr_2$ with Ph_3P in acetonitrile at 80 °C in the presence of O_2 gave $[FeBr_3(OPPh_3)_2]$[289]. Similarly, oxidation of iron with Ph_3PO and CCl_4 in MeCOEt gave $[Fe(Ph_3PO)_2Cl_3]$[290]. Passing O_2 through a solution or suspension of $FeCl_2$, $FeSO_4$, etc., or iron powder in acetonitrile containing KCl or HCl, etc., in the presence of Ph_3P gave $[FeX_3(OPPh_3)_2]$ ($X = Cl$, Br, NCS)[302,303].

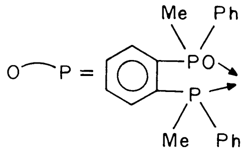
The binuclear complex $[(FeCl_2L)_2O]$ ($L = Ph_3PO$)[295] was obtained from the reaction of either $[FeCl_2(OPPh_3)_2]$ or $[FeCl_2(PPh_3)_2]$ with O_2 in benzene[295]. Mixed anion complexes, $[Fe(NO_3)_2XL_2]$[301] were obtained from the reaction of $[Fe(NO_3)_2X]_2$ ($X = Cl$, I) with PPh_3 and O_2 or Ph_3PO; these represent the first examples of transfer of 'O' from NO_3 to Ph_3P in cyclohexane[301]. X-ray analysis for $X = Cl$ has shown that the NO_3^- is asymmetrically bonded[301]. The reaction of $[Fe(NCS)_3(OPPh_3)_2]$ with $HgCl_2$ gave $[Fe(NCS)_3(OPPh_3)_2(HgCl_2)_3]$ involving an Fe—NCS—Hg linkage. Each of the three NCS groups bonds to an $HgCl_2$ molecule[300].

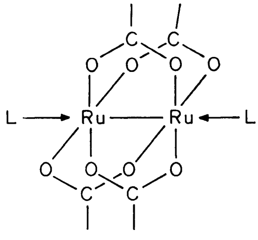
Iron(III) halide complexes, $[FeX_3L_2]$ ($X = Cl$, Br; $L = Ph_3PO$, etc.), have been shown to exist as ionic complexes, $[FeL_4X_2][FeX_4]$, with a *trans*-octahedral cation and a tetrahedral anion[291,292,304], as confirmed by X-ray analysis[304] of $[FeCl_2(OPPh_3)_4][FeCl_4]$.

Reaction of $[Ru(CO)_4X_2]$ with Ph_3PO formed monosubstituted octahedral complexes, $[Ru(CO)_3X_2L]$[305]. Inner-sphere oxidation of the coordinated Ph_3P in $[Ru(PPh_3)_3Cl_2]$ gave $[Ru(OPPh_3)_3Cl_2]$[306]. Some mixed-ligand complexes of ruthenium(II) that have been reported are $[RuCl_2LL']$ ($L = o\text{-}C_6H_4\{PMePh\}_2$; $L' = o\text{-}C_6H_4\{PMePh\}\{OPMePh\}$)[307], $[Ru(NO_3)_3(NO)(OPPh_3)(PPh_3)]$[308] and $[(bipy)(py)Ru(OPPh_3)]^{2+}$ [309]. X-ray analysis of $[RuCl_2LL']$ has shown a *trans*-octahedral geometry[307] with an unusually short Ru—P distance *trans* to O (2.219 versus 2.310–2.346 Å for Ru—P *trans* to one another (**32a**). In the bipyridyl complex, transfer of oxygen from $[(bipy)_2(py)RuO]^{2+}$ to Ph_3P takes place[309]. In the nitrosyl complex $[Ru(NO)(NO_2)L_2(OH)]$ ($L = n\text{-}Bu_3PO$)[310], L lies *trans* to NO and the *trans* effect of L decreases in the order $L\text{-}Bu^n_3PO > py > NH_3 > H_2O$. A mixed-valence complex, $[Ru^{II}Ru^{III}(\mu\text{-}OAc)_4(OPPh_3)_2](BF_4)\cdot CH_2Cl_2$ was obtained from the reaction of $[Ru_2(\mu\text{-}OAc)_4(thf)BF_4$ and Ph_3PO[311a]. Other mixed-valence complexes that have been reported include $[Ru_2(\mu\text{-}O_2CCH_3)_4(OPR_3)_2](PF_6)$ ($R = H$, F, Cl, etc.). X-ray analysis of $[Ru_2(\mu\text{-}O_2CCH_3)_4(OPPh_3)_2\cdot ClCH_2CH_2Cl$ has shown a dimeric structure (**32b**) with Ru—Ru bonding and Ph_3PO in the terminal positions[311b].



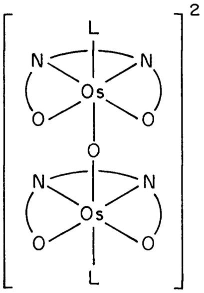
(32a)



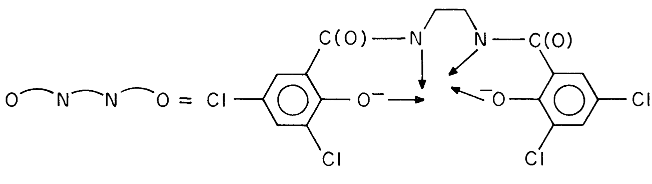


(32b)

Reduction of $[Os(OEP)O_2]$ by Ph_3P in CH_2Cl_2 gave $[Os(OEP)L_2]$ ($L = Ph_3PO$, H_2OEP = octaethylporphyrin)[312]. An X-ray study has shown a *trans*-octahedral structure with normal Os—O (from Ph_3PO) bonding (2.036 Å). Similarly, *cis* and *trans* isomers of $[\mathrm{Os(bipy)_2L_2}]^{2+}$[313] and $[\mathrm{Os}(\eta^4\text{-CHBA-DCB})\mathrm{L}]$ $\{\mathrm{L} = \mathrm{Ph_3PO}$, $\mathrm{H_4CHBA\text{-}DCB}$ = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene$\}$[314] have been reported. In the latter complex, the *trans* isomer contains planar amido-N-ligands and the *cis*-α-isomer contains non-planar amido-N-ligands. Finally, treatment of $\mathrm{K_2[OsO_2(OH)_4]}$ with $[\text{2-OH-3,5-}\mathrm{Cl_2C_6H_2CONHCH_2}]_2$ in methanol followed by reduction with $\mathrm{Ph_3P}$ in thf gave complex **33**[315].



(33a)



(33b)

ii. Cobalt sub-Group. Table 7 contains a number of complexes of cobalt(II) halides (or other anions). Generally, the complexes involve 1:2 metal: ligand ratios. A few 1:4 complexes, *trans*-$[\mathrm{CoL_4X_2}]$ ($\mathrm{X} = \mathrm{Cl}$, $\mathrm{ONO_2}$; $\mathrm{L} = \mathrm{R_3PO}$; $\mathrm{R} = \mathrm{Bu}^n$, $\mathrm{CH_2OH}$) are also known[234]. A number of different routes have been reported for their preparation: (a) direct reaction of metal salt with a ligand; (b) reaction of a metal salt with a phosphine oxide ligand in the molten state, e.g. $[\mathrm{CoCl_2(OPPh_3)_2}]$[351,352]; (c) autoxidation of cobalt(II)–alkylphosphine complexes, $[\mathrm{CoX_2L_2}]$ ($\mathrm{L} = \mathrm{Et_3P}$, $\mathrm{X} = \mathrm{Cl}$, Br, I; $\mathrm{L} = \mathrm{Ph_3PO}$, $\mathrm{X} = \mathrm{Cl}$ in an organic solvent[347]; (d) inner-sphere oxidation of the complexes using $\mathrm{H_2O_2}$, e.g. $[\mathrm{CoBr_2(PPh_3)_2}]$[348], or by thermal heating, e.g. $[\mathrm{Co(PPhR_2)_2X_2}]$ $[\mathrm{Co(PPh_2R)_2X_2}]$ ($\mathrm{X} = \mathrm{Cl}$, Br, I; $\mathrm{R} = \mathrm{Et}$, Pr, Bu)[349] and $[\mathrm{Co(PPh_3)_2X_2}]$ ($\mathrm{X} = \mathrm{Cl}$, Br, I)[350]; (e) oxidation of

TABLE 7. Complexes of the cobalt sub-Group

Complex	X	L	Ref.
A $[\mathrm{CoX_2L_2}]$	Cl, Br, I, NCS, $\mathrm{NO_3}$	L[a]	73, 230, 234, 316–336
	Cl, I. NCS	$\mathrm{RPh_2PO}$[b]	337
B $[\mathrm{CoX_2L(PPh_3)}]$	Cl, Br, I, NCS	$\mathrm{Ph_3PO}$	326, 328, 338–341
C $[\mathrm{CoX_2L}_n]$	(i) $\mathrm{(NC)_2CC(O)NH_2}$[c], $\mathrm{NCNC(O)NH_2}$[d]	$\mathrm{Ph_3PO}(n = 2)$	341
	(ii) hfa	$\mathrm{Bu_3PO}(n = 2)$	238, 342
	(iii) tta	$\mathrm{R_3PO}(n = 1)$	343
	(iv) CN	$\mathrm{Me_3PO}(n = 1)$	344
		$\mathrm{R_3PO}(\mathrm{R} = \mathrm{Et, Bu}$, Ph; $n = 0.5)$ α	344
	(v) $\mathrm{SO_3CF_3}$	$\mathrm{Bu_3PO}$, $\mathrm{Ph_3PO}$ ($n = 4\text{–}6$)	345
	(vi) $\mathrm{CF_3CH_2O}$	$\mathrm{Ph_3PO}(n = 1)$	346
D $[\mathrm{CoClXL}]$	$\mathrm{CF_3CH_2O}$	$\mathrm{Ph_3PO}$	346

[a] $\mathrm{L} = \mathrm{Me_3PO}$, $\mathrm{Et_3PO}$, $\mathrm{Pr^i_3PO}$, $\mathrm{Bu^n_3PO}$, $\mathrm{Ph_3PO}$, $\mathrm{Cy_3PO}$, $(p\text{-}\mathrm{MeC_6H_4})_3\mathrm{PO}$, $\mathrm{Bz_3PO}$.
[b] R = 2-pyridylmethyl.
[c] Carbamyldicyanomethanide.
[d] Carbamylcyanamide.

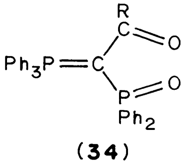
cobalt metal with Ph$_3$PO in a mixture of CCl$_4$ and MeCOEt, e.g. preparation of [CoCl$_2$(OPPh$_3$)$_2$][290]; and (f) replacement of Ph$_3$P from its complexes of Ph$_3$PO, e.g. [CoX$_2$(OPPh$_3$)$_2$] obtained from [CoX$_2$(PPh$_3$)$_2$] and Ph$_3$PO (X = I, NCS)[338,340]. Routes b–f are less common, although interest persists in route d.

X-ray analyses of [CoCl$_2$(OPMe$_3$)$_2$][319] and [Co(O$_2$NO)$_2$L$_2$] (L = Me$_3$PO, Ph$_3$PO)[353,354a] have shown them to involve distorted tetrahedral and *trans*-octahedral structures, respectively. The angles at oxygen, i.e. P—O—Co lie between 133 and 140°[353a]. A nitro complex, [CoL$_2$(NO$_2$)$_2$] (L = Ph$_3$PO), presumably has a similar structure[355]. Powder X-ray data have been reported for some cobalt(II) complexes, viz. [CoCl$_2$L$_2$] (L = Ph$_3$PO, BzPh$_2$PO, Bz$_2$PhPO, Bz$_3$PO)[320,328] and [Co(NCS)$_2$L$_2$] (L = Ph$_3$PO, Ph$_2$BzPO)[356]. The nitrato complexes [M(O$_2$NO)$_2$(OPPh$_3$)$_2$] (M = Co, Zn) are isomorphic[357]. The single-crystal ESR and polarized electronic spectra of [CoCl$_2$(OPPh$_3$)$_2$] have shown highly distorted tetrahedral geometry about the cobalt centre (g values: $g_1 = 5.67$, $g_2 = 3.59$ and $g_3 = 2.16$)[318]. The X-ray analysis of [CoCl$_2$L$_2$] {L = Ph$_2$P(O)py, py = 2-pyridyl} has shown a distorted octahedral structure with ligand L chelating via O and N[354b].

A 3:4 and 1:1 complex of cobalt(II), viz. [CoL$_2$X]$_2$[CoX$_4$] {X = Cl, Br; L = Me$_2$NCH$_2$P(O)Ph$_2$} and [Co(LH)Cl$_3$] {LH$^+$ = Ph$_2$P(O)CH$_2$CH$_2$N$^+$Me$_2$(H)}, have also been reported[358]. The cation [CoL$_2$X]$^+$ is 5-coordinate and the anion tetrahedral. The latter complex was obtained from CoCl$_2$ and Ph$_2$P(O)CH$_2$CH$_2$NMe$_2$ and the origin of the protonation of NMe$_2$ is not known. [CoCl$_3$(LH)] has a tetrahedral structure with LH coordinating via its PO group. Reaction of CoCl$_2$ with Ph$_2$P(O)CH$_2$NMe$_2$ in the presence of HCl gave [(LH)$_2$CoCl$_4$]. Similarly, [Co(NCS)$_2$L$_2$] {L = Me$_2$N(CH$_2$)$_n$P(O)Ph$_2$; $n = 1,2$} are also known. For $n = 1$ a distorted octahedral structure and for $n = 2$ tetrahedral geometry have been suggested. In the latter complex there was no coordination by PO groups[358].

The mixed-ligand complexes [CoX$_2$LL′] (Table 7) were obtained from the reaction of [CoX$_2$(PPh$_3$)$_2$] (X = Cl, Br, I, NCS) and Ph$_3$PO. The lability of the Co—PPh$_3$ bond was high for X = NCS. Complexes C and D (Table 7) have been poorly studied so only a few comments can be made. Thermal studies on [Co(hfa)$_2$(OPBu$_3$)$_2$][238,342] have shown that it is stable in the gas phase. Before decomposition on heating, the anion hfa first changes from the bidentate to the monodentate form. In the solution phase three forms of the hfa complex were identified[342].

The interaction of CoCl$_2$ with L (L = Ph$_3$PO, Ph$_2$Bu^{n}PO, topo, etc.) was studied in solution phase[227,359–363]. Although normally the complexes formed had a 1:2 stoichiometry, complexes with other stoichiometries, viz. 1:1, 1:3 and 1.4, were also formed in some cases, for example in the CoCl$_2$–topo system[360,364]. Some other observations that have been noted include the following: (a) Co—O bonds were more covalent when R was alkyl than when R was an aryl group[359,362,363]; (b) the ligand-field effects of various ligands were similar[359]; and (c) the complex-forming tendency in different solvents was in the order MeNO$_2$ > (thf + CCl$_4$) > acetate ester > BuOH > Me$_2$CO > MeCN. Finally, the formation of [CoLCl$_2$] (L = **34**) was also established from solution-phase studies[365].

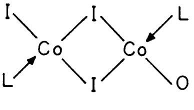


(34)

Cobalt(II) perchlorate and fluoroborate also form several complexes of the type [CoL$_4$](ClO$_4$)$_2$ (L = Bz$_3$PO, Bz$_2$PhPO, BzPh$_2$PO, Bu$_3$PO, Ph$_3$PO[137,327,331,334],

$[CoL_4](BF_4)_2$ ($L = R_3PO$; R = Et, Pr, Bu)[234], $[CoL_6](ClO_4)_2$ ($L = Cy_3PO$)[229,230], $[CoL_4X_2]$ {$L = Ph_3PO$, BF_4, Me_3PO, Ph_3PO[230,232,233,366] $(p\text{-}Me_2NC_6H_4)_3PO$; $X = ClO_4$[229]} and $[CoL_4X]X$ ($X = BF_4$, ClO_4; $L = Me_3PO$, $MePh_2PO$)[231,234]. The complexes $[CoL_4]^{2+}$, $[CoL_4X]^+$ and $[CoL_4X_2]$ have been assigned tetrahedral, square-pyramidal and octahedral geometries respectively, but an X-ray study is needed to confirm coordination by either the BF_4^- or ClO_4^- anions. Reaction of $[Co(PMe_3)_4](Ph_4B)_2$ in acetonitrile gave $[Co(NCCH_3)_2(OPMe_3)_4](Ph_4B)_2$ and its X-ray analysis showed a *trans*-octahedral cation[367]. An intermediate $[Co(PMe_3)_4(O_2)](Ph_4B)_2$ was also detected.

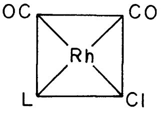
Dimeric cobalt(II) complexes, $[Co_2I_4L_2]{\cdot}2C_6H_6$($L = Ph_3PO$) and $[Co_2(CO)_6(R^1R^2P(O)(C{\equiv}CR^3)]$ ($R^1 = R^2 = Ph$; $R^3 = Me_3C$, Ph)[368,369] have been reported. The iodo complex was obtained from CoI_2 and Ph_3PO in O_2-free benzene. The same product was obtained from the reaction of the phosphine complex $[CoI_4(PPh_3)_2]$ with Ph_3PO. X-ray analysis of the iodo complex confirmed the dimeric structure **35** with C_6H_6 molecules lying in the lattice. There is antiferromagnetic coupling between the cobalt centres[368]. In the alkynephosphine oxide complexes, there is Co—O bonding and the alkyne groups are uncoordinated. Similarly, complexes of the type $[Co(OPBu_3)_4][Co(CO)_4]_2$, $[Co(OPMe_3)_6][Co(CO)_4]_2$[370] and $[Co_4(SPh)_6Cl_2(PPh_3)(OPPh_3)]$[371] have been reported. X-ray analysis of the Ph_3PO complex[371] showed that the $Co_4S_6Cl_2$ core is that of a nearly regular Co_4 tetrahedron inscribed in an irregular octahedron of bridging sulphur atoms, resulting in an adamantane-type cage. Cobalt(III) complexes, $[CoCl_3(OPPh_3)]$[60] and $[CoI_2L_2]I$ ($L = Cy_3PO$)[229] are also known. The iodo complex was obtained by oxidation of $[CoI_2L_2]$ with I_2 in ethanol.



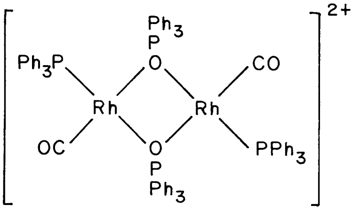
(35)

A number of rhodium(III) complexes have been reported: $[RhLCl]_n$, $[Rh(CO)_2LCl]$ ($L = Ph_3PO$)[372]; *cis*-$[RhCl(CO)_2L]$ (L = topo)[373]; *cis*-$[RhCl(CO)_2L]$ ($L = cy_3PO$)[374] $[\{Rh(HDMG)L\}_2O_2]$[375], $[Rh(cod)(OPR_3)(PPh_3)](ClO_4)$(R = Ph, substituted phenyl), $[Rh(cod)(OPR_3)_2](ClO_4)$, $[Rh(CO)_2(OPR_3)_2](ClO_4)$, $[Rh(CO)(OPR_3)_2(PPh_3)](ClO_4)$, $[Rh(CO)(OPR_3)(PPh_3)_2](ClO_4)$[376], $[Rh_2(\mu\text{-}OPR_3)_2(CO)_2(PPh_3)_2](ClO_4)_2$ and $[Rh_2(\mu\text{-}OPR_3)_2(cod)_2](ClO_4)_2$[376].

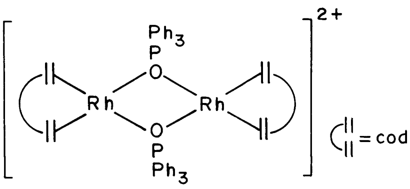
An X-ray study of *cis*-$[RhCl(CO)_2L]$($L = cy_3PO$)[374] has shown a *cis*-square planar structure about rhodium (**36**). Other complexes with same stoichiometry are believed to possess similar structures. $[Rh_2(\mu\text{-}OPR_3)_2(CO)_2(PPh_3)_2](ClO_4)_2$ and $[Rh_2(\mu\text{-}OPR_3)_2(cod)_2](ClO_4)_2$ complexes[376] are thought to possess bridging ligands (**37** and **38**).



(36)

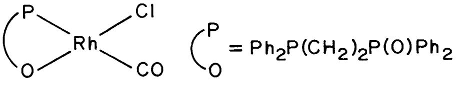


(37)

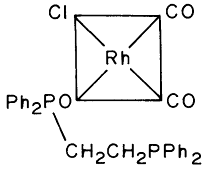


(38)

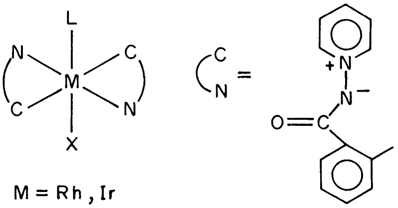
Thermal heating of solid samples of $[Rh(PPh_3)_3Cl]$, $[Rh(PPh_3)_3NO]$[377], $[RhL_3Cl_3]$ $\{L = Ph_2P(CF_3)$, $Ph_2PC_2F_5\}$[378] and $[Rh(CO)L(PPh_3)_2(ClO_4)$ ($L = py$, γ-picoline, etc.)[379] led to inner-sphere oxidation of PPh_3 to $OPPh_3$ forming corresponding phosphine oxide complexes. The ligand $Ph_2PCH_2CH_2P(O)Ph_2$ formed a rhodium(I) complex, *cis*-$[RhCl(CO)L]$ (**39**), which on reaction with CO gave a trace of *cis*-$[RhCl(CO)_2L]$[380] (**40**). The PO—Rh bond is stronger in **39** than in **40**. A complex $[Rh(NO_3)(NO)_2(OPPh_3)]$[381] was later reinvestigated and found to be $[Rh(NO_3)_2(NO)(Ph_3P)_2]$[382]. Rhodium(III) and iridium(III) complexes of stoichiometry $[RhL_2(OPBu_3)Cl]$ and $[IrL_2(OPPh_3)Cl]$ (**41**) ($L = C_6H_4CONR'$, R' = pyridino) have been reported[383]. The iridium complex reacted with CO reversibly forming $[IrL_2(CO)Cl]$.



(39)



(40)



(41)

iii. Nickel sub-Group. Nickel(II) forms several complexes as listed in Table 8. The complexes can be prepared by direct reactions as usual. However, complexes A can also be prepared by other routes: (a) inner-sphere oxidation of $[NiX_2L_2]$ by H_2O_2 ($X = Br$, I; $L = Ph_3P$)[348], air (X = halogen; $L = Et_3P$)[408], $NaClO_2$ ($X = Cl$; $L = Cy_3P$, Ph_3P)[389] and thermal heating ($X = Cl$, Br, I, NCS, $L = Ph_3P$, Ph_2EtP, $PhEt_2P$, Me_2PhP, etc; $X = NO_3$, $L = Et_2PhP$)[393,409–412] and (b) reaction of $NiCl_2$ with molten Ph_3PO[351,352]. $[Ni(NO_2)Cl(OPPh_3)]$ was obtained *in situ* from $[NiX_2L_2]$ and $NaNO_2$ and, on bubbling CO through the solution, $[Ni(NO)ClL_2]$ was formed. Here the CO has reacted with NO_2 to form CO_2 and NO. Further reaction of $[Ni(NO)ClL_2]$ with O_2 gave exclusively $[Ni(NO_2)XL_2]$[396]. Dimeric complexes (D) were obtained on treatment of $[NiX_2(PPh_3)_2]$ with NOCl in a benzene–cyclohexane mixture[398]. For $X = NCS$, the dimer $[Ni(OPPh_3)XCl]_2$ reacted with NOCl forming $[NiLCl_2]_2$[397].

Complexes A–C are suggested to have tetrahedral structures for X = halogen or NCS and octahedral structures for $X = NO_3$, hfa or tta[238,329,343,393]. For $L = Me_2PhPO$,

TABLE 8. Complexes of the nickel sub-Group

	Complex	X	L	Ref.
A	$[NiX_2L_2]$	Cl, Br, I, NO_3	Ph_3PO, Cy_3PO, Et_3PO, p-Tol_3PO	321, 322, 329, 348, 384–392
		Cl	L^a	392
		NO_3	L^b	393, 394
		Cl, Br	$(R_2NCH_2)_3PO$, $Ph_2P(O)CH{=}CH_2$, $Me_2P(O)CH_2R$ (R = Cl, MeO, PhO)	66, 227, 395
		Cl, I, NCS	RPh_2PO^c	337
		$(NC)_2CC(O)NH_2$	Ph_3PO	341
		hfa, tta	Bu_3PO, topo, Ph_3PO	238, 343
B	$[NiX_2L(Ph_3P)]$	Br	Ph_3PO	385
C	$[Ni(NO_2)XL_2]$	Cl	Ph_3PO	396
D	$[NiLXCl]_2$	NCS	Ph_3PO	397
		Cl, Br, NO_3	Ph_3PO	398
E	$[NiL_4X_2]$	Cl, l, NCS, NO_3	$(HOCH_2)_3PO$, Bu_3PO, Ph_3PO	228, 234
F	$[NiL_2X]_2[NiX_4]$	Cl, etc.	$Ph_2P(O)CH_2NMe_2$	357
G	$[NiCl_3(LH)]$	—	LH^d	357
H	$[NiX_2L_n]$	CF_3SO_3	Bu_3PO, Ph_3PO($n = 4$–6)	345
I	(i) $[NiX_2L_4]$	ClO_4	Et_3PO, Ph_3PO	137, 230, 322, 360, 399
	(ii) $[NiL_4]X_2$	ClO_4	Bu_3PO, $BzPh_2PO$	137, 401, 402
	(iii) $[NiL_4X]X$	ClO_4	Me_3PO, $MePh_2PO$	231, 232, 234, 403
	(iv) $[NiL_5]X_2$	BF_4	Me_3PO	234
	(v) $[NiX_2L_n]$	BF_4	Ph_3PO($n = 4,5$)	233
	(vi) $[NiL_2X]$	SO_4	Ph_3PO	276
J	(i) $[Ni(O_2CR)_2L]_2{}^e$	—	Ph_3PO	404, 405
	(ii) $[Ni(O_2CC_6H_4R)_2L]_2{}^f$	—	Ph_3PO	406
K	$[(C_6H_5)_2NiL_2]$	—	Ph_3PO	407

[a] $L = Ph_2EtPO$, Bz_2PhPO, $BzPh_2PO$, Bz_3PO.

[b] $L = Ph_2P(O)CH{=}C{=}CH_2$, $Me_2P(O)CH{=}C{=}CMe_2$, $Me_2P(O)C{\equiv}CPh$.

[c] R = 2-pyridylmethyl.

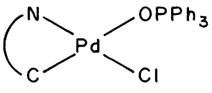
[d] $LH = Ph_2P(O)CH_2CH_2\overset{+}{N}HMe_2$.

[e] $R = Et$, Pr, $ClCH_2$, Cl_2CH, Cl_3C.

[f] $R = H$, 4-CH_3, 2-Cl, 4-NO_2.

Pr_2PhPO, Bu_2PhPO, Bu_3PO and X = Cl, Br, I, the A-type complexes are assigned a *trans*-square-planar geometry[411]. Various other structures that have been suggested are square-pyramidal for cations of complexes F[357] and for complexes I(iii) ($L = Me_3PO$, $MePh_2PO$)[231,232,403] and I(iv)[234], ligand-bridged square-pyramidal dimeric for complexes I(ii) with $L = BzPh_2PO$[400,401] and tetrahedral with $L = Bu_3PO$[137,402], halogen-bridged dimeric for complexes D, *trans*-octahedral for complexes E and carboxylate-bridged dimeric for complexes J. The carboxylate complexes J involve a metal–metal exchange interaction similar to that in copper(II) acetate. An increase in Cl substitution in the chloroacetate moiety decreased the magnetic interaction between the nickel centers[405]. In complex G, $[NiCl_3(LH)]$, the ligand $Ph_2P(O)CH_2CH_2\overset{+}{N}(H)Me_2$ binds to nickel(II) via the PO group only[357]. Only one diorganonickel(II) complex, $[Ni(C_6F_5)_2(OPPh_3)_2]$[407], is known (Table 8).

Air oxidation of diamagnetic $[Pd(PPh_3)L_2]$ ($L = Ph_2PC_6H_4X$; X = F, Cl, Me, MeO, CO_2H) gave a paramagnetic species $[Pd(OPPh_3)L_2]$[413]. Similarly, inner-sphere oxidation of *trans*-$[PdL_2X_2]$ ($L = Ph_3P$, Ph_2EtP; X = Br, I) and *cis*-$[Pd(Ph_2EtP)_2Cl_2]$[414] gave the corresponding phosphine oxide complexes. A series of palladium(II) nitrate complexes, $[Pd(NO_3)_2L_2]$ ($L = R_3PO$, R = Pr, Bu, Ph, isopentyl) were prepared by extraction from HNO_3 solutions of the metal salt[415]. Other palladium(II) complexes, including those of organopalladium(II) are $[(PdCl_2)_4L_2]$ $\{L = (o\text{-}XC_6H_4)_2PhP(O)$; $X = PhC{\equiv}C\}$[416], $[PdL(OPPh_3)Cl]$ (**42**, $HL = C_6H_4CONR'$; R′ = pyridino)[383], $[Pd(ONO_2)_2(OPPh_3)PPh_3]$[417], $[Pd(C_6F_5)_2(OPPh_3)_2]$[418] and $[Pd(C_6F_5)(AsPh_3)_2(OPPh_3)](ClO_4)$[419]. The X-ray crystal structure of the nitrate complex has shown a *trans*-square-planar structure[417]. *cis*-$[PdL_2]X_2$ complexes $\{X = NO_3, PF_6; L = Ph_2P(O)CH_2PPh_2\}$[420] have also been reported.



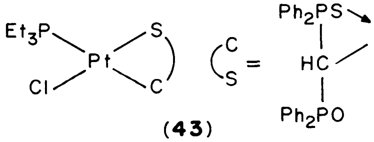
C⌒N as in **41**

(42)

The monodentate ligand Ph_3PO forms complexes with platinum(II) of the type (A)$[PtRL_2L'](ClO_4)$($R = C_6F_5$, Ph; $L = Et_3P$, Ph_3AS; $L' = Ph_3PO$)[421-424] and (B) $[PtL(Ph_3PO)Cl]$ ($HL = C_6H_4CONR'$, R′ = pyridine), analogous to palladium(II) above[383].

Unsymmetrical phosphorus ligands, such as $Ph_2P(O)(CH_2)_nPPh_2$($n = 1, 2$) form *cis*-$[PtL_2]X_2$ complexes ($X = NO_3$, PF_6, BF_4)[419]. Similarly, *cis*- and *trans*-$[PtCl(PR_3)L]X$ {R = Et or Bu; $X = ClO_4$, BF_4; $L = Ph_2PCH_2P(O)R'_2$; R′ = Ph, $CHMe_2$, CMe_3} are known[425]. These complexes on treatment with NaH form *cis*- and *trans*-$[PtCl(PR_3)\{Ph_2PCHP(O)R'_2\}]$. An X-ray structure of the *trans* isomer with $R' = CMe_3$ has been reported. It is notable that the Pt—O bond is weaker than the Pt—S bond in analogous complexes[425].

Finally, reaction of $[Pt_2Cl_4(PEt_3)_2]$ with $Ph_2P(O)CH_2P(S)Ph_2$ gave $[PtCl(PEt_3)L]^{+}$[426], which on treatment with 1,8-bis(dimethylamino)naphthalene gave **43**. A platinum(II) complex, $[Pt_2(\mu\text{-}S)(\mu\text{-}L)(\eta'\text{-}L')]$ $\{L = Ph_2PCH_2PPh_2$; $L' = Ph_2PCH_2P(O)Ph_2\}$[427] was found to possess no Pt–O interaction.



(43)

g. Complexes of the copper Group (IB). Table 9 shows various types of complexes of copper(II). Only a few copper(I), silver(I), gold(I) and gold(III) complexes have been reported. Apart from the usual methods of preparation, some indirect methods have been used which are briefly described as follows: (a) oxidation of copper metal with Ph_3PO and CCl_4 in MeCOEt gave $[CuCl_2L_2]$ and $[Cu_4OCl_6L_4]$[290,454]; (b) reaction of copper(II) chloride with molten Ph_3PO gave $[CuCl_2(OPPh_3)_2]$[351]; (c) grinding of $CuCl_2$ and Ph_3PO to a fine powder for some time gave $[CuCl_2L_2]$[352]; (d) reaction of copper(II) chloride with Ph_3P in acetone gave a mixture of Ph_3PO, $[CuCl_2(OPPh_3)_2]$, $CuCl_2(OPPh_3)_4{\cdot}2H_2O$ and $[Cu_4OCl_6L_4]$[455,456] (separated by chromatography). It may

TABLE 9. Complexes of the copper Group (IB)

	Complex	X	L	Ref.
A	$[CuX_2L_2]$	Cl, Br, NO_3	Ph_3PO, Cy_3PO, Ph_2BzPO, $PhBz_2PO$, Bz_3PO, $Ph_2P(O)CH{=}CH_2$	66, 322, 428–434
B	$[CuCl_2L]$	—	$[Me_2P(O)CH_2]_2O$, $[Me_2P(O)CH_2OCH_2]_2$ $[Me_2P(O)CH_2OC_2H_4]_2O$	435
C	$[CuX_2L_4]\cdot 2H_2O$	Cl, Br	Ph_3PO	429, 436–438
D	(i) $[CuX_2L_4]$	NO_3	Ph_3PO	366
	(ii) $[CuX_2L_4]$	Cl, NO_3	$(HOCH_2)_3PO$	234
E	$[Cu_4OX_6L_4]$	Cl	Ph_3PO	429, 439–446
		Br	Ph_3PO	444
F	$[CuX_2L]$	(i) hfa, tta, tfa, acac, $Et_2NC(S)$, etc.	Ph_3PO, topo	238, 343, 447–450
		(ii) HA[a]	Bu_3PO	97
G	$[CuX_2L_n]$	(i) hfa, dbm, tta, cupferron	Bu_3PO topo($n = 1,2$)	238, 451
		(ii) CF_3SO_3	Bu_3PO, topo($n = 4,6$)	345
H	$[CuX_2L_2]$	2,4,6-$X_3C_6H_2O_2$ (X = Cl, Br)	Ph_3PO	452
I	(i) $[CuL_4]X_2$	ClO_4	Me_3PO, Bu_3PO, Ph_2BzPO, $PhBz_2PO$, Bz_3PO	137, 343, 432
	(ii) $[CuL_4X]X$	ClO_4	Me_2PO, Ph_3PO, $MePh_2PO$	229–232, 453
	(iii) $[CuX_2L_4]$	BF_4	Bu_3PO, Ph_3PO	233, 234
	(iv) $[CuL_5]X_2$	BF_4	Me_3PO	234

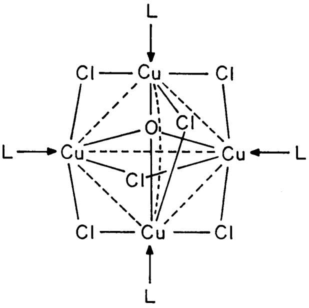
[a] HA = 5-methoxy-5-methyl undecane-2,4-dione.

be added that sometimes in the direct reaction of a metal salt with a ligand, unexpected products were obtained. For example, reaction of copper(II) chloride with Ph_3PO under different conditions gave $[CuCl_2L_2]$, $2[CuCl_2L_3]$ and $(Cu_4OCl_6L_4]$[457]. A complex with a quaternary cation, namely $(Ph_2P(O)CH_2CH_2NEt_2(H))^+[CuCl_2]^-$ is also known[458,459]; X-ray analysis has confirmed this formulation.

X-ray study has shown a slightly elongated tetrahedron for $[CuBr_2(OPPh_3)_2]$[428], with angles at oxygen, viz. Cu—O—P, being 144.0° and 154.8°. Similarly, for $[CuCl_2(OPPh_3)_2]$, a compressed tetrahedral geometry (C_2 symmetry) was inferred from single-crystal ESR and polarized electronic spectra[429,431]. $[Cu(O_2NO)_2(OPPh_3)_2]$ has *trans*-rhombic octahedral geometry[434]. Other complexes of type A and also complexes of type B (coordination via PO only have been assigned a distorted tetrahedral geometry (Table 9).

Complexes C exhibit coordination isomerism: $[CuCl_2(OH_2)_2](Ph_3PO)_4$[429,436,437] (isomer I) and $[CuCl_2(OPPh_3)_4]\cdot 2H_2O$ (isomer II)[438]. Isomer I has a tetrahedral geometry (X-ray) about copper with no coordination by Ph_3PO. Each H_2O interacts with Ph_3PO via hydrogen bonding. In isomer II, H_2O is not coordinated and the complex has a *trans*-octahedral geometry. On heating, isomers I and II formed $[CuL_2X_2]$[460]. Complexes D presumably have *trans*-octahedral structures with monodentate NO_3 in mutually *trans* positions.

One of the most widely studied compounds is $[Cu_4OCl_6L_4]$ (L = Ph_3PO) (complexes E). Apart from the methods mentioned earlier, this cluster compound can be readily obtained by refluxing $[CuCl_2(OPPh_3)_2]$ in methyl isobutyl ketone[446]. X-ray study has shown that the copper atoms are at the vertices of an almost regular tetrahedron (**44**). Each copper is surrounded by a slightly distorted trigonal bipyramid[440–442,446]; six bridging 'Cl' atoms form an octahedron about the central oxygen. There is antisymmetric super-exchange between orbitally degenerate magnetic ions[445]. Further, the EPR spectrum has shown separation of the $S = 2$ state from the $S = 1$ state (ground state) of $14 \pm 1\,cm^{-1}$ (zero-field splitting, $0.53 \pm 0.01\,cm^{-1}$)[443].



(**44**)

The 1:1 adducts $[CuX_2L]$ (complexes F and G) either possess square-pyramidal geometry or dimeric octahedral structures involving bridging via oxygen or sulphur donor atoms of the anions. The 1:2 adducts G have *trans*-octahedral structures. However, none of these have been characterized by X-ray studies. The triflate complexes $[Cu(SO_3CF_3)_2L_n]$ ($n = 4,6$) have only been poorly studied. The Lewis acidity of copper(II) β-diketonates, CuX_2, towards the ligands decreased in the order $Cu(hfa)_2 > Cu(tta)_2 > Cu(tfa)_2 > Cu(acac)_2$.

In copper(II)–dithiocarbamate adducts (F)[448], low-temperature ESR studies showed that the axial binding to copper by L weakens the Cu—S bonding in the square-plane. Phenoxo complexes (H) are also believed to possess *trans*-octahedral geometries[452] and on thermal degradation they form $[Cu_4OCl_6L_4]$. For the perchlorate or fluoroborate complexes, tetrahedral, square-pyramidal, or octahedral structures have been assigned for I(i), I(ii, iv) and I(iii), respectively. For $[CuL_4]$ $(ClO_4)_2$, a square-planar structure has been suggested when L = Me_3PO[343], whereas when L = Bu_3PO the structure is believed to be between tetrahedral and square-planar.[137]

The unsymmetrical phosphorus–sulphur ligands $Ph_2P(O)CH_2CH_2SR$ (R = Et, Ph) also formed complexes of the type $[CuL_2]{\cdot}X_2(X = ClO_4)$, $[CuL_2](BF_4)_2$—(R = Et) and $\{[CuL'_2]X{\cdot}[CuL_2]X_2\}$ $\{L' = Ph_2PCH_2CH_2SEt;\ L = Ph_2P(O)CH_2CH_2SPh\}$[461]. Complexes $\{[CuL'_2]X{\cdot}[CuL_2]X_2\}$ are double salts and the presence of $[CuL'_2]X$ induces asymmetry in the $g_\perp$ line of $[CuL_2]X_2$ ($X = ClO_4$, BF_4) species which showed $g_\parallel = 2.220$ and $q_\perp = 2.089$; the double salt complexes showed three g values (2.269, 2.064 and 2.034). From solution-phase studies, species of the type $[CuLCl]^+$ $\{L = Me_2P(O)CH_2R;\ R = Cl$, OMe, OPh[227], Ph_3PO, $Ph_2P(O)CH_2Ac$, $Ph_3P{=}CHP(O)Ph_2$[364]$\}$ and $[CuL_2Cl]^+$ $\{L = Me_2P(O)CH_2OPh\}$[227] were detected.

Addition of Me_3P to a rapidly dehydrated copper(II) Y-zeolite reduced the copper(II) to copper(I), which on treatment with O_2 was deoxidised forming $[Cu(Me_3PO)_4]^{2+}$ species in the supercages of the Y-zeolite's lattice[462].

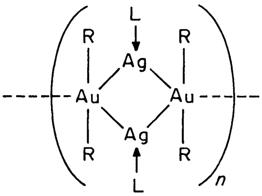
A large number of adducts of copper(II) carboxylates with Ph_3PO have been reported: $[Cu_2(O_2CR)_4L_2]$ {R = Me, Et, Pr[343,463,464], FCH_2, $ClCH_2$, Cl_2CH, Cl_3C, F_3C, etc.[465–467], $BrCH_2CH_2$, MeCHBr, $MeC(Cl_2)$, $ClCH_2CH_2$, MeCH(Cl)[464,468–470]; PhC≡C[471], $R'C_6H_4$, R′ = H, 4-Me, 2-Cl, 4-NO_2[406], 2-F, etc.[464]} and $[Cu(O_2CCX_3)_2(Ph_3PO)_2]$ (X = F, Cl)[472].

X-ray analyses of $[Cu_2(O_2CCH_2CH_2Cl)_4(OPPh_3)_2]$[469] and $[Cu_2(O_2CCHClMe)_4(OPPh_3)_2]$[470] have shown dimeric structures (**46**) similar to that of copper(II) acetate. Magnetic moment, ESR and other studies have revealed antiferromagnetic exchange interactions between the copper(II) centres of the carboxylate complexes. In one case, viz. $[Cu_2(PhC{\equiv}CO_2)_4L_2]$[471], there was inter-dimer antiferromagnetic interaction.

Recently 1:2 adduct of substituted glycine, namely $[CuA_2L_2]$ (HA = *N*-formyl-L-phenylalanylglycine; L = Ph_3PO) was reported to have a *trans*-octahedral structure[473]. However, an ESR study revealed the existence of monomeric and dimeric forms of the adduct.

A few tetrameric copper(I)–phosphine oxide complexes, $[CuLX]_4$ (L = Ph_3PO, *p*-tol_3PO; X = Cl, Br, I), were formed by the thermal decomposition of $[Cu(PPh_3)X]$ in O_2[474] and oxidation of $[CuX(p\text{-}tol_3P)]$ with H_2O_2[475]. Similarly, reaction of Ph_3P with $CuCl_2$ in Me_2CO gave $[CuClL_n]$ (n = 1–3; L = Ph_3PO)[456]. Reaction of CuCl with $Ph_2P(O)CH(R)Li^+$ {from BuLi + $Ph_2P(O)CH_2R$} led to *trans*-metallation of copper(I) forming $CuCH(R)P(O)Ph_2$ (R = H, Pr, etc.)[476].

The *β*-tri-*α*-methylindolphosphine oxide $(C_6H_4NHCMe{=}C)_3PO$ and *β*-triindolylphosphine oxide, $(C_6H_4NHCH{=}C)_3PO$, were reported to interact with $AgNO_3$, but no details were given[477]. Other silver(I) complexes reported are $[Ag(NO_3)L]$, $[AgXL_5]$ (X = ClO_4, BF_4, PF_6), $[AgL_4]^+(SbF_6)^-$ (L = Ph_3PO)[478] and $(R_2AuAgL)_n$[479] (R = C_6F_5, $C_6F_3H_2$; L = Ph_3PO; **45**).



(**45**)

Gold(I, III) complexes of the type $[Au(Ph_3PO)(Ph_3P)](ClO_4)$,[480] $[(C_6F_5)_2Au(Ph_3P)(Ph_3PO)](ClO_4)$[481] and $(HL_2)[AuX_4]$ (X = Cl, Br; L = Ph_3PO)[482–84] have been reported. Au X-ray study of $(H(Ph_3PO)_2)[AuCl_4]$[485] showed a hydrogen-bonded centrosymmetric interaction with Ph_3PO.

h. Complexes of the zinc Group (IIB). Various complexes of this group are given in Table 10. Most of the adducts have 1:1 or 1:2 metal to ligand ratios, although a few complexes with other stoichiometries have also been reported. For example, zinc(II) forms $[ZnX_2L_n]$ (X = SO_3CF_3; n = 4–6) complexes[345]. X-ray analysis of $[ZnCl_2(OPPh_3)_2]$ showed a distorted tetrahedral geometry about zinc(II)[486]. Other A complexes are also suggested to have similar structures.

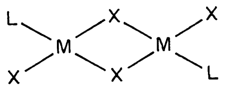
For B complexes, $[MX_2L]$, when the anion is halogen, a dimeric structure (**46**) is suggested. When the anion is tta, hfa or bfa, square-pyramidal or dimeric octahedral structures (**47a** and **b**) have been suggested. The unsymmetrical phosphorus ligands $Ph_2P(O)CH(R)PPh_2$ chelate to a metal centre via P and O donor atoms, forming

TABLE 10. Complexes of the zinc Group (IIB)

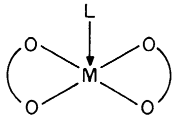
	Complex	M	X	L	Ref.
A	$[MX_2L_2]$	Zn	Cl, Br, I, NO_3, CH_3COO	L[a]	16, 66, 73, 227, 230, 322, 486–490
			$(NC)_2CC(O)NH_2$	Ph_3PO	341
		Cd	I	Ph_3PO	16, 230, 490
		Hg	Cl	Ph_3PO, $Ph_2P(O)R$ $(R = CH_2{=}CH)$	16, 66, 491, 492
B	$[MX_2L]$	Zn, Cd	tta, bfa, hfa	Ph_3PO, topo	343, 449, 493, 494
		Cd	Cl	$(HOCH_2)_3PO$	234
		Cd, Hg	Cl, Br	$R_3PO(R = HOCH_2)$ $Ph_2P(O)CH(R)PPh_2$ $(R = H, Pr^n)$[b]	143
		Hg	Cl, Br	Me_3PO, Ph_3PO, p-Tol_3PO	491, 492, 495
C	$[MX_2L_n]$	Zn	CF_3SO_3	Bu_3PO, Ph_3PO $(n = 4–6)$	345
D	$[ML_4]X_2$	Zn	BF_4, ClO_4, SbF_6	Me_3PO, Bu_3PO, Cy_3PO	137, 234, 496
		Cd	SbF_6	Cy_3PO[c]	497
E	$[ZnL_4X]X$	—	ClO_4	Me_3PO, $MePh_2PO$, Ph_3PO	229, 231 232
F	$[ML_4X_2]$	Zn, Cd, Hg	BF_4, ClO_4, $N(SO_3F)_2$	Me_3PO, Ph_3PO	233, 234, 498

[a] $L = Me_3PO, Ph_3PO, R_2P(O)CH{=}CH_2$ $(R = Bu^n, Ph)$, $Me_2P(O)CH_2R$ (R = Cl, MeO, PhO).
[b] ^{31}P NMR study.
[c] ^{31}P, ^{113}Cd NMR study.

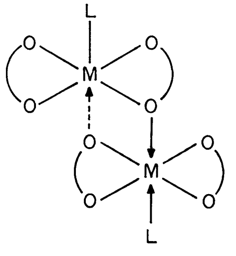
tetrahedral complexes, $[MX_2L]$[143]. For complexes D–F, tetrahedral, square-pyramidal or octahedral structures have been suggested.



(46)

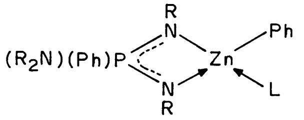


(47a)

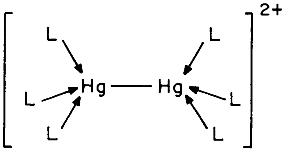


(47b)

Using ^{31}P and ^{113}Cd NMR, the formation of $[CdL_4](SbF_6)_2$ $(L = Cy_3PO)$ was detected[497], and insoluble product, $[CdL_3(SbF_6)_2]$ $(L = Cy_3PO)$ was isolated. From another solution-phase study, the order of metal–ligand interaction was found to be Zn–O > Cd–O > Hg–O[499,500]. Recently, an adduct of a substituted glycine, viz. $[ZnA_2(OPPh_3)_2]$ (HA = *N*-formyl-L-phenylalanylglycine), with a *trans*-octahedral structure was reported[473]. A few reactions of organo-zinc(II) and -mercury(II) have also been reported[473]. For instance, reaction of *N,N,N″,N″*-tetrakis(trimethylsilyl)diamidophosphonimidate, $R_2N(P{=}NR)_2(R = Me_3Si)$ with Ph_2Zn formed a 3-coordinate complex $[(R_2N)(Ph)P(NR)_2Zn]$, which further reacted with Ph_3PO forming a 1:1 adduct (**48**)[501]. Similarly, $(C_6F_5)_2Hg$ and $[(O_2N)_3C]_2Hg$ formed 1:1 adducts with Ph_3PO[502,503]. From another study (solution phase)[503], the Lewis acidity of R_2Hg towards Ph_3PO was indicated to decrease in the order $R = o\text{-}HC_6F_4 > C_6F_5 > p\text{-}HC_6F_4 \approx p\text{-}MeOC_6F_4$. Only a few mercury(I) complexes, $[Hg_2L_6(ClO_4)_2]$ $(L = Ph_3PO)$[498,505], $[Hg_2L_4(ClO_4)_2]$[506] and $[Hg_2L_5(SiF_6)$ $(L = Ph_3PO)]$[506], have been reported. An X-ray study of $[Hg_2L_6(ClO_4)_2]$ showed a dimeric structure (**49**), the geometry about each mercury being approximately tetrahedral.



(48)



(49)

i. Complexes of the lanthanides. Numerous complexes of the lanthanides have been reported (Table 11). Lanthanide halides generally form 6- or 7-coordinate $[MX_3L_n]$ $(n = 3, 4)$ complexes. There is a tendency to extend the coordination number from 6 to 7 either by reaction with an additional ligand or absorbing moisture or solvent molecules. An iodo complex, $[SmL_4I_3]$, showed ionization forming $[SmL_4I_2]I$[515], probably for steric reasons. A thermal study of the complexes $[MCl_3L_3(H_2O)]$[518] revealed an increase in thermal stability from holmium to samarium. Cerium(IV) complexes had low thermal stability, decomposing between 45 and 80 °C; decomposition was rapid in water also[510].

An interesting feature noted in lanthanide chemistry was the abstraction of halogens with a Lewis acid from the $[ML_3X_3]$ complexes. Coordination of R_3PO to the metal weakens the M—X bonds and thus ionic complexes such as $[MClL_5][FeCl_4]_2$[520] and $[MCl_2L_4][CuCl_3]$[521,522] are formed. X-ray analysis of the gadolinium complex showed a *trans*-octahedral structure for $[GdCl_2L_4]^+$ and a trigonal planar $CuCl_3^-$ anion[522]. Similarly, X-ray analysis showed an octahedral structure for $[LaClL_5]^{2+}$ [520] and *trans*-octahedral structures for $[CeCl_4L_2]$ $(L = Ph_3PO)$[509] and $[SmI_2L_4]I$ $(L = Ph_2MePO)$[515].

The nitrate complexes B in Table 11 involve chelation by the NO_3 groups and hence the coordination number varies from 7 to 10. X-ray studies of $[La(O_2NO)_3L_3]\cdot EtOH$[523], $[Nd(O_2NO)_3L_2]\cdot EtOH$[530], $[Eu(O_2NO)_3L_3](Me_2CO)_2$[531] and $[Eu(O_2NO)_3L_2(EtOH)]$[531] $(L = Ph_3PO)$ have shown 9-coordination about the metal centre, whereas $[Ce(O_2NO)_4L_2]$ $(L = Ph_3PO)$[527] has 10-coordinate cerium. Here the general tendency of the metal ion is to extend the coordination number up to 9 readily and owing to this various complexes acquire solvent molecules. Preliminary X-ray data on $[Nd(NO_3)_3(Ph_3PO)_3]$ showed that the complex exists in two phases[529].

The metal thiocyanate complexes showed coordination numbers similar to those in the metal halides. The complexes possess M—NCS bonding as expected. An X-ray study of $[Nd(NCS)_3L_4]$ $(L = Ph_3PO)$ has shown that it possesses C_s symmetry. The perchlorate complexes also have coordinating ClO_4^- groups. For example, in $[Nd(O_2ClO_2)_2L_4](ClO_4)$[522], an X-ray study has confirmed the chelation by the ClO_4 groups as deduced from IR spectrometry for several complexes. The geometry of the neodymium complex involves a distorted delta dodecahedron. The complexes $[ML_6]^{3+}$ $(L = Me_3PO)$[543] are other examples where six monodentate R_3PO ligands coordinate to the metal.

TABLE 11. Complexes of the lanthanides

	Complex	M	L	Ref.
A	$[MCl_4L_2]$	Ce	Ph_3PO	507–509
	$[MCl_4L_2]EtOH$	Ce	Ph_3PO	510
	$[MCl_3(OMe)L_2]$	Ce	Ph_3PO	510
	$[MCl_3L_n]\cdot m BuOH$ ($m = 1, 2$)	Nd	topo, Ph_3PO, Ph_2BzPO ($n = 1$–4)	511–514
	$[ML_4I_2)I$	Sm	Ph_2MePO	515
	$[MCl_3L_n]$	Sm	Ph_3PO ($n = 3, 4$)	512, 513
	$[MX_3L_n]\cdot S$ ($S = 0$, 0.5 or 2 $C_4H_8O_2$; $X = Cl$, Br).	Eu, Dy, Er	Ph_3PO, Ph_2BzPO, Ph_2EtPO ($n = 3$)	516, 517
	$[MCl_3L_3]\cdot H_2O$	Nd, Sm, Eu, Gd, Ho	Ph_3PO	518
	$[MCl_3L_4]$	Sm, Tb, Dy	Ph_3PO	518
	$[MCl_3L_3]$	La–Nd, Sm, Gd, Dy, Er	topo, Ph_3PO	519
	$[MClL_5][FeCl_4]_2$	Y, La–Er, except Pm, Tm, Lu	Ph_3PO	520
	$[MCl_2L_4][CuCl_3]$	Y, Ln, except Pm, Tm, Yb, Lu	Ph_3PO	521, 522
B	$[M(O_2NO)_3L_3]\cdot EtOH$	La	Ph_3PO	523
	$[M(O_2NO)_4L_2]$	Ce	Ph_3PO	524–527
	$[M(O_2NO)_3L]$	Nd	Me_3PO, Et_3PO, Ph_3PO, Bz_3PO, Ph_2BzPO, $PhBz_2PO$	528
	$[M(O_2NO)_3L_3]$	Nd	Ph_3PO	512, 529
	$[M(O_2NO)_3L_2]\cdot EtOH$	Nd	Ph_3PO	512, 530
	$[M(NO_3)_3L_2]\cdot EtOH$	Y	Ph_3PO	512
	$[M(O_2NO)_3L_2]\cdot EtOH$	Sm	Ph_3PO	512
	$[M(O_2NO)_3L_3]\cdot 2Me_2CO$	Eu	Ph_3PO	531–533
	$[M(O_2NO)_3L_2\cdot EtOH]$	Eu	Ph_3PO	531–533
	$[M(NO_3)_3L_3]$	La–Lu	R_3PO ($n = 3, 4$; R = isoamyl)	534
		Sm, Yb, Y	Pr_3PO	534
	$[M(NO_3)_3L_2]\cdot EtOH$	Ln except Pm	Ph_3PO	512, 535
	$[M(NO_3)_3L_n]\cdot S_m$ [S = EtOH, Me_2CO; $m = 1, 2$)	Y, Ln	Ph_3PO ($n = 3, 4$)	535
	$[M(NO_3)_2L_4](NO_3)$	Ln	Ph_3PO	535
	$[M(O_2NO)_3L_3]$	La–Yb	Bu^n_3PO, topo	519, 536
C	$[M(NCS)_3L_4]$	Ce, Pr, Nd, Eu, Gd, Tb, Dy	Ph_3PO, topo, $PhBz_2PO$	537, 538
	$[M(NCS)_3L_n]$	Sm, Er	Ph_3PO ($n = 3, 4$)	512
	$[M(NCS)_3L_n]$	Y, La–Lu, except Pm, Tb, Yb	Ph_3PO, Bu_3PO, topo, Pr_3PO, R_3PO (R = isoamyl; $n = 3, 4$)	513, 519 534, 539
D	$[M(ClO_4)_3L_4]$	La	Ph_2EtPO	516
	$[M(OClO_3)_2L_4](ClO_4)$	Ce	Bu^n_3PO	137

	$[M(ClO_4)_3L_4]$	Nd	$Ph_xBz_{3-x}PO$, Ph_2EtPO ($x = 0$–3)	516, 540
	$[M(O_2ClO_2)_2L_4](ClO_4)\cdot S$ ($S = EtOH$, Me_2CO)	Nd	Ph_3PO	541, 542
	$[M(ClO_4)_3L_4]$	Eu, Er	Ph_3PO, Bz_3PO, Ph_2BzPO, Ph_2EtPO	516–517
	$[ML_6](ClO_4)_3$	La, Gd, Eu, Lu, Y	Me_3PO	543
	$[ML_4(OClO_3)_2](ClO_4)$	La–Lu	Bu^n_3PO	544
	$[ML_4(O_2ClO_2)](ClO_4)_2$	Y, Gd–Er	Bu^n_3PO	544
	$[ML_4(OClO_3)](ClO_4)_2$	Yb	Bu^n_3PO	544
E	$[ML_6](PF_6)_3$	La, Ce, Nd, Eu, Gd, Tm, Lu, Y	Me_3PO, $MePh_2PO$	543, 545
	$[ML_5(PF_6)_3]$	La, Eu, Gd, Tb, Dy	$CyPh_2PO$	545
F	$[MA_3L_2]$[a]	Ce, Pr, Nd, Sm, Eu, Dy, Tb, Er	Ph_3PO	546
G	$[M(OOCCF_3)_3L]$	La–Lu, Y	Ph_3PO	547
H	$[MA_3L]$ (HA = Hacac, Hba, Hdbm, Htta)	Ce	Ph_3PO, topo	548–552
	$[M(tta)_2(NO_3)_2L_2]$	Ce	Ph_3PO	553
	$[M(dbm)_2(NO_3)_2L]$	Ce	Ph_3PO	525
	$[MA_4L]$ (HA = Hacac, Hba, Hdbm)	Ce	topo, Ph_3PO	551
	$[MA_3L]$[b] (HA = Hdpvm)	Ce	Ph_3PO	554, 555
	$[MA_3L_2]$ (HA = Htta, Hhfa)	Nd, Eu	Et_3PO, topo, Ph_3PO	49, 51, 556–561
	$[MA_3L]$[c]	Eu	Et_3PO, Ph_3PO	499, 562
	$[MA_2(O_2NO)L_2]$ (HA = Htta, Hdbm, Hba)	Eu, etc.	Ph_3PO, Bu_3PO	570, 571
	$[MA_3L]$ (HA = Hdbm, Hacac, Hba, Hdpvm)	Nd, Pr, Er, Gd, Ha, Tn, Yb, Y	topo, Ph_3PO	52, 53, 554, 555, 563–566
	$[MA_3L_n]$ (HA = Htta, etc.)	La, Nd, Pr, Er, Gd, Dy, Ho, Yb, Tm	topo, Ph_3PO ($n = 1, 2$) $PhMe_2PO$, $MePh_2PO$, $EtPh_2PO$ ($n = 2$)	567, 568
	$[MA_3L_n]$ (HA = Hacac)	Y, La, Pr, Sm, Gd, Dy	Ph_3PO ($n = 2$ for Y, 3 for others)	569
I	$[MA_3L_2]\cdot 2H_2O$[d]	La	Ph_3PO	572
J	$[M(PMBP)_4L]$	Ce	Ph_3PO, Bu_3PO	573
	$[M(PMBP)_3L_n]$	Pr–Gd	Ph_3PO ($n = 1, 3$)	574, 575
K	$[MA_3L]$[e]	Y, La, Eu, Lu	Ph_3PO	576, 577
	$[MA_2(PPh_2)L]$[e]	Y, La, Eu	Ph_3PO	576
	$[M_2A_4(O_2)L_2]$[e]	La, Pr, Sm, Eu, Lu	Ph_3PO	577
L	$[MA_3L]$[f]	Ce, etc.	Et_3PO, Ph_3PO	54, 578
	$[M(SO_3Cl)_3L_2]$	Ce, Nd, Sm, Gd, Dy, Ho, Er	Ph_3PO	579–581

---

[a] HA = 5-chlorosalicylic acid.

[b] HA = Hdpvm–dipivaloylmethane.

[c] HA = 1-trifluoromethoxy-1,1-difluoro-5,5-dimethylhexane-2,4-dione, Hdpvm, etc.

[d] HA = *N*-nitrosophenylhydroxylamine.

[e] HA = HN $(SiMe_3)_2$.

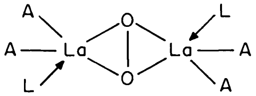
[f] HA = 2,6-$Me_3CC_6H_3OH$, 2,6-di-*tert*-butyl-4-methylphenol, 2,6,4-$(CMe_3)_2MeC_6H_2OH$.

Hexafluorophosphate complexes (E) probably do not contain the coordinated anion whereas complexes G have coordinating carboxylate groups, the salicylate complexes being 8-coordinate and the trifluoroacetate complexes 9-coordinate. However, X-ray analysis is needed to confirm such possibilities. All the trifluoroacetate complexes decomposed at 300 °C forming metal trifluoride compounds. A polymeric europium(III) complex, $Eu_4A_3 \cdot 9H_2OL$ ($L = Ph_3PO$) (H_4A = benzene-1,2,4,5-tetracarboxylic acid), has also been reported[582].

Several adducts of metal β-diketonates have been reported (complexes H, Table 11.) The coordination number varies from 7 to 8 with coordination number 9 being shown only by $[CeA_4L]$ adducts. The adducts $[Ce(tta)_4L]$[550,551] were unstable and were reduced to $[Ce(tta)_3L]$ (L = topo, Ph_3PO), whereas other adducts were stable. X-ray studies of $[M(tta)_3(OPPh_3)_2]$ (M = Nd, Eu)[557,561] and $[Eu(dbm)_2(O_2NO)(OPPh_3)_2]$[571] showed dodecahedral structures for these complexes. However, an X-ray study of $[PrA_3L]$ (HA = dipivaloylmethane) showed that it has a pentagonal bipyramidal structure[554,555]. Europium(III) complexes $[EuA_3L_n]$ ($n = 1,2$) fluoresce[570,583].

A thermal study of $[MA_3L]$ (HA = Hdbm)[563] revealed that the adducts sublime in vacuum; the decomposition temperature of the adducts increases as the lanthanide increases in atomic number. A mass spectral study of $[EuA_3(OPPh_3)]$ $\{HA = RC(O)CH_2C(O)CMe_3;\ R = CF_3,\ CF_3OCF_2,\ C_3F_7\}$, the complexes with $R = CF_3OCF_2$ and CF_3 showed dimer formation in the gas phase[584].

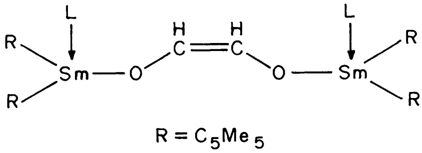
N-Nitrosophenylhydroxylamine, 4-benzoylpyrazolone and chlorosulphate complexes (I–K) formed 7- to 9-coordinate complexes. Using $(Me_3Si)_2N^-$ or Ph_2P^- as the anions, novel 4-coordinate complexes, and peroxo complexes, were obtained (Table 11). The diphenylphosphido complexes were obtained from $[MA_3L]$ and Ph_2PH $\{HA = HN(SiMe_3)_2\}$. An X-ray study of $[La_2A_4(O_2)L_2]$ $\{L = Ph_3PO,\ HA = HN(SiMe_3)_2\}$[577] showed that it exists as a centrosymmetric dimer (**50**), each Lanthanum has a distorted tetrahedral environment if the fourth side is considered to be occupied by the peroxo group, O_2^{2-}. Similarly, 4-coordinate peroxo complexes(M) have been reported[54,578].



(**50**)

Reaction of $Na[M(S_2PR_2)_4]$ (M = La–Lu, except Pm) with Ph_3PO gave dithiophosphinate adducts, $[MA_3L_2]$ and $[MA_2L_3]$ ($A = S_2PR_2$) complexes (R = EtO)[585–586]. X-ray analysis showed 8-coordinate square-antiprism geometry about lanthanum and a pentagonal bipyramidal geometry about samarium.

A few organosamarium(II) and-(III) complexes, $[(C_5Me_5)_2SmL(thf)]$ ($L = Ph_3PO$)[572] and $[(C_5Me_5)_2SmL(OCH{=}CHO)SmL(C_5Me_5)_2]L$[588], have been reported. The latter was obtained from the reaction of $[(C_5Me_5)_2SmH]_2$ and CO in the presence of Ph_3PO and it exhibited *cis–trans* isomerism. X-ray analysis of the *cis* isomer showed a distorted tetrahedral geometry about each samarium (**51**).



$R = C_5Me_5$

(**51**)

j. Complexes of the actinides. Several complexes of the actinides reported are given in Tables 12 and 13. Whereas only a few organolanthanide complexes were formed, a large number of organoactinide complexes have been reported (Table 13). As discussed earlier, some indirect methods of preparation also gave phosphine oxide complexes. For instance, oxidation of $(Ph_3PH)_2[UCl_6]$ with chlorine gave $[UCl_4L_2]$ ($L = Ph_3PO$)[602]. Similarly, $[UBr_4(OPPh_3)]$ was obtained from the reaction of UCl_4 with bromine in the presence of Ph_3PO[599] and $[PuBr_3L_2]$ from $PuCl_3$ and bromine in the presence of Ph_3PO[599]. Air oxidation of Ph_3P in the presence of $[UO_2X_2]$ ($X = Cl$, Br) gave $[UO_2X_2L_2]$ ($L = Ph_3PO$)[624]. From Table 12, it can be seen that a maximum of six phosphine oxide molecules can coordinate to an actinide. As Me_3PO is a small molecule it has low steric hindrance and hence six molecules can be accommodated about the central metal, unlike Ph_3PO, where only four molecules are accommodated about the metal.

An X-ray study of $[ThCl_4(OPPh_3)_3]$[594] showed 7-coordinate geometry in an approximately capped octahedral environment with one oxygen in the capping position and three chlorine atoms in the capped face. Similarly, X-ray analysis of $[UCl(OPMe_3)_6]Cl_3$[609] showed a distorted monocapped trigonal antiprismatic structure or distorted monocapped octahedral structure.

An X-ray study showed a *trans*-octahedral geometry for $[UBr_4(OPPh_3)_2]$[590] and *cis*-octahedral for $[UCl_4(OPPh_3)_2]$[603]. The latter complex exists in the two different crystal phases, α and β[590,608a], the β-phase being a metastable phase of the α-form. Heating $[UCl_4(OPMe_3)_2]$ at 100 °C for 6–7 h gave β-$[UCl_4L_2]$[598]. X-ray analysis of $[UCl_5(OPPh_3)]$[612] and $[UO_2Cl_2(OPPh_3)_2]$[616] showed distorted octahedral geometries. In the latter, the ligands display a *trans*-octahedral disposition.

A thermodynamic study of the interaction of UCl_4 with Ph_3PO revealed that the UCl_4–$OPPh_3$ interaction was weaker than the UCl_4–dmso interaction[715] ($\Delta H = -35.9$ versus $-45.3\ \mathrm{kcal\,mol^{-1}}$). In the solution phase $[UO_2Cl_2(topo)_2]$ undergoes restructuring:

$$2[UO_2Cl_2L_2] \rightleftharpoons [UO_2ClL_3]^+[UO_2Cl_3L]^-$$

None of the perchlorate, sulphate and halogeno sulphate complexes of thorium, uranium and neptunium (Table 12) have been studied by X-ray analysis making it difficult to confirm coordination by the perchlorate groups, although XSO_3^- groups ($X = F, Cl, CF_3$) are probably bidentate. In some thorium(IV) and neptunium(V) complexes, H_2O is coordinated: $[ThL_5(OH_2)](ClO_4)_4$[632] and $[NpO_2L_4(OH_2)]ClO_4$[627,635]. Only two borohydride complexes of the actinides have been reported, $[U(BH_4)_4L_2]$[638,639] and $[U(BPh_4)_2(NO_3)_2L_5]$[640]. An X-ray study of $[U(BH_4)_4L_2]C_6H_6$ ($L = Ph_3PO$) showed a *trans*-octahedral geometry[639]. C_6H_6 was lying as solvate molecules. The U—BH_4 distances (2.55 and 2.75 Å) reveal bi- and tri-dentate BH_4^- ions. In the solution phase, $[U(BH_4)_4L_2]$ exists as a mixture of *cis* and *trans* isomers.

Among the nitrate and thiocyanate complexes (Table 12), only one 1:1 adduct, $[Th(NO_3)_4(OPPh_3)]$, was obtained by electrochemical synthesis, the other complexes being obtained by routine methods. X-ray studies of $[Th(O_2NO)_4L_2]$ ($L = Ph_3PO$)[642] and $[Th(O_2NO)_4{\cdot}2.67Me_3PO]$[640] showed chelation by the NO_3^- groups and 10-coordinate thorium. Similarly, an X-ray study of $(Ph_4P)\ [Th(O_2NO)_5(OPMe_3)_2]$[640] showed a 12-coordinate polyhedron.

X-ray studies of $[U(NO_3)_4L_2]$ ($L = Ph_3PO$)[650] and $[UO_2(NO_3)_2L_2]$ $\{L = Bu_3PO$, $(2\text{-}O_2NC_6H_4)Ph_2PO\}$[645,658] showed distorted *trans*-octahedral and 8-coordinate geometries, respectively. In the complex $[U(NO_3)_4L_2]$, the NO_3^- group is unidentate and in the uranyl nitrate complexes it is bidentate with a linear UO_2^{2+} moiety. An X-ray photoelectron study[648] of the former complex also revealed distortion in the geometry and its decomposition pattern was suggested as

$$[U(NO_3)_4L_2](s) \rightarrow [UO_2(NO_3)_2L_2](s) + \text{gases}$$

TABLE 12. Complexes of the actinides

	Complex	X (or H_mA)	n	L	Ref.
A	(i) $[ThX_4L_n]$	Cl, Br	2, 3	Me_3PO, Et_3PO, Et_2PhPO, $EtPh_2PO$, Ph_3PO, Pr^i_3PO, $MePh_2PO$	589–596
		Cl	3, 5	Me_2PhPO	596
		Cl, Br	5, 6	Me_2PhPO, Me_3PO	592, 596–598
	(ii) $[Th(OEt)Br_3L_n]$	—	2,3	Ph_3PO	593
	(iii) $[Th(OH)Cl_3L_2]\cdot H_2O$	—	—	Ph_3PO	71
B	(i) $[PaX_4L_n]$	Cl, Br	2	Ph_3PO	590, 595
		Cl	6	Me_3PO	598
	(ii) $[PaCl_5L_5]$	—	—	Ph_3PO, Ph_2BzPO	102, 110
	(iii) $[Pa(OEt)_2X_3L]$	Cl, Br	—	Ph_3PO	110
	(iv) $[PaOX_3L_2]$	—	—	Ph_3PO	110
C	(i) $[UCl_3L]$	—	—	Ph_3PO	60
	(ii) $[UX_4L_n]$	Br	1	Ph_3PO	599
		Cl, Br	2	R_3PO (R = Ph, Pr^i, Et, Me, Bu, Bz) Et_2PhPO, Me_2PhPO, Ph_2MePO	507, 590–592, 596, 598, 600–607
		Cl	3,4	Me_3PO, Me_2PhPO, $MePh_2PO$, Bz_3PO	596, 598 601, 607
		Cl, Br	6	Me_3PO, Me_2PhPO	592, 597, 598, 608b, 609
		I	2	Ph_3PO	610
	(iii) $[UX_5L_n]$	F, Cl, Br	1,2	Ph_3PO	110, 611–613
	(iv) $[U(OEt)_2X_2L]$	Cl, Br	—	Ph_3PO	614
	(v) $[UF_{5-x}Cl_xL_n]$ $(0 \leqslant x \leqslant 5)$	—	1,2	Ph_3PO	613, 615a
	(vi) $[UF_4L_2]$ (SbF_6)	—	—	Ph_3PO	615b

D	(i) $[NpX_4L_n]$	Cl, Br	2	Me_3PO, Ph_3PO	590, 595, 598
		Cl	3–3.5	Ph_2MePO	607
		Cl	6	Me_3PO	598
	(ii) $[PuX_4L_n]$	Cl, Br	2	Ph_3PO, $MePh_2PO$	590, 595, 598, 599, 607
		Cl	3	Me_2PhPO	607
			6	Me_3PO	598
E	(i) $[UO_2X_2L_n]$	Cl, Br, I, NCS, NO_3	2	Et_3PO, Ph_3PO, Bu_3PO, topo, Bz_3PO	71, 616–625
		F	1.5–3	topo	626
		I	3, 4	Bu_3PO	623
		F	1.33	Bu_3PO	623
	(ii) $[NpO_2ClL_n]$	—	4	topo	627
	$[NpO_2Cl_2L_n]$	—	2	topo	628
	(iii) $(R_4N)[MO_2X_3L]$ ($R = C_{10}H_{21}$; M = U, Np)	Cl, Br	—	Bu_3PO, topo	628–630
F	(i) $[ThX_4L_n]$	ClO_4	4, 5	Pr_3PO, Ph_3PO	631
	(ii) $[ThL_5(H_2O)]X_4$	ClO_4	—	Ph_3PO	632
	(iii) $[UX_4L_n]$	ClO_4	4–6	Me_3PO, Pr_3PO, Ph_3PO	631
	(iv) $[UO_2X_2L_n]$	ClO_4	2,4	Bu_3PO, Me_3PO, Pr_3PO, Ph_3PO	632, 634
	(v) $[NpO_2L_4(H_2O)](ClO_4)$	—	—	topo	627, 635
G	(i) $[ThX_4L_2]$	SO_3F, SO_3Cl	—	Ph_3PO	579, 637
	(ii) $[UO_2XL_n]$	SO_4	2.5–3	Bu_3PO	633
	(iii) $[UO_2X_2L_n]$	SO_3Cl, SO_3CF_3	1, 2	topo, Ph_3PO	579, 636
	(iv) $[UO_2L_5](SO_3CF_3)_2$	—	—	topo	636
H	(i) $[UX_4L_2]$	BH_4	—	Ph_3PO	638, 639
	(ii) $[UX_2(NO_3)_2L_5]$	BPh_4	—	Me_3PO	640
I	(i) $[Th(X)_4L_n]$	NO_3	1	Ph_3PO	641
			2	Ph_3PO, Bu_3PO, topo, $(2\text{-}O_2NC_6H_4)Ph_2PO$	642–645
			2.67	Pr_3PO	644
			2.67–5	Me_3PO	640, 644, 646
			3	topo, R_3PO (R = 2-ethylhexyl)	647

(continued)

TABLE 12. (*continued*)

	Complex	X (or H_mA)	*n*	L	Ref.
	(ii) $[Th(NO_3)_2L_5X_2]$	BPh_4	—	Me_3PO	640
	(iii) $(Ph_4P)[Th(X)_5L_2]$	NO_3	—	Me_3PO	640
	(iv) $[U(X)_4L_n]$	NO_3	2–5	Ph_3PO, Pr_3PO, Me_3PO	640, 644, 646, 648–651
	(v) $[UO_2(X)_2L_2]$	NO_3	—	R_3PO^a, RPh_2PO ($R = 2\text{-}O_2NC_6H_4$)	617, 618, 620, 622, 626, 634, 643–645, 648, 652–660, 739b
	(vi) $[UO_2XL'L]_2X_2$ $\{L' = (BuO)_3PO\}$	NO_3	—	Bu^n_3PO	661, 662
	(vii) $[NpX_4L_n]$	NO_3	2–3	Bu_3PO, Ph_3PO, Pr_3PO, Me_3PO	644
	(viii) $[NpO_2(NO_3)L_3]$	—	—	topo	627
	(ix) $[Pu(NO_3)_4L_2]$	—	—	Ph_3PO	739c
J	(i) $[ThX_4L_n]$	NCS	4	Ph_3PO, Pr^i_3PO, Bz_3PO	591, 663
		NCS	6	Me_3PO	663
	(ii) $[U(X)_4L_n]$	NCS	4	Me_3PO, Ph_3PO, Me_2PhPO, $MePh_2PO, Pr^i_3PO$, Bz_3PO	591, 596, 663–665
	(iii) $[UX_4L_n]$	NCSe	4	Bu_3PO	666
	(iv) $[UO_2(NCS)_2L_n]$	—	2, 3	Ph_3PO, Bu_3PO	618, 620, 633
	(v) $[UO_2(NCS)_2L_2]\cdot Me_2CO$	—	—	Ph_3PO	667
	(vi) $(R_4N)[UO_2(NCS)_3L_n]$ ($R = C_{10}H_{21}$)	—	2	Bu_3PO	668
	(vii) $[M(NCS)_4L_n]$ ($M = Np$, Pu)	—	4	Me_3PO, Ph_3PO, Me_2PhPO, $MePh_2PO$	663, 669
K	(i) $[M(O_2CR)_4L_n]$ ($M = Th, U$; $R = CH_2Cl$, $CHCl_2$, CCl_3, CF_3)	—	1–4	Ph_3PO, Me_3PO, Me_2PhPO, $MePh_2PO$	670–672
	(ii) $[Th(O_2)AL_n]$	$o\text{-}C_6H_4(COOH)_2$, $2,6\text{-}C_5H_3N(COOH)_2(CH_2COOH)_2$	1, 2	Ph_3PO	79, 673, 674
	(iii) $[U(O_2)_2A_2L]$	$H_2NNHC(S)SCH_2Ph^b$	—	Ph_3PO	176

	(iv) $[\{UO_2(NO_3)L_2\}_2(\mu\text{-}O_2)]$	—	—	Ph_3PO	675
	(v) $[UO_2A_2L_n]$	CH_3COOH	1.5–2	Ph_3PO, Bu_3PO, topo, $Bu_3PO, Pr^i_2PhPO, Bz_3PO$	622, 625, 626, 633, 654, 657, 676–679
	(vi) $[UO_2A_2L]$	RCOOH ($R = Me, Me_2CH, Me_3C$)	—	$Ph_3PO, Pr^i_2PhPO, RPh_2PO$ ($R = 2\text{-}O_2NC_6H_4$)	645, 679
	(vii) $[UO_2A_2L]_2$	MeCOOH	—	Ph_3PO	657, 677, 681
	(viii) $[UO_2AL]$	$(COOH)_2$	—	R_3PO[c]	633, 682, 683
	(ix) $[UO_2AClL_2]\cdot CH_2Cl_2$	Cl_3CCOOH	—	Ph_3PO	684a
L	(i) $[ThA_4L]$	Htta	—	topo, Ph_3PO	49–51
	(ii) $[MA_4L]$ (M = Th, U)	HA[d]	—	Ph_3PO	684b
	(iii) $[MA_2(NCS)_2L_n]$ (M = Th, U)	Hacac	2	Pr^i_3PO	685
	(iv) $[ThA_m(NO_3)_{4-m}L_n]$ ($m = 1, 2$)	Htta, Hdbm, Hbfa, Hba	2	Ph_3PO	553, 686, 687
	(v) $[UA_2Cl_2L_n]$	Hacac	1, 2	Ph_3PO	688, 689
	(vi) $[UO_2A_2L]$	Htta, Hbfa, Htfa	—	Ph_3PO, topo, Bu_3PO, $Me_3PO, (2\text{-}EtC_6H_{12})_3PO$	49, 51, 449, 493, 690–693
		MeCOCH(R)COMe ($R = H, Me, Et, PhCH_2, Cl, NO_2, CN$)	—	Ph_3PO	694
		$R^1COCH_2COR^2$ ($R^1, R^2 = Me, CF_3, Bu^t$)		Me_3PO	695
	(vii) $[UO_2A_2L]\cdot C_6H_6$	Hacac	—	Ph_3PO	696
	(viii) $[UO_2A_2L_n]$	Htta, Hacac	2, 3	topo, Ph_3PO	49–51, 343
	(ix) $[NpA_4L_n]$	Hhfa, Hpvtfa[e], Htta	1–3	Me_3PO, topo, Ph_3PO	697–699
	(x) $[NpO_2A_2L]$	Hhfa, Htfa, Hpvtfa, Hdpvm	—	Me_3PO	698, 700, 701
	(xi) $[MA_3L]$ (M = Pu, Am, Cm)	Htta	—	Ph_3PO, topo	702, 703

---

[a] R = Me, Et, Pr, Bu, Ph, *n*-octyl, isopentyl, nonyl, decyl, hexadecyl, *sec*-octyl.

[b] *S*-Benzyldithiocarbazate.

[c] R = Me, Et, Bu, Ph, isoamyl, octyl, nonyl, decyl.

[d] HA = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione.

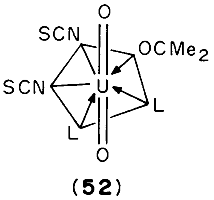
[e] Hpvtfa = Pivaloyltrifluoroacetylacetone.

TABLE 13. Complexs of the organoactinides

	Complex	X	L	Ref.
A	$[(\pi\text{-cp})ThX_3L_n]$ $(n = 1,2)$	Cl, Br	Ph_3PO	704
	$[(\pi\text{-}C_9H_7)ThX_3LL']$ $(L' = \text{thf})$	Cl, Br	Ph_3PO	683
	$[(\pi\text{-cp})MCl_3L_2]$ $(M = Np, Pu)$	—	Ph_3PO, Me_2PhPO) $MePh_2PO$, Ph_3PO	705, 706
	$[(\pi\text{-cp})M(NCS)_{3-n}L_n]$ $(M = Np, Pu; n = 2,3)$	—	Ph_3PO, Me_2PhPO, $MePh_2PO$, Ph_3PO	669
B	$[(\pi\text{-}MeC_5H_4)_3UL]$	—	Ph_3PO	707
C	(i) $[(\pi\text{-cp})UX_3L_n]\cdot x\text{thf}$ $(x = 0,1)$	Cl, Br	$Ph_3PO (n = 2)$	419, 708, 709
		Cl	Ph_3PO, Me_2PhPO, $MePh_2PO (n = 2)$	710
		NCS	$Me_2PhPO (n = 3)$	710
		BH_4	Ph_3PO	711
	(ii) $[(\pi\text{-}C_5Me_4Et)UCl_3L_2]$	—	Ph_3PO	712
D	(i) $[(\pi\text{-}C_9H_7)UX_3L]\cdot\text{thf}$	Cl, Br	Ph_3PO	683
	(ii) $[(\pi\text{-}C_9H_7)UX_3L_2]$	Cl, Br	Ph_3PO	683
E	(i) $[(\pi\text{-cp})_2UX_2L_2]$	Cl, Br	Ph_3PO	709
	(ii) $[(\pi\text{-cp})_2UCl(\text{acac})L_2]$	—	Ph_3PO	713
	(iii) $[(\pi\text{-cp})UCl(\text{acac})_2L]$	—	Ph_3PO	689
	(iv) $[(\pi\text{-cp})UCl_2(HBR_3)L]$ $(R = \text{pyrazol-1-yl})$	—	Ph_3PO	714
	(v) $[(\pi\text{-cp})UCl_2(H_2BR_2)L_2]$	—	Ph_3PO	714
	(vi) $[(\pi\text{-cp})UCl(H_2BR_2)_2L_2]$	—	Ph_3PO	714

For $[UO_2(NO_3)_2L_2]$ $(L = Ph_3PO)$[657], only preliminary X-ray data have been reported. In $[UO_2(NO_3)L'L]_2(NO_3)_2$ $(L^1 = \text{tbp}; L = Bu^n_3PO]$[661,662], bridging by L′ with unidentate nitrate groups has been suggested.

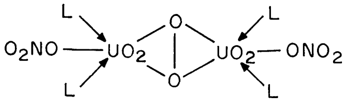
As expected, thiocyanate or selenocyanate groups are N-bonded. The geometry about uranium in $[U(NCS)_4L_4]$ $(L = Me_3PO,Ph_3PO)$[664,665] was shown as square-antiprismatic by X-ray analysis. The structure of $[UO_2(NCS)_2L_2(Me_2CO)]$ $(L = Ph_3PO)$[667] is pentagonal bipyramidal (**52**) with a coordinated Me_2CO group.



(52)

The carboxylate and peroxo complexes of only thorium and uranium are known (Table 12). The peroxo complexes are very stable and inert towards oxidation. The peroxo complex $[\{UO_2(NO_3)L_2\}_2(\mu\text{-}O_2)_2]$ has a dimeric structure (**53**)[675]. X-ray analyses have not been reported for any thorium(IV) carboxylate complexes; however, X-ray analysis of $[UO_2AClL_2]CH_2Cl_2(HA = Cl_3CCOOH;\ L = Ph_3PO)$[684] has shown a pentagonal bypyramidal geometry with apical oxygens of UO_2^{2+} moiety. An X-ray study of a 1:1 adduct has confirmed the dimeric structure of $[UO_2(OAc)_2L]_2$ $(L = Ph_3PO)$[677].

For the 1:2 uranyl acetate adduct $[UO_2(OAc)_2L_2]$ (L = Ph_3PO), only preliminary X-ray data (crystals monoclinic) are available[657]. The complexes are thermally stable, e.g. $[UO_2A_2L]$ (HA = Me_3CCOOH, $Me_2CHCOOH$, L = Ph_3PO)[680] sublime in vacuum. In the thermal study of uranyl oxalate complexes, $[UO_2AL]$[682] (L = R_3PO), it was noted that heating splits off R_3PO. The oxalate decomposed either prior to the loss of R_3PO or simultaneously.



L = Ph_3PO

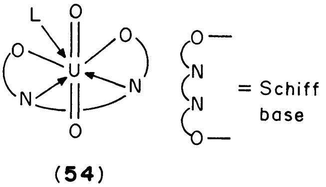
(53)

A series of adducts of actinide β-diketonates are known (Table 12). An X-ray study of $[Th(O_2NO)_3(dbm)(OPPh_3)_2]$[687] has shown an irregular 10-coordinate polyhedron. X-ray analyses of $[UO_2(tta)_2(topo)]$[691], $[UO_2A_2(OPPh_3)]$ {HA = $CH_3COCH(Cl)COCH_3$}[694] and $[UO_2(acac)_2(OPPh_3)]C_6H_6$[696] have shown pentagonal bipyramidal geometry with linear UO_2^{2+} moieties. The benzene in the last complex lies as a solvate although solvation of the actinide diketonates is a rare observation.

^1H NMR study revealed *cis–trans* isomeric forms for $[MO_2A_2L]$ (M = U, Np; HA = Htta, Hbfa, etc.; L = Bu_3PO, Me_3PO)[692,701]·$[UCl_2(acac)_2L]$ (L = Ph_3PO)[689] also showed fluxional behaviour, undergoing ligand exchange with the free ligand to form the $[UCl_2(acac)_2L_2]$ species. Mass spectral study of $[UO_2A_2L]$ (HA = Htfa, $R^1COCH_2COR^2$, R^1,R^2 = Me, CF_3, Bu^t)[693,695] and $[NpO_2A_2L]$[698,700] showed that the complexes were stable and formed molecular ions (dominant abundance). Also, the presence of the ligand in a metal β-diketonate facilitates the cleavage of β-diketone during fragmentation[693].

Interestingly, the bis(trimethylsilylamide)-stabilized 3-coordinate uranium complex $[U\{N(SiMe_3)_2\}_3L]$ in the presence of Ph_3PO[716]. A few pyrazolone complexes, $[Th(pmbp)_4(topo)]$[717], $[UO_2(pmbp)_2(topo)]$[717] and $[UO_2A_2(topo)]$ (HA = 1-phenyl-3-methyl-4-acetylpyrazol-5-one)[718], have been reported as having 7-coordinate uranium and 9-coordinate thorium geometries.

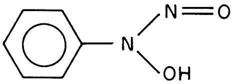
N-(2-Carboxyphenyl)salicylideneimine (H_2A) forms a stable peroxy complex, $[ThA(O_2)(OPPh_3)]$[674]. Tetradentate Schiff bases form 7-coordinate pentagonal bipyramidal complexes: $[UO_2AL]$ (**54**, L = Ph_3PO, H_2A = $HOC_6H_4CH{=}NC_6H_4N{=}CHC_6H_4OH$, $HOC_6H_4CH{=}NC_2H_4N{=}CHC_6H_4OH$ and $HOC_6H_4CH{=}NC_3H_6{-}N{=}CHC_6H_4OH$[993]; $HOC_6H_4CH{=}NCH_2CH_2N{=}CHC_6H_4PH$[720] and $HOC_6H_4{-}N{=}CHCH{=}NC_6H_4OH$[721]). A terdentate Schiff base, $C_6H_4(2\text{-}OH)CH{=}NCH_2C_6H_4(2\text{-}OH)$($H_2A$) formed a 6-coordinate complex, $[UO_2A(OPPh_3)]$[722].



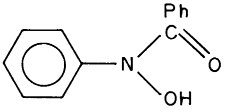
(54)

N-Nitrosophenylhydroxylamine (HA, **55**) formed $[ThA_4(OPPh_3)]$ and $[UO_2A_2L]\cdot 3H_2O$[572]. Similarly, 2-hydroxypyridine *N*-oxide, 2-hydroxypyridine-2-thione and

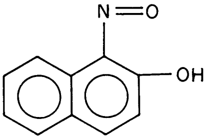
N-phenylbenzoylhydroxamic acid (HA, **56**) formed 7-coordinate $[UO_2A_2(OPPh_3)]$ complexes^{572,723,724}, whereas 1,2-naphthoquinone-1-oxime (HA, **57**) formed the 8-coordinate complex $[UO_2A_2(OPPh_3)(OH_2)]^{739d,e}$ as confirmed by X-ray analysis. Oxamic acids, namely *N*-phenylbenzo-, *N*-phenylcinnamo- and *N*-phenylphenylaceto-hydroxamic acids also formed the adducts $[UO_2A_2(OPPh_3)]^{725}$. 2-Hydroxycyclohepta-2,4,5-trien-1-one (tropolone, HA, **58**) formed the chelate complex $[UO_2A_2(OPPh_3)]^{726-728}$. A few 8-coordinate complexes of hydrotris(pyrazol-1-yl)borate (HA) of the type $[M(NCS)_2A_2L_n]$ (L = Me_3PO, Ph_3PO, Me_2PhPO, $MePh_2PO$, M = Th, $n = 2$; L = Me_3PO, M = U, $n = 2$; M = U, L = Ph_3PO, Me_2PhPO, $MePh_2PO$, $n = 1)^{729}$ are known. Here when $n = 1$, the complexes have one bidentate and one tridentate pyrazol-1-yl ligand.



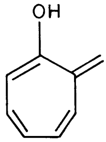
(55)



(56)



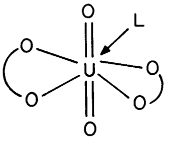
(57)



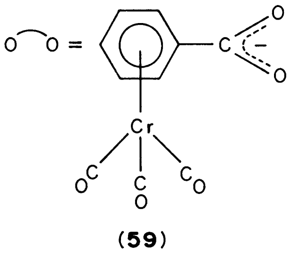
(58)

A number of adducts of uranyldithiocarbamates and phosphorodithioato and other sulphur-containing anions have been reported, viz. $[UO_2A_2L_2]$ HA = *N*,*N*-dialkyldithiocarbamic acid, e.g. Et_2NCSSH, L = Ph_3PO, $Bu^n_3PO^{654,730-733}$, {HA = R_2PS_2H, R = MeO, PhO, etc., L = Ph_3PO^{734}; HA = MeC(O)SH, $PhCS_2H$, L = $Ph_3PO^{654,735}$; HA = Me_2CS_2H, L = Ph_3PO^{735}}. X-ray studies of $[UO_2(S_2CNEt_2)_2(OPPh_3)]^{730,731}$ and $[UO_2(S_2CMe_2)_2(OPPh_3)]^{735}$ have shown irregular pentagonal bipyramidal structures with linear UO_2^{2+} moieties lying along the z-axis. A 1:2 adduct of the $(NC)_2N^-$ anion $[UO_2(N(CN)_2)_2(OPPh_3)_2]^{736}$ has also been reported.

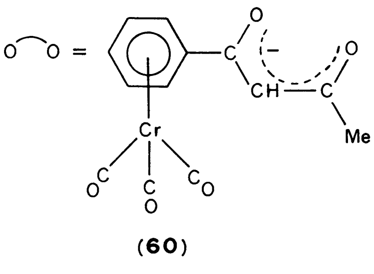
A few complexes with anions derived from ferrocene and chromium carbonyl derivatives are known: $[UO_2A_2L]$ {**59–62**; HA = $Cr(CO)_3(PhCOOH)$, $Cr(CO)_3(PhC(O)CH_2C(O)Me)$, L = Bu_3PO, Ph_3PO^{737}; HA = (π-cp)(π-C_5H_4R')Fe,R' = $CH_2CO_2^-$, $Fe(C_5H_4COCH_2COPh)_2$, L = Bu_3PO,Ph_3PO}^{738,739a}.



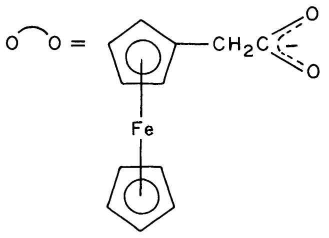
(59–62)



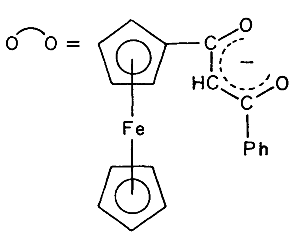
(59)



(60)

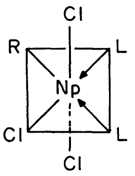


(61)



(62)

Adducts of the organoactinides (Table 13) with π-cyclopentadienyl or its substituted derivatives and π-indenyl and π-C_9H_7 as the organic moieties are known. Only a few adducts of thorium, neptunium and plutonium have been reported as compared with many for uranium. X-ray analysis of [π-$cpNpCl_3(OPMePh_2)$] showed a *cis*-octahedral structure (**63**) about neptunium[705].



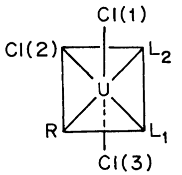
R = π−cp

(63)

The adduct [(π-$MeC_5H_4)_3U(OPPh_3)$][707] was obtained from the reaction of [$(MeC_5H_4)_3U$]·thf and Ph_3PO and confirmed by X-ray analysis. Interestingly, similar reactions with Ph_3PS, Bu_3PSe and Bu_3PTe gave bridging chalcogenide complexes, [{$(MeC_5H_4)_3U$}$_2$E] (E = S, Se, Te).

NMR (^1H, ^{31}P) studies have revealed the existence of two isomers of [(π-cp)$UCl_3(OPPh_3)_2$][419]. This and other complexes, namely [(π-cp)$U(BH_4)_3L_2$][711] and [(π-cp)$UCl(acac)_2L$][689] (L = Ph_3PO), exhibit fluxional behaviour involving exchange phenonomena between coordinated and free Ph_3PO ligands. The lability of the U—$OPPh_3$ bond in organouranium(IV) adducts was further demonstrated by preparing [(π-cp)UCl_3L_2] from [(π-cp)$_3UCl$] and [UCl_4L_2] (L = Ph_3PO)[1109] as well as the disproportionation of [(π-$C_9H_7)UX_3(OPPh_3)_2$] in solution to give [(π-$C_9H_7)_3UX$], [UX_4L_2] and L.[683]

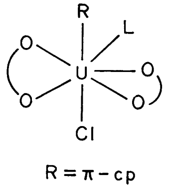
An X-ray study of [(π-cp)UCl_3L_2]thf (L = Ph_3PO)[708] showed a highly distorted *mer*-octahedral structure with the L ligands in *cis* positions (**64**); the angles ∠Cl(2)UCl(3)



R = π−cp

(64)

and ∠Cl(1)UL(1) are 158.1° and 162.7°, respectively, whereas the others lie between 78° and 87°. An X-ray study of $[(\pi\text{-cp})UCl(acac)_2(OPPh_3)]$[689] showed a pentagonal bipyramidal geometry (**65**). X-ray analysis of the indenyl complex $[(\pi\text{-}C_9H_7)UBr_3(OPPh_3)(thf)]$[683] showed a structure similar to that of $[(\pi\text{-cp})UCl_3L_2]thf$[708], the only difference being that one ligand position is occupied by a thf molecule.



(65)

2. *Main Group elements*

a. Complexes of the boron Group (IIIA). Boron(III) halides and boranes form a number of tetrahedral 1:1 adducts with R_3PO ligands, viz. $[BX_3L]$ [X = F, L = Me_3PO, Et_3PO, Pr_3PO, Bu_3PO, Ph_3PO[41,740–743]; X = Cl, L = Me_3PO, Et_3PO, Ph_3PO[41,740,744,745]; X = Br, L = Me_3PO[740]; X = I, L = Ph_3PO[746]); $(BF_2ClL]$, $[BFCl_2L]$, $[BF_2BrL]$, $[BFBr_2L]$ (L = Me_3PO)[740]; $[(0.5)B_2H_6L]$ (L = R_3PO, R = Me, Ph)[747], $[B_{10}H_{12}(OPR_3)_2]$(R = Ph or alkyl)[748]: $[L{\cdot}H_2B(NMe_3)](PF_6)$ (L = Me_3PO)[749] and $[Me_3P(OH)](BF_4)_2$[750]. Most of these complexes were studied using NMR spectroscopy (^1H, ^{13}C, ^{11}B, ^{19}F, ^{31}P)[41,740,743,744]. The complex $BF_3(OPMe_3)$ was stable and distillable, but in water ligand replacement takes place[741]. $BI_3(OPPh_3)$ is moisture sensitive.[746] The X-ray structure of $Ph_3PO{\cdot}BF_3$ shows a tetrahedral structure with a B—O—P angle of 134.5°[751].

The complexes $[(0.5)B_2H_6(OPR_3)]$ (R = Me, Ph) are in fact $BH_3(L)$ adducts[747]. The hydroxyphosphonium salt $[Me_3P(OH)](BF_4)_2$ (prepared from BF_3, HF and Me_3PO) is stable and sublimes without decomposition. The materials $[B_{10}H_{12}(R_3PO)_2]$ ignite when brought into contact with HNO_3, and reduce $AgNO_3$ to silver. This material is useful as a reducing agent, a high-energy fuel and a curing agent for natural or synthetic rubber[1281].

Aluminium halides form adducts $[AlX_3L]$ (X = Cl, L = Me_3PO, Et_3PO, Bu^n_3PO, Ph_3PO[41,60,752,753]; X = Br, L = Ph_3PO[41]), $[AlCl_3(OPMe_3)(OEt_2)]$[752] and $[AlCl_3L_n]$ {$n = 2$ for Ph_3PO, $Ph_2P(O)CH{=}CH_2$, $n = 6$ for Me_3PO}[66,752]. NMR data (^{13}C, ^{27}Al, ^{31}P) and X-ray data for $[AlX_3(OPPh_3)]$[41,751] supported tetrahedral structures about aluminium with linear Al—O—P bonding (180°), of which these complexes represent the first examples.

Organoaluminium(III) forms stable adducts of the type $[R_3Al(L)]$ (R = Me, Et, L = Me_3PO, Et_3PO, Ph_3PO[754–756]; R = HC≡C, L = Ph_3PO)[757]; $[Me_2AlOC(Me){=}CHCMe_3(OPPh_3)]$[249]. $[Me_3Al(OPMe_3)]$ was found to be distillable, but stable below 150 °C, and had a low solubility in non-polar solvents[758,759]. The adducts $[Et_3AlL]$ (L = Me_3PO, Et_3PO) are isosteric with hexaalkyldisiloxanes[754]. Similarly, the adduct $[Al(OR)_3(OPMe)_3]$ (R = $SiMe_3$)[299] is known. The enthalpy of adduct formation between Me_3Al and L was high for Me_3PO versus Ph_3PO (Me_3PO, $\Delta H = -32.0\,\text{kcal mol}^{-1}$; Ph_3PO, $\Delta H = -28.69\,\text{kcal mol}^{-1}$)[755].

The adducts formed with gallium(III) are $[GaX_3L_n]$ (X = Cl, Br, I, $n = 1$, L = Ph_3PO[41,760–762]; X = NCS, NCSe, $n = 3$, L = Pr_3PO, Ph_3PO[763,764]); $[Me_3Ga(OPMe_3)]$[759] $[R_3GaL]$ (R, L = Me, $OPMe_3$; HC≡C, Ph_3PO)[757,759] and $[Ga(OR)_3$-

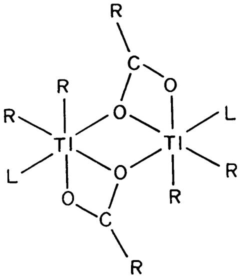
(OPMe$_3$)] (R = SiMe$_3$)[299]; [Me$_3$Ga(OPMe$_3$)] was stable and distillable[759]. NMR (^{13}C, ^{31}P, ^{71}Ga) and X-ray studies of [GaCl$_3$(OPPh$_3$)] showed a tetrahedral structure, again with a linear Ga—O—P moiety (180°) similar to that of [AlCl$_3$(OPPh$_3$)][41].

Indium(I) perchlorate gave an 1:4 adduct, [InL$_4$] (ClO$_4$) (L = Ph$_3$PO)[765]. Indium(III) halides and pseudohalides formed 1:2 and 1:3 adducts of the type [InX$_3$L$_2$] (X = Cl, Br, I, NCO, SO$_3$F, L = Ph$_3$PO[766–768]; X = Cl, Br, L = Me$_3$PO, Ph$_2$MePO, Ph$_3$PO[769]), [InCl$_3$L$_2$(MeOH)] (L = Me$_3$PO)[769], [InCl$_3$L$_2$(OH$_2$)]H$_2$O (L = Me$_3$PO)[769], [InX$_3$L$_3$] (X, L = Cl, Me$_3$PO, Me$_2$PhPO, MePh$_2$PO, NCS, NCSe, NCO, Pr$_3$PO, Ph$_3$PO[764,767,771,772]) and [(C$_6$F$_5$)$_3$InL] (L = Ph$_3$PO)[773].

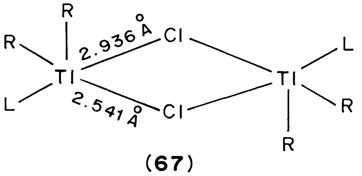
The complexes [InX$_3$L$_2$] (X = Cl, Br) exist as ionic complexes, [InX$_2$L$_4$][InX$_4$] (L = Ph$_3$PO, Ph$_2$MePO; X = Cl, Br)[769]. The cations presumably have *trans*-halogen groups. X-ray studies of [InCl$_3$L$_2$(MeOH)], [InCl$_3$L$_2$(OH$_2$)]H$_2$O (L = Me$_3$PO)[769] and [InCl$_3$L$_3$] (L = PhMe$_2$PO) have shown *fac*-octahedral structures, whereas [InCl$_3$L$_3$] (L = Me$_3$PO) has a *mer*-octahedral structure[769]. A mixed heterometallic In–Co complex, [L$_3$In][Co(CO)$_4$]$_3$ (L = Ph$_3$PO) (^{59}Co NMR), has been reported[770].

Thallium(III) halides and mixed halides form adducts of the type [TlX$_3$L$_2$] (X = Cl, Br; I, L = Ph$_3$PO)[774–777] [TlBr$_2$XL$_2$] (X = Cl, I), [TlCl$_2$IL$_2$] (L = Ph$_3$PO)[778–779], [TlClBrIL$_2$] (L = Ph$_3$PO)[780] and [HL$_2$]$^+$ [TlCl$_4$]$^-$ (L = Bu$^n_3$PO)[781]. An initial attempt to isolate [TlI$_3$L$_2$] failed and instead [TlI$_3$L$_3$] (L = Ph$_3$PO) was isolated[774]. [TlX$_3$L$_2$] adducts were formulated (X = Br, I) as [TlBr$_2$L$_4$][TlBr$_4$] and [TlI$_2$L$_4$][TlL$_4$L$_2$][774]. However, X-ray analysis of [TlBr$_3$L$_2$] and [TlClBrIL$_2$] (L = Ph$_3$PO)[775,778,780] confirmed the non-ionic nature of the complexes. The geometry about thallium is slightly distorted trigonal bipyramidal with *trans*-Ph$_3$PO groups.

Mono-, di- and tri-organothallium(III) form complexes such as [RTlX$_2$L] (R = Ph, *p*-tol; X = Cl, Br, O$_2$CCCl$_3$; L = Ph$_3$PO)[782,783], [R$_2$TlXL$_4$] (X = Cl, Br, O$_2$CCF$_3$, O$_2$CC$_6$F$_5$, acac, hfa, tfa, dbm, R = C$_6$F$_5$, *p*-HC$_6$H$_4$, $n = 1$; X = NO$_3$, $n = 2$, L = Ph$_3$PO)[784–788], [R$_2$Tl(O$_2$SR′)L] (R = C$_6$F$_5$; R′ = Ph, *p*-MeC$_6$H$_4$; L = Ph$_3$PO)[789] and [R$_3$TlL] (R = C$_6$F$_5$, 3, 5-H$_2$C$_6$F$_3$, L = Ph$_3$PO)[790]. X-ray analyses of [(C$_6$F$_5$)$_2$·Tl(O$_2$CC$_6$F$_5$)L][787] and [(*p*-HC$_6$F$_4$)$_2$TlClL] (L = Ph$_3$PO)[788] revealed dimeric structures with unsymmetrical C$_6$F$_5$CO$_2$ and chloro bridging. The thallium has a distorted octahedral structure with unsymmetrically bonded C$_6$F$_5$CO$_2$ groups. In **66** each thallium has a distorted octahedral structure with unsymmetrically bonded C$_6$F$_5$CO$_2$ groups, and in **67** each thallium has approximately trigonal bipyramidal geometry with two R and more tightly held Cl groups in the equatorial plane.



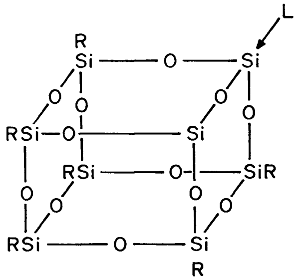
(66)



(67)

b. Complexes of the silicon Group (Si,Ge,Sn,Pb)(IVA). Silicon(IV) complexes have been reported of the type [SiX$_4$L$_n$] ($n = 2, 4$; X = F, Cl, Br; L = Ph$_3$PO, Me$_3$PO)[791–793], [SiBr$_2$L$_4$(ClO$_4$)$_2$][791], [SiL$_4$(ClO$_4$)$_4$][791] and [Me$_3$SiClL] (L = Ph$_3$PO)[794]. The 1:4 (M:L) complexes were shown to possess cations of the type [SiX$_2$L$_4$]$^{2+}$ or [SiL$_4$]$^{4+}$ [791]. Further, the formation constant for $[SiCl_4(OPPh_3)_2]$ was higher ($180\,l\,mol^{-1}$) than for $[Me_3SiClL]$ ($60 \pm 5\,l\,mol^{-1}$)[794].

Reaction of Me_3Al or $(Me_2CHO)_3Al$ with $R_7(Si_7O_9)(OH)_3$ (R = cyclohexyl) gave quantitatively $[R_7(Si_7O_{12}Al)]_2$, which on further reaction with Ph_3PO gave **68**, characterized by X-ray analysis[795]. Compound **68** represents the first well characterized example of aluminium-containing polyhedral silsesquioxanes proposed as models for the secondary building units of aluminosilicate minerals and zeolites.

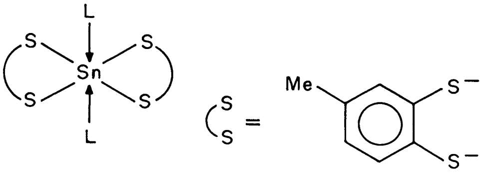


(68)

The only known germanium(IV) complex is $[GeCl_4(OPMe_3)_2]$[73]. In comparison with tin(IV), there are a few complexes with tin(II). Tin(II) forms complexes of the type $[SnX_2L_n]$ (X = Cl, Br, NCS, ClO_4, $n = 1$, L = Ph_3PO[796,797]; X = Cl, Br, L = Ph_3PO, $n = 2$[797]]. A ^{31}P NMR study revealed the formation of $[SnL_m](SbF_6)_2$ ($m = 2, 3$; L = Ph_3PO)[798]. $[SnCl_2(OPPh_3)]$ behaves as a ligand in the complexes $[Mn(SnCl_2L)_5Cl]Cl$ (M = Ru, Os), $[Rh(SnCl_2L)_4(SnCl_3)Cl]Cl$ and $[Ir(SnCl_2L)_5Cl]Cl$[306]. Recently, $[SnLI_2]$ (L = dimethyl(phthalimidomethyl)phosphine oxide) was also used as a ligand, forming $[PtCl_2(SnLI_2)_2]$[799].

Tin(IV) halides form 1:2 adducts with R_3PO ligands of the type $[SnX_4L_2]$ (X = F, Cl, Br, I; L = R_3PO, R = Me, Et, Bu, Cy, Ph[63,64.73,800–816], L = $R_2R'PO$, R = Et, R′ = Et, Pr, Cy[811,817,818]; R = Ph, R′ = $CH{=}CH_2$[66]; R = Me, R′ = Me, etc., R = Ph, R′ = Me[820]; L = $RR'R''PO$, R, R′, R″ = Ph, Me, *i*-Pr[821]], $[SnCl_3(O_2CCH_3)L]$ (L = Ph_3PO)[822] and $[SnCl_3(OCH_2CF_3)L]$ (L = Ph_3PO)[823]. The geometry about tin is variable for $[SnX_4L_2]$ complexes. Mössbauer data suggest *cis*-octahedral structures[812,815,816]. However, X-ray studies showed a *trans*-octahedral structure in $[SnBr_4L_2]$ (L = Ph_3PO)[806], but a *cis*-octahedral structure for $[SnI_4(OPPh_3)_2]$[807], and $[SnCl_4(OPPh_3)_2]$[824]. An NMR study of $[SnCl_4L]$ (L = $R_2R'PO$, R = Me, R′ = Me, etc.)[819] revealed *cis–trans* isomerism. Similarly, NMR data (^{31}P, ^{119}Sn) for $[SnX_4L_2]$ (X = Cl, Br; L = Bu^n_3PO) complexes revealed that $[SnCl_4L_2]$ predominantly exist in the *trans*-octahedral form with the *cis* isomer in low abundance[825]. The formulation of $[SnCl_xBr_{4-x}L]$ and $[SnCl_xBr_{5-x}L]^-$ (L = Bu^n_3PO) has been established by NMR spectrometry[825]. X-ray analysis of the acetatotrichlorotin(IV) adduct $[SnCl_3(O_2CCH_3)(OPPh_3)]$[822] showed an octahedral structure with CH_3CO_2 acting as a chelating agent.

A sulphur-containing spirocyclictin(IV) complex $[SnX_2(OPPh_3)_2]$ (H_2X = toluene-3, 4-dithiol) (**69**) has been reported[826]. Monoorganotin(IV) forms 1:1 and 1:2 complexes of the type $[RSnX_3L_2]$ {R, X, L = Me, Et, Bu^n, Ph, Cl, Br, I, Ph_3PO[807,812,816,824,827–830]; Bu^n, Cl, Cy_3PO[827,830]; $R'CO_2CH_2CH_2$, Cl, topo, Ph_3PO (R′ = Me, Bu)[831], Me, Ph, Cl, Br, Bu^n_3PO[832]}; $[PhSnCl_2BrL]$, $[PhSnClBr_2L]$ (L = Bu_3PO)[832], $(Et_4N)[RSnCl_4L]$ (L = Ph_3PO)[833] and $[RSnCl_3L]$ (L = Et_3PO, Ph_3PO)[834]. For $[EtSnX_3L_2]$ (X = Cl, Br, I; L = Ph_3PO), X-ray analysis established *trans*-octahedral structures. Mössbauer data favoured a *cis*-octahedral structure for $PhSnCl_3L_2$ (L = Ph_3PO)[816,827]. Similarly, a

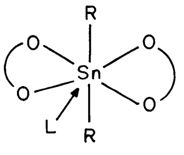


(69)

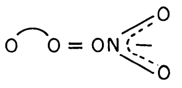
trans-octahedral was suggested for [$BuSnCl_3L_2$] (L = Ph_3PO, Cy_3PO)[827,830], a *cis*-octahedral structure (wrt, R, L) for (Et_4N) [$RSnCl_4L$] and a trigonal bipyramidal structure was suggested for [$PhSnCl_2BrL$] and [$PhSnClBr_2L$] (^{31}P, ^{119}Sn NMR)[832].

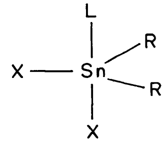
Diorganotin(IV) forms 1:1 and 1:2 complexes of the type (A) [R_2SnX_2L] [R, X, L = Et, Bu, Ph, *p*-$MeOC_6H_4$, Cl, Br, NCS, Ph_3PO, Bu_3PO[827,830,835–840]; Et, Bu, Cl, Cy_3PO[830]], (B) [Et_2SnX_2L] (L = Et_2RPO; R = Bu; X = Cl, etc.)[841], (C) [$R_2SnX_2L_2$] (R = Me, Et, $H_2C{=}CH$, Bu, Ph, *p*-MeC_6H_4, $PhCH_2$, Cl, Br, I, NCS, $OCOCF_3$, Ph_3PO[812,816,827,837,839,842–851]; $R'CO_2CH_2CH_2$, Cl, Br, Et_3PO, Bu_3PO, topo, Ph_3PO[344,831,834,836,840]), (D) [$PhMeSnCl_2(OPPh_3)$][852] and (E) [Me_2SnL_4] $(Ph_4B)_2$, [$Me_2SnL_2(OAsPh_3)_2$] $(BPh_4)_2$ (L = Ph_3PO)[728,853,854].

Complexes A were formed by the direct reaction of diorganotin(IV) compounds with a ligand whereas complexes B were formed on thermal heating of [Et_2SnX_2[$Et_2P(OR)$]], wherein $Et_2P(OR)$ isomerized to Et_2RPO. An X-ray study of the nitrate complex [$Ph_2Sn(O_2NO)_2(OPPh_3)$] revealed a pentagonal bipyramidal structure (**70**)[855]. On the basis of Mössbauer data, trigonal bipyramidal geometry with R groups in the equatorial plane are suggested for complexes A (**71**)[836,837,839]. An NMR study (^{31}P, ^{119}Sn) of the exchange of free and coordinated Bu^n_3PO in [Ph_3SnX_2L] (X = Cl, Br) revealed that the exchange was rapid at room temperature but slow at 60 °C. When [Ph_2SnX_2] and L were mixed, the formation of [$Ph_2SnClBrL$] complexes was detected[836,838].



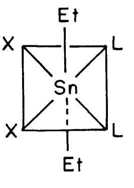
(70)



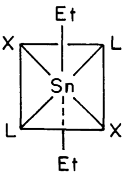


(71)

Mössbauer and IR data supported a *trans* disposition of the R groups in complexes C–E. X-ray studies of [$Et_2SnX_2L_2$] (X = Cl, I; L = Ph_3PO)[847,848] revealed the existence of *cis* and *trans* isomers (**72**, **73**). NMR studies (^{31}P, ^{119}Sn)[836,840] also revealed the formation of 1:2 complexes [$Ph_2SnX_2L_2$] (X = Cl, Br; L = Bu_3PO, Ph_3PO), while another study revealed partial dissociation of the complexes [$R_2SnCl_2L_2$] (L = Et_3PO, Ph_3PO)[344,834].

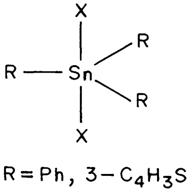


(72)



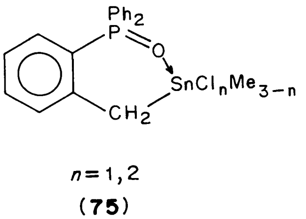
(73)

Triorganotin(IV) forms complexes of the type (A) $[R_3SnXL]$ (R, X, L = Me, Bu, Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, 3-furyl, 3-thienyl, Cl, Br, NCS, NCO, NO_3, N_3, $OCOCF_3$, O_2COCCl_3, $Ph_3PO^{794,839,846,851,856-871}$; Et, Ph, etc., Cl, Br, I, Et_3PO, $MePh_2PO$, Et_2BuPO, $Ph_3PO^{834,841,872-875}$), (B) $[R_2R'SnXL]$ (R_2R', X, L = Bu_2Ph, Ph_2Bu, Cl, Br, $Ph_3PO)^{876}$ and (C) $[R_3SnL_2]X_2$ (R_3, L, X = Me_3, Bu_3, Bu_2Ph, Ph_2Bu, Ph_3PO, BF_4, $BPh_4)^{853,876,877}$. The formation of $[Et_3SnXL]$ (L = Et_2RPO) takes place via $[Et_3SnXL']$ (L' = $Et_2(OR)P\}$ involving isomerization of L' to $L^{841,875}$. Other complexes were formed by usual methods. Mössbauer and NMR data for numerous complexes have favoured *trans*-trigonal bipyramidal geometries for A–C complexes with R_3 groups in the equational plane. X-ray analyses of $[Ph_3Sn(ONO_2)(OPPh_3)]^{864,865}$ and $[Sn(C_4H_3S)_3Br(OPPh_3)]^{869,870}$ have confirmed the proposed structures (**74**) for A, B and cations of C. The carboxylate groups O_2COCR_3 (R = F, Cl) were also unidentate^{867,868}.



(**74**)

Triphenyltin phosphinylacetate, $[Ph_3SnO_2CCH_2P(O)Ph_2]$, forms a 1:1 adduct with $[Ph_3SnCl]^{878}$. A few organotin(IV) complexes involve intramolecular coordination $(\mathbf{75})^{879}$. A few lead(II) complexes $[PbL_m]$ $(SbF_6)_2$ have been reported ($m = 2$, 3; L = Ph_3PO); their existence was established by a ^{31}P NMR study^{798}. Lead(IV) chloride formed 1:2 whereas lead(IV) acetate and dihydrogenphosphate formed 1:1 adducts with $Ph_3PO^{880,881}$. $[Pb(H_2PO_4)_4(OPPh_3)]$ is a superior oxidizing agent to $Pb(OAc)_4(OPPh_3)$ for organic compounds owing to the higher thermal and moisture stability of the former. However, hot water hydrolyses the $[Pb(H_2PO_4)_4(OPPh_3)]$ adduct^{881}.



(**75**)

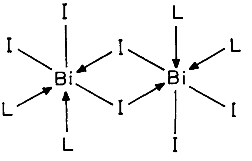
Diorganolead(IV) adducts have been reported: (A) $[Ph_2PbX_2L_n]$ (X, L = Cl, Br, I, Ph_3PO for $n = 1$, Br, I, Ph_3PO for $n = 2^{840,882}$; NCSe, Ph_3PO for $n = 2^{883}$) and (B) $[Me_2PbX_2L]$ (L = R_3PO, R = Me, Et, Bu^n, Ph; X = quinolin-8-olate, $YC_6H_4CO_2$, Y = H, *o*-Me, *m*-Me, *p*-Me, *p*-MeO$)^{884}$. The complexes A were labile, particularly for X = Br, I and solvents such as MeOH, Me_2CO replaced Ph_3PO^{882}. Trigonal bipyramidal structures were suggested for $n = 1$ and octahedral for $n = 2$. Complexes B studied by NMR (Job's method) are 7-coordinate and the stability constants decreased in the order R = Me > Et > Bu^n > Ph^{884}. A few triorganolead(IV) adducts, $[R_3PbXL]$ (R = Me, Ph; X = Cl, NCO; L = Ph_3PO) with trigonal bipyramidal geometry are also known^{851,885}.

c. Complexes of the phosphorus Group (P, As, Sb, Bi) (VA). The phosphorus(V) complexes $[PF_5L]$ ($L = Bu_3PO$, Ph_3PO) and *trans*- $[PF_4(OPBu_3)_2]^+F^-$ have been studied using ^{19}F and ^{31}P NMR[886]. ^{31}P NMR revealed the basicity order of the ligands to be $Bu_3PO > Ph_3PO > Bu_3P$. Similarly, arsenic complexes of the type (A) $[AsCl_3(OPMe_3)]$, (B) $[AsCl_5(OPMe_3)]$[491,492], (C) $[AsCl_5(OPPh_3)_2]$[887] and (D) $[Me_3POH)$ $[AsF_6]$[750] have been reported. Complex C was prepared at 0 °C and evolved Cl_2 at room temperature. Fresh samples were weakly paramagnetic, possibly owing to a low concentration of an arsenic(IV) species as an intermediate in the solid-state reduction of arsenic(V) to arsenic(III)[887]. Complex D, obtained from Me_3PO, HF and AsF_5, decomposed on heating, forming $[(Me_3PO)AsF_5]$[750].

Antimony(III) and antimony(V) form complexes of the type (A) $[SbX_3L_n]$ {$X = Cl$, Br, I; $L = R_3PO$, R = Me, Ph, $Ph_2P(O)CH{=}CH_2$; $n = 1$ or 2[66,491,492,888–890,907], (B) $[SbCl_5L]$ ($L = R_3PO$, R = Me, Ph, Bu^n)[59,64,491,492,891–895], (C) $[SbCl_3Br_2L]$ ($L = Ph_3PO$)[896], (D) $[SbF_nCl_{5-n}L]$ ($L = R_3PO$; R = Bu, Ph; $n = 1–5$)[897], (E) $[Sb(OR)Cl_4L]$ ($L = Ph_3PO$; R = Me, Et, ClC_2H_4, $Cl_3C_2H_2$, $F_3C_2H_2$)[823,898–900], (F) $[SbCl_4(NR_2)L]$ ($L = Ph_3PO$; $R = SO_2F$)[901], (G) $[Sb(SO_3CF_3)_3L]$ ($L = Ph_3PO$)[902] and (H) $[L_2H]^+$ $[SbCl_6]^-$ and $(L_3 \cdot H_3O)^+$ $[SbCl_6]^-$ ($L = Ph_3PO$)[903]. Similarly, a number of organoantimony(V) complexes are known: (I) $[R_3SbL_2]$ $(ClO_4)_2$ ($L = Ph_3PO$; R = Me, Ph)[904], (J) $[R_2SbCl_3L]$ (R = Me, Et, Ph; $L = Ph_3PO$)[905] and (K) $[R_nSbX_{5-x}L]$ (X = F, Br; $L = Ph_3PO$, R = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4; $n = 1–3$)[906].

A single-crystal X-ray study of $[SbCl_5(OPMe_3)]$ showed a distorted octahedral structure[892]. The angle Sb—O—P of 139° reveals considerable deviation from the tetrahedral angle at oxygen. For other complexes of type B, and also for complexes C–F, J and K, octahedral and in the case of $[R_3SbL_2]$ $(ClO_4)_2$[904] trigonal bipyramidal structures are suggested. As expected, the Lewis acdity of the metal halides decreased as the halide increased in atomic number, i.e. $F > Cl > Br > I$[897,906].

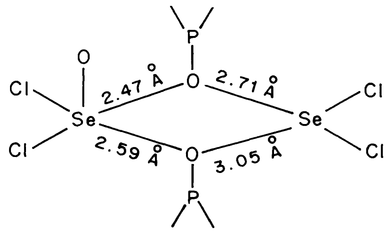
Bismuth(III) and bismuth(V) form complexes of the type (A) $[BiCl_3L_n]$ ($n = 1–3$; $L = Ph_3PO$)[890,907,908], (B) $[BiI_3L_2]$ ($L = Ph_3PO$)[909], (C) $[Ph_3BiL_2]X_2$ ($X = ClO_4$, PF_6; $L = Ph_3PO$)[910]; (D) $[Ph_3BiL_2]_2O(ClO_4)_2$ ($L = Ph_3PO$)[910] and (E) $[Bi(SO_3CF_3)_3L]$ ($L = Ph_3PO$)[902]. For complex B an iodo-bridged dimeric structure (**76**) and for complex D an oxygen-bridged dimeric structure have been suggested. However, X-ray analyses should be extended to further compounds.



(**76**)

d. Complexes of the selenium Group (Se, Te) (VIA). There are only two complexes of selenium(V) with R_3PO ligands, $[SeOCl_2(OPMe_3)]$[491] and $[SeOCl_2(OPPh_3)]_2$[911]. An X-ray study of the latter revealed a distorted square-pyramidal geometry about the selenium atom. Ph_3PO acts as a bridge, but the Se---O—P bonds differ significantly (**77**). The former complex presumably has a similar structure.

Tellurium(IV) chloride forms hygroscopic $[TeCl_4L_n]$ adducts ($L = Ph_3PO$, Me_2PhPO; $n = 1,2$)[897]. Similarly, a series of hygroscopic organotellurium(III) and (IV) adducts have been reported: (A) $[(p\text{-}RC_6H_4)TeClL]$ (R = MeO, PhO; $L = Ph_3PO$)[912], (B) $[RTeCl_3L_n]$ ($n = 1,2$, L, R = topo, Ph, *p*-$PhOC_6H_4$[913]; $n = 1$, L, $R = Ph_3PO$, Me_2PhPO, Ph, 4-$MeOC_6H_4$, 4-BrC_6H_4, *p*-HOC_6H_4[897,914]) and (C) $[Ph_2Te(ONO_2)_2(OPPh_3)]$[915]. For



(77)

complexes B and C (except for $n = 2$), 5-coordinate monomeric distorted octahedral structures have been suggested (one site occupied by a lone pair).

3. *Alkali and alkaline earth elements*

a. Complexes of the alkali metal Group(IA). Alkali metals also form complexes, although the number of investigations is small. From solution-phase studies, formation of species of the type [ML]X $\{M = Li,\ X = Cl,\ Br,\ ClO_4,\ L = Ph_3PO$ or $Ph_2P(O)CH_2Ac;\ M = Na,\ L = Ph_3PO,\ X = I\}$[365,916–918] was established. Other complexes studied in the solid state include (A) $[LiL_n]X$ ($L = Ph_3PO$, $n = 4$, $X = Br$, ClO_3, PF_6, ReO_4, IO_4, SbF_6, $AuCl_3$, $SnCl_3$, $GaCl_4$; $L = Ph_3PO$, $n = 5$, $X = I$, NO_3, BF_4, BrO_3)[478]; (B) $[NaL_5X]$ ($L = Ph_3PO$; $X = I$, ClO_4, IO_4, BPh_4)[478], (C) $[Me_3SiOML]_4$ ($M = Li$, Na, K; $L = Me_3PO$)[919] and (D) $[(15\text{-crown-}5)Na(Me_3PO)]^+[(CO)_3Fe(\mu\text{-}Bu^t_2P)Rh(CO)(PMe_3)]^-$ [920]. For complexes A and B with $n = 5$, 5-coordinate square-pyramidal geometry, and for complexes A with $n = 4$, tetrahedral geometry have been suggested. In complex C, each alkali metal is tetrahedrally surrounded.

Alkali metal complexes in the zero-valent state, such as [ML] and $[M_2L]$ ($L = Ar_3PO$), have also been reported[921].

b. Complexes of the alkaline earth metal Group (Be, Mg, Ca) (IIA). Only two beryllium(II) complexes, $[BeL_2(NO_3)_2]$ and $[BeL_4](BF_4)_2$ ($L = Ph_3PO$) are known[922]. In contrast, more complexes have been reported for magnesium(II) and calcium(II), namely $[ML_nX_2]$ $\{M = Mg,\ Ca,\ L = Me_3PO,\ Ph_3PO,\ Bu^n_3PO,\ n = 4,\ X = ClO_4,\ BF_4$[137,232,233,923]; $M = Mg,\ Ca,\ L = Me_3PO,\ Ph_3PO,\ n = 5,\ X = ClO_4$[923]; $M = Ca,\ L = (HOCH_2)_3PO,\ n = 6,\ X = BF_4$[234]$\}$, $[MgL_5(OH_2)](ClO_4)_2$ ($L = Me_3PO$, Ph_3PO)[923] and $[MgL_2Cl_2]_n$ $\{L = (HOCH_2)_3PO\}$[234]. An X-ray study of $[MgL_5](ClO_4)_2$ ($L = Me_3PO$)[924] showed a square-pyramidal geometry with a shorter axial Mg—O bond (1.94 Å); compared with the basal Mg—O bonds (2.03 Å); this is attributed to O → Mg π-bonding along the axial bond. The aquated analogue $[MgL_5(OH_2)](ClO_4)_2$[925] has an octahedral structure. Each cation is hydrogen-bonded to two ClO_4^- anions via the coordinated H_2O molecules. For the 1:4 complexes, 5-coordinate species of the type $[ML_4(OClO_3)](ClO_4)$ with presumably a square-pyramidal geometry have been suggested from spectral and other studies[232,923]. For $[MgL_2Cl_2]_n$, a polymeric structure was suggested[234].

A ^{31}P NMR study on the exchange of the Ph_3PO with the coordinated ligand in $[Mg(OPPh_3)_5]^{2+}$ revealed that magnesium has harder Lewis acid character relative to zinc in $[Zn(OPPh_3)_4]^{2+}$ [926]. The interaction of $CaCl_2$ with $Me_2P(O)CH_2R$ ($R = Cl$, OMe, OPh) in MeCN has also been reported[227]. Reaction of Ph_3PO with Mg^{2+} in chlorophyll a and b involves replacement of the keto groups of the chlorophyll[927a].

B. Di-, Tri- and Tetra-tertiary Phosphine Oxides

Most of the complexes reported are with di-tertiary phosphine oxides, a small number of complexes with tri-tertiary phosphine oxides and a few complexes with tetra-tertiary phosphine oxides.

1. Transition elements

a. Complexes of scandium and titanium Groups(IIIB and IVB). Scandium(III) on reaction with the bidentate ligand $dpeO_2$ gave an octahedral complex, $[Sc(dpeO_2)_3]\cdot(ClO_4)_3$[55]. Similarly, the tri-tertiary phosphine oxide $\{Ph_2P(O)\}_3CH$ formed complexes with scandium(III) and yttrium(III) of stoichiometry $[ML_3]$ (where L is the anion $\{Ph_2PO\}_3C^-)$[927b]. One PO end of the anion is uncoordinated and thus it acts as a bidentate ligand in these complexes. ^{31}P NMR study revealed the lack of lability of Sc—OP or Y—OP bonds so that there was no exchange of the coordinated and uncoordinated PO groups or with the added lithium salt, $\{Ph_2P(O)\}_3C^-Li^+$. The value of the ^{89}Y–^{31}P coupling was 6.5 Hz (for Y, $I = \frac{1}{2}$), the first reported value for such coupling.

Reaction of zirconium(IV) chloride with $dpeO_2$ gave a *cis*-octahedral complex, $[ZrCl_4(dpeO_2)]$[75]. The tridentate ligand $[Ph_2P(O)CH_2]_2P(O)Ph(L)$ formed complexes with zirconium(IV) and halnium(IV), $[ZrCl_4L]$, $[M(OH)_2Cl_2L]\cdot 8H_2O$ and $[Zr(OH)_2L](ClO_4)_2$[928].

b. Complexes of the vanadium, chromium and manganese Groups (VB–VIIB). The reaction of vanadyl halides, $VOX_2\cdot nH_2O$, with dpe gave $[(VOX_2)_2(dpeO_2)]\cdot nH_2O$ ($n = 1,4$; X = Cl, Br)[929] in which dpe was oxidized to $dpeO_2$, probably by the metal salt. When anhydrous vanadyl chloride, $VOCl_2$ (from V_2O_5 and HCl in EtOH), was reacted with $dpeO_2$ a 1:1 adduct, $[VOCl_2(dpeO_2)]$, was formed[86].

Hexacarbonyls of Group VIB metals, $[M(CO)_6]$, undergo substitution reactions with $dpmO_2$ forming monomeric *cis*-octahedral $[M(CO)_4(dpmO_2)]$ and dimeric *fac*-$[M_2(CO)_6(dpmO_2)_3]$[930]. Similarly, with $\{Ph_2P(O)CH_2\}_2P(O)Ph$, *cis*-$[M(CO)_4L]$ and *fac*-$[M(CO)_3L]$ were formed[930]. Oxidation of bisphosphine complexes $[M(CO)_4(dpe)]$ with halogens (Cl_2 and Br_2) in $CHCl_3/CCl_4$[931] gave $[MoOX_3L]$ and $[MO_2X_2L]$ (M = Mo, W; X = Cl, Br; L = $dpeO_2$). Whereas molybdenum(V) complexes are precipitated from the reaction mixture, the M^{VI} complexes must be obtained from the filtrate. Molybdenum(V) complexes show normal magnetic behaviour ($\mu = 1.65$–1.73 BM, $T = 100$–300 K). Halogen oxidation of $[M_2(CO)_6(dpmO_2)]$ and $[M(CO)_3L]$ $\{L = (Ph_2POCH_2)_2P(O)Ph\}$ also gave 7-coordinate complexes, $[M(CO)_3(dpmO_2)X_2]$ and $[M(CO)_3LX_2]$ (X = Br, I)[932].

Treatment of the molybdenium(V) complex $MoOX_3(dpeO_2)$ (X = Cl, Br) with hydrogen peroxide in ethanol gave diamagnetic peroxo complexes $[MoO(O_2)_2(dpeO_2)]$[174]. Two nitrosyl complexes, $[Mo(NO)(dpeO_2)X_2]$ (X = Cl, Br), are also known[933].

The reaction of manganese(II) halides with dpm, dpe and *cis*-$Ph_2PCH{=}CHPPh_2$ gave phosphine oxide complexes, $[MnX_2L]$ $\{X = Cl, Br, I; L = dpmO_2, dpeO_2$, *cis*-$Ph_2P(O)CH{=}CHP(O)Ph_2\}$ and an ionic complex, $[Mn(dpmO_2)_2]Br_2$[222,934]. Similarly, reactions of manganese(III) chloride with dpm, dpe, dpp and *cis*-$Ph_2PCH{=}CHPPh_2$ also gave similar phosphine oxide complexes, $[MnCl_2L]$ (L = $dpmO_2$, $dpeO_2$, etc.); $MnCl_3$ chlorinated R_3P to form R_3PCl_2, which on hydrolysis gave R_3PO[935].

Reactions of $[Re(CO)_5X]$ and $K_2[ReOX_5]$ (X = Cl, Br, I) with $dpeO_2$ gave the octahedral complexes $[Re(CO)_3LX]$ and $[ReOX_3L]$, respectively[259a,268]. Heating the complexes $[ReOX_3L]$ (L = dpe, *cis*-$Ph_2PCH{=}CHPPh_2$) gave the corresponding phosphine oxide complexes. Similarly, on heating $H_2L[ReCl_6]$ in Me_2CO containing HCl the $[ReCl_4L']$ complex was formed $\{H_2L^{2+} = (H)Ph_2\overset{+}{P}CH_2CH_2\overset{+}{P}(H)Ph_2$; $L' = dpeO_2\}$[262b]. In $[Re(CO)_3LX]$ the ligand L is unidentate, whereas in the other complexes it is bidentate.

c. Complexes of the iron, cobalt and nickel Groups(VIII)

i. Iron sub-Group. Reactions of iron(II) salts with di-tertiary phosphine oxides formed complexes (A) $[FeX_2L(H_2O)_2]\cdot mH_2O$ $\{m = 0,1;$ X = Cl, Br, NCS; L = $Ph_2P(O)\cdot$

$(CH_2)_nP(O)Ph_2$; $n = 1,2,4,6\}$, (B) $[FeL_3]I_2 \cdot mH_2O$($n = 1,4$ for L; $m = 1,2$), (C) $[FeL_2I_2] \cdot mH_2O$ ($n = 2$ for L, $m = 0,1$) and (D) $[Fe(CO)_2LI]I \cdot mH_2O$ ($n = 1,2,4,6$ for L; $m = 1,2$)[936,937]. The complexes had a tendency to absorb moisture; complexes D were light sensitive and showed low μ value (3.85–3.95 BM)[937]. The carbonyl groups in D lie in *cis* positions in a trigonal bipyramidal geometry. For complexes A–C octahedral geometry is suggested.

Iron(III) halides generally formed mixed octahedral–tetrahedral complexes of the type $[FeL_2X_2][FeX_4]$ $\{X = Cl$, Br; $L = Ph_2P(O)(CH_2)_nP(O)Ph_2$; $n = 1,2,4,6\}$[938–940], although a complex of the type $[FeL_3][FeCl_4]_3$ is also known[941]. Similarly, with iron(III) isothiocyanate, nitrate and perchlorate, complexes with various stoichiometries, e.g $[Fe(NCS)_3L]$ ($n = 2,4,6$ for L) $[Fe(NCS)_2L_2](NCS)$ ($n = 1$ for L), $Fe(NO_3)_3L$ ($n = 4,6$ for L), $[Fe(NO_3)_2L_2](NO_3)$ ($n = 2$ for L), $[FeL_3](ClO_4)_3$ ($n = 1$ for L), etc., are known[940,942].

The thiocyanate complexes showed low μ values (5.34–5.58 BM) compared with the typical values shown by other complexes. For the complexes $[FeL_2X_2][FeX_4]$, *trans*-octahedral cations (with respect to X) showed $g_{\perp}$ values of about 6; however, their $g_{\parallel}$ values (ca 2) merged with the strong ESR band due to the $[FeX_4]^-$ species at $g \approx 2$[943]. Interestingly, $[FeL_2Cl_2][FeCl_4]$ ($L = dpeO_2$) which showed only one g value of ca 2 was shown by X-ray analysis to possess *cis*-octahedral geometry for the cation[291b,944].

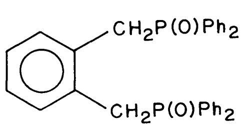
Thermal heating of the complexes FeX_3L ($X = Cl$, Br, $L = Ph_2PCH_2CH_2PPh_2$ and *cis*-$Ph_2PCH{=}CHPPh_2$) formed phosphine oxide complexes $[FeL_2X_2]$ $[FeX_4]$[945a]. A tetradentate ligand, $C\{CH_2P(O)Ph_2\}_4$ (L), formed complexes $[(FeCl_3)_2L]$ and $[(FeCl_3)_4L]$[945b]. Two complexes of osmium(II) of stoichiometry *cis*-$[OsL(bpy)_2]^{2+}$ $\{L = dpmO_2$, *cis*-$Ph_2P(O)CH{=}CHP(O)Ph_2\}$ were reported recently[313].

ii. Cobalt sub-Group. Several cobalt(II) high-spin complexes of the type (A) $[CoLX_2]$ $\{L = Ph_2P(O)(CH_2)_nP(O)Ph_2$; $n = 2$–4; $X = Cl$, Br, I, NCS, $ONO_2\}$[946–948], (B) $[Co(NO)IL]$ ($L = dpeO_2$)[949], (C) $[CoL_2\{(Ph_2P(O))_2N^-\}]$[950], (D) $[\{Co(S_2N_2H)_2\}_2 \cdot (dpeO_2)]$[951], (E) $[Co(dpeO_2)(O_2NO)_2]$[948,952]. (F) $[CoL_2(H_2O)_2](ClO_4)_2$ ($n = 2,4$ for L)[948,952], (G) $[Co(dpmO_2)_3](ClO_4)_2$[953,954], (H) $[CoL'_2](ClO_4)_2 \cdot 3H_2O$ $\{L' = (Ph_2P(O) \cdot CH_2)_2P(O)Ph\}$[955], (I) $[CoL'_3](ClO_4)_2 \cdot 4H_2O$[955] and (J) $[CoL_3][CoX_4]$ $\{X = Cl$, Br, I, $L = dpmO_2$[946,954]; $X = Cl$, $L = Bu^n_2P(O)CH_2P(O)Bu^n_2$[941]$\}$ have been reported. X-ray analysis of complexes B and D showed distorted tetrahedral and square-pyramidal structures, respectively; for complexes A–C distorted tetrahedral structures and for complexes E–I octahedral structures are suggested. The ligand $\{Ph_2P(O)CH_2\}_2P(O)Ph$ is tridentate in complex H and bidentate in complex I.

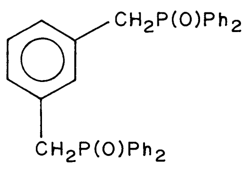
An interesting feature in cobalt(II) phosphine oxide chemistry is the tendency of $dmpO_2$ and $Bu^n_2P(O)CH_2P(O)$ Bu^n_2 ligands to form octahedral complexes with six-membered chelate rings (complexes G and J). When the anions are halogens, the formation of mixed octahedral–tetrahedral complexes takes place, e.g. complexes J. The higher steric requirements of seven- to nine-membered chelate rings formed by ligands with $n = 2$–4 generally favour coordination by two ligand molecules per metal ion.

A mixed valence complex, $[Co^{I}(CO)L_2]_2[Co^{II}_2(\mu\text{-}L')Cl_6]$ ($L = dpe$; $L' = dpeO_2$) was obtained from the reaction of $CoCl_2 \cdot 6H_2O$ with dpe, CO and zinc powder in air[956]. An x-ray study showed tetrahedral geometry for each cobalt atom of the anion with $dpeO_2$ acting as a bridge; the cation has trigonal bipyramidal geometry. Using the ligands **78**, **79**, **80** and **81**, a series of complexes, $[CoLCl_2]$ (L = **78**, **81**), $[CoL_3](ClO_4)_2$ (L = **79**), $[(CoCl_2)_3L_2]$ (L = **80**) and $[CoL_2](ClO_4)_2$ (L = **80**), were reported[957,958]. $[CoL_3](ClO_4)_2$ have octahedral while the other complexes have tetrahedral structures. On heating $[CoLX_2]$ complexes ($X = Cl$, Br, I, NCS; L = dpe, *cis*-$Ph_2PCH{=}CHPPh_2$) the corresponding phosphine oxide complexes were formed[959,960].

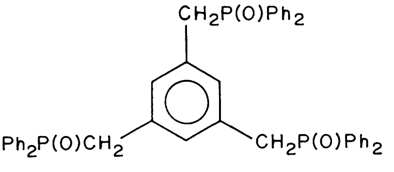
A series of square-planar rhodium(I) complexes $[Rh(cod)L](ClO_4)$, *cis*-$[Rh(CO)_2L] \cdot (ClO_4)$, $[Rh(CO)L(Ph_3P)](ClO_4)$ and $[Rh(CO)L(Ph_3P)_2](ClO_4)$ $\{L = Ph_2P(O)(CH_2)_n \cdot P(O)Ph_2$; $n = 1,2\}$ (IR, ^{31}P NMR) have been reported[961].



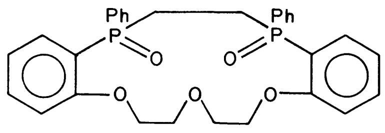
(78)



(79)



(80)



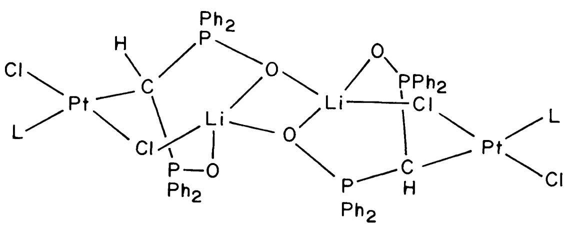
(81)

iii. Nickel sub-Group. A number of high-spin nickel(II) complexes have been reported: (A) $[NiX_2L]$ $\{X = Cl, O_2NO; L = Ph_2P(O)(CH_2)_nP(O)Ph_2; n = 2,3\}$^{389,946,948,962}, (B) $[NiL_3]X_2 \cdot mH_2O$ ($n = 1$ for L; X = Cl, Br, I)^{963}, (C) $[NiL_2(H_2O)_2](ClO_4)_2$ ($n = 2,4$ for L)^{948,962}, (D) $[NiL'_2](ClO_4)_2 \cdot 5H_2O$^{955}, (E) $[NiL'_3](ClO_4)_2 \cdot 4H_2O$ $\{L' = (Ph_2P(O)CH_2)_2 \cdot P(O)Ph\}$^{955}, (F) $[NiL_3][MX_4]$ $\{M = Ni, X = Cl, Br, I, n = 1,2$ for L; X = Cl, $L = Bu^n_2P(O)CH_2P(O)Bu^n_2$; M = Zn, X = Cl, $n = 1$ for L$\}$^{941,946,954,962,963}. The complexes A–E have been assigned octahedral structures with halogen-bridging and bi-coordination by NO_3^- groups. L′ acts as a tridentate in complex D, but bidentate in E. The F-type complexes have mixed octahedral–tetrahedral structures similar to those of their cobalt(II) analogues.

On heating the phosphine complexes $[MLX_2]$ (L = dpe, *cis*-$Ph_2PCH{=}CHPPh_2$; M = Ni, Pd; X = Cl, Br, NCS)$^{412,959,960,964-966}$, the corresponding phosphine oxide complexes were formed. Significantly, palladium(II)–phosphine complexes required higher temperatures for their oxidation than cobalt(II) or nickel(II) complexes. $[PdL(NCS)(SCN)]$ (L = dpe) did not undergo oxidation of dpe to $dpeO_2$^{966}.

Whereas $NiCl_2$ with *cis*-$Ph_2P(O)CH{=}CHP(O)Ph_2$ formed $[NiCl_2L]$, there was no reaction of $NiCl_2$ with the *trans* analogue of the ligand^{967}. The *trans* ligand reacted with $NiCl_2$ only in the molten state, although in thf solution some interaction of $NiCl_2$ with *trans* ligand was detected.

The anionic phosphine oxide ligand $\{Ph_2P(O)\}_2CH^-$ (L) formed a series of palladium(II) and platinium(II) complexes: $[MCl_2(R_3P)LM']$ (M = Pd, R = Et, M′ = Li; M = Pt, R = Et, Bu^n, M′ = Li, Na)^{968}. The reaction of $[(Et_3P)PtCl_2L(Li)]$ with $[Pd_2Cl_2(Et_3P)_4](BF_4)_2$ formed an unstable complex, $[(Et_3P)Cl_2Pt(\mu\text{-}L)_2Pd(Et_3P)_2](BF_4)$ {in which Li^+ was replaced by $Pd(Et_3P)_2^{2+}$}. The X-ray crystal structure of $[Pt(Et_3P)\cdot$



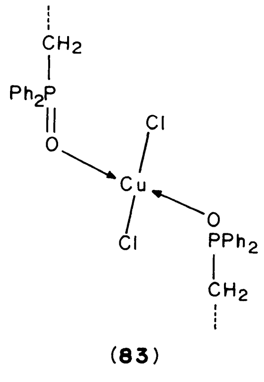
(82)

$Cl_2L(Li)]$ showed that the anionic ligand L was bound to platinum via the methine carbon with a square-planar geometry about platinum (**82**). Two PO groups, one chloride and one oxygen from an adjacent molecule complete tetrahedral geometry about lithium. From ^{1}J ^{195}Pt–^{31}P values (^{31}P NMR) in the range 2750–2827 Hz, it was inferred that methine carbon exerts a low *trans* effect in comparison with the normal carbon bonded ligands[968–970]. It is interesting that Li^+ ions remain intimately associated with the complex in solution.

d. Complexes of the copper Group(IB). Copper(II) forms complexes of the type (A) $[CuX_2L]$, (B) $[CuL_2](ClO_4)_2$ (L = dpeO$_2$; X = Cl, Br, NO_3)[948,952], (C) $[CuL_2](ClO_4)_2 \cdot 2H_2O$, (D) $[CuL_3](ClO_4)_2 \cdot 4H_2O$ (L = $\{Ph_2P(O)CH_2\}_2P(O)Ph$)[955], (E) $[CuL_2][CuCl_4]$ {L = dpmO$_2$, $RPhP(O)CH_2CH_2P(O)PhR$, R = *o*-$MeOC_6H_4$, L = **79**, **81**}[957,958,971] and (F) $[CuX_2L]$, (G) $[(CuX_2)_2L]$ {L = $R_2P(O)CH_2P(O)R_2$, R = Ph, *n*-Oct, X = F_3acac, F_6acac, i.e. tri- and hexa-fluoroacetylacetonates}[972]. For R = *n*-Oct, complexes of stoichiometry $[CuX_2L_2]$ were also formed.

Other complexes of copper(II) studied in the solid and solution phases have formulae of the type $[CuCl_2L]$ {L = $R_2P(O)(CH_2)_nP(O)R_2$, $n = 1$ for R = Ph, $n = 1,2,6$ for R = Bu}[973–975], $[CuCl_2L_2Me_2CO]$ (L = dpmO$_2$)[975], $[CuCl_2L]$, $(CuCl_2)_2L]$, $[CuCl_2L_2]$ {L = $Ph_2P(O)CH(R)P(O)Ph_2$, R = H, $CH_2CH_2CO_2H$, $CH_2CH_2P(O)Ph_2$, etc.}[976], $[CuClL]Cl$ {L = $Ph_2P(O)C(R)(R')P(O)Ph_2$, R = H, R′ = Cl, Br, I, Ph, CH_2Ph, etc.[976]; L = $(XC_6H_4)_2P(O)CH_2P(O)(C_6H_4X)_2$, X = H, *m*-$CF_3$, etc.[977]}.

An X-ray analysis of $[CuCl_2L]$ (L = dpeO$_2$) showed that the geometry about copper(II) is highly distorted tetrahedral (the ClCuO angle being 140.2°, ClCuCl 100.3° and OCuO 90.6°, 97.1°), with L acting as a bridging bidentate ligand (**83**)[978,979]. The single crystal ESR and polarized electronic absorption spectra also suggest a compressed tetrahedral geometry about the copper(II)[980–983]. The one-electron orbital sequence derived was $d_{xy} > d_{xz} > d_{yz} > d_{x^2-y^2} \approx d_{z^2}$. Interestingly, $[CuCl_2L]$ (L = dpmO$_2$) has a different structure[984]. An X-ray study showed that it exists as $[CuL_3][Cu_2Cl_6]$, where the cation is octahedral and the anion has a halogen-bridged dimeric structure with each copper having distorted tetrahedral geometry. The short axial distances (2.001–2.002 Å) versus the longer equational ones (2.063–2.256 Å) for the cation reveal slight compression of the octahedron. Thus complexes A, B, C and E are assigned distorted tetrahedral geometry, whereas D, F and other complexes with similar stoichiometries probably have distorted octahedral geometries. The only complex of gold(I) is $[LAu(PPh_3)](ClO_4)$ (L = dpeO$_2$)[481].



(**83**)

e. Complexes of the zinc Group (IIB). The interaction of Group IIB metals with *bis*(phosphine oxide) ligands has been studied mainly using ^{31}P NMR spectrometry.

The formation of octahedral $[ZnL_n]^{2+}$ $\{L = dpmO_2, n = 3; L = (Ph_2P(O)CH_2)_2P(O)Ph, n = 2\}$ and tetrahedral $[ZnL_2]^{2+}$ ($L = dpmO_2$) was established by varying the L: Zn ratio[998]. No species formed by the interaction of zinc(II) with $Ph_2P(O)CH_2CH_2P(O)Ph_2$ could be detected, owing to the high lability of the system under the experimental conditions.

Similarly, cadmium(II) and mercury(II) formed $[ML_m]^{2+}$ ($M = Cd, Hg; L = dpmO_2, dpeO_2; m = 2,3$) and $[CdL_2]^{2+}$ $\{L = (Ph_2P(O)CH_2CH_2)_2P(O)Ph\}$ (^{31}P, ^{113}Cd NMR)[999,1000]. For L: M $\geqslant 3$ octahedral species were detected and for L: M $= 2$ tetrahedral species were formed. It is significant that the Cd^{II}–$Ph_2P(O)CH_2CH_2P(O)Ph_2$ system was not labile, unlike the zinc(II) system (see above), probably owing to large bite of the seven-membered chelate ring giving a worse fit for zinc(II) than cadmium(II) because of their size difference.

f. Complexes of the f-block elements. This group of elements has been poorly studied and no X-ray analyses have been reported for any complex. Lanthanon(III) chlorides form complexes of the type $[M_2Cl_6L_3]\cdot H_2O$ ($M = La, Nd, Sm; L = dpeO_2; x = 0$–$2$)[985], $[NdCl_3L]\cdot H_2O$ ($L = dpmO_2, dpeO_2$)[985,986] and $[NdCl_3L_3]$ ($L = dpmO_2$)[986]. Similarly, lanthanon(III) nitrates form complexes of the type $[M_2(NO_3)_6L_3]\cdot xH_2O$ $\{M = La, Nd, Sm; L = Ph_2P(O)(CH_2)_nP(O)Ph_2; n = 2,4\}$[987]. The NO_3^- groups are coordinated, but their dentacy has not been established. Other complexes of lanthanides include $[M(NO_3)_3L]$ $\{M = La, Nd, Gd, Ho, Lu; L = O(CH_2CH_2OC_6H_4OCH_2P(O)Ph_2)_2$ and $1,2\text{-}(Ph_2P(O)CH_2O)_2\text{-}4\text{-}Me_3CC_6H_3\}$[988] as well as $[(ML_n)_2(B_{12}H_{12})_2]$ ($n = 4, M = La; n = 3.5, M = Pr, Nd, Sm; n = 3, M = Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu$)[989].

Thorium(IV) forms complexes of the type $[Th(NO_3)_4L]$ $\{L = Cy_2P(O)CH_2P(O)Cy_2\}$, $[Th(NO_3)_4L_2]$ ($L = dpeO_2$), $[Th_2(NO_3)_8L_3]$ $\{L = dpmO_2, dpeO_2, R_2P(O)CH_2P(O)R_2; R = 2\text{-ethylbutyl}\}$[644,647,990]. Similarly, a number of uranium(IV) and uranium(VI) complexes have been reported: $[UCl_4L]$, $[UO_2X_2L]$ $\{X = Cl, Br, I$ or $NO_3, R_2P(O)(CH_2)_nP(O)R_2; R = Ph, Hex^n, n = 1$–$4; R = Bu^n$, 2-ethylbutyl, $n = 1\}$[655,991–996] and $[(UO_2)_2(NO_3)_4L_3]$ $\{L = Ph_2P(O)CH_2P(O)Ph_2\}$[644]. Apart from the usual methods, some complexes were formed indirectly. For example, reaction of $[Th(NO_3)_4]$ with dpe[990] and of $[UO_2Cl_2]$ with dpm and dpe[996] gave the corresponding phosphine oxide complexes. The UCl_4 complexes are paramagnetic ($\mu = 1.50$–2.02 BM). X-ray studies are recommended.

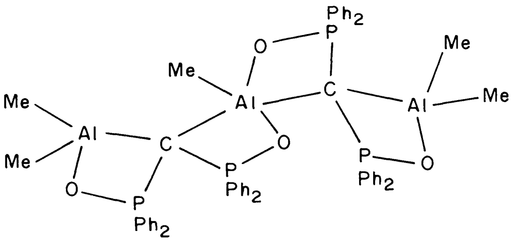
Formation of 1:1, 2:1, 3:1, 4:1 and 6:1 (L:M) complexes of $[UO_2(NO_3)_2]$ with $R_2P(O)EP(O)R_2$ ($R = Ph, Bu, Et, PhMe; E = CH_2, CH_2CH_2$, *cis*- and *trans*-$CH{=}CH$) has also been reported[997]. Here all the ligands except *trans*-$Ph_2P(O)CH{=}CHP(O)Ph_2$ were chelating whereas the latter ligand was unidentate.

The organouranium(IV) and neptunium(IV) complexes $[(cp)MX_3L]$ $\{M = U, Np; X = Cl, Br; L = Ph_2P(O)CH_2CH_2P(O)Ph_2\}$ are also known[709,994].

2. Main Group elements

a. Complexes of the boron Group (IIIA). Reaction of $Me_3Al_2Cl_3$ with $Ph_2P(O)CH_2\cdot P(O)Ph_2(L)$ gave $[(AlCl_3)_2(L)]$ with a tetrahedral structure about each aluminium centre[1001]. An unusual product, $[Al(CH_3)]\{Ph_2P(O)CP(O)Ph_2\}_2[Al(CH_3)_2]_2$, was obtained from the reaction of $AlMe_3$ with $Ph_2P(O)CH_2P(O)Ph_2$ in PhCl[1002]. Here the Al–R and C—H bonds of the CH_2 group were cleaved. X-ray analysis showed that the central aluminium atom is 5-coordinate, whereas the other two are 4-coordinate (**84**).

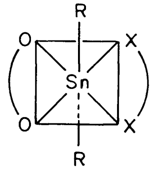
Indium(III) and thalium(III) formed complexes of the type $[InCl_3L]$ ($L = dpeO_2$), $[InL_3](ClO_4)_3$ ($L = dpmO_2, dpeO_2$)[1003,1004], $[TlX_3L]$, $[TlClBr_2L]$, $[TlClI_2L]$ and $[TlBrI_2L]$ ($L = dpeO_2$)[1005]. Thallium(III) complexes were obtained from the reaction of thallium(I) halides with the ligand followed by oxidation with Br_2 or I_2 in CH_3CN.



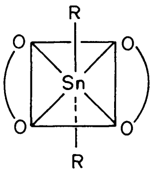
(84)

b. Complexes of the tin and lead Group (IVA). Interaction of tin(II) and lead(II) hexafluoroantimonates with $dpeO_2$ and $(Ph_2P(O)CH_2)_2P(O)Ph$ in liquid SO_2 (studied by ^{31}P NMR) revealed the formation of $[ML]^{2+}$ species[978]. The lead(II) complexes showed low coordination shifts and were more labile than the tin(II) complexes. Tin(IV) halides form 1:1 adducts $[SnX_4L]$ $\{L = Ph_2P(O)(CH_2)_nP(O)Ph_2;\ X = Cl,\ Br,\ I;\ n = 2,4\}$[1006–1008]. Mössbauer data favoured *cis*-octahedral structures. $SnCl_4$ forms a 2:1 adduct with the tetradentate ligand $C(CH_2P(O)Ph_2)_4$ $[(SnCl_4)_2L]$[945a].

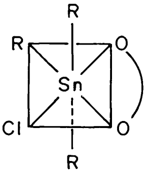
One of the most thoroughly studied group of complexes is that of organotin(IV). Several complexes have been reported: (A) $[R_2SnX_2L]$ $\{X = Cl$, Br, NCS, R = Me, Et, Oct, Ph, etc., $L = dpmO_2$, $dpeO_2$, $dpbO_2$; X = Cl, R = Et, Pr, Bu, $L = cis\text{-}Ph_2P(O)\cdot CH{=}CHP(O)Ph_2\}$[835,1009–1017], (B) $[(Bz_2SnCl_2)_2L]$ $(L = dpeO_2,\ dpbO_2)$[1018], (C) $[R_2SnL_2](BPh_4)_2$ (R = Me, Ph; $L = dpmO_2$, $dpeO_2$)[1009,1017,1019], (D) $[R_3SnXL]$ (X = Cl; R = Me, Ph; $L = dpmO_2$)[1009,1017,1019], (E) $[(Ph_3SnCl)_2L]$ $(L = dpmO_2$, $dpeO_2)$[1017,1020a] and (F) $[R_3SnL](BPh_4)$ (R = Me, Bu, Ph; $L = dpmO_2$, $dpeO_2$)[1011,1019,1020b,c,1021]. Based on Mössbauer data, complexes A and C were assigned *trans*-octahedral structures (**85**, **86**)[1009–1013,1022–1024]. In contrast, the $[Ph_2SnX_2L]$ (L = phen, bipy) complexes have *cis* dispositions of the phenyl groups[1025]. The *cis* or *trans* disposition of R groups is influenced by the electronic and steric factors of all the groups attached to tin[1026]. For complexes D and F, *mer* configurations (**87**, **88**) have been assigned. Finally, for the complexes B and E, ligand-bridged structures with R groups in the equatorial plane of a trigonal bipyramid have been suggested (**89**).



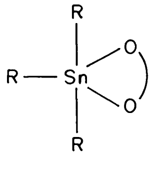
(85)



(86)

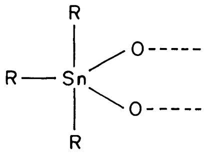


(87)

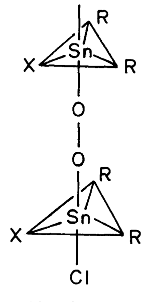


(88a)

or



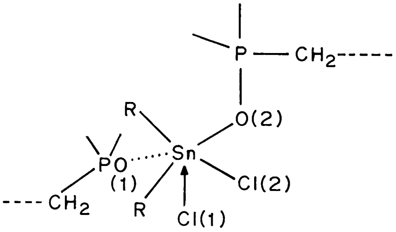
(88b)



X = Cl, R

(89)

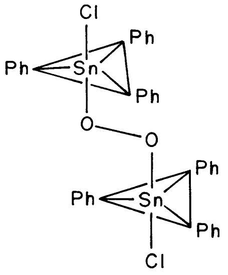
X-ray studies have been reported for a number of tin(IV) complexes. The geometry about tin in $[Bu^n_2SnCl_2L]$ ($L = dpmO_2$) is highly distorted *trans*-octahedral (**85**)[1015]. For $L = dpeO_2$ the mode of binding changes from chelation (as in the $dpmO_2$ complex) to bridging forming a polymeric structure[1020a]. The geometry may be viewed as a highly distorted tetragonal pyramid with $Cl_{(2)}$ at the apex or irregular octahedron if $O_{(1)}$ is considered as part of the environment (**90**). The C—Sn—C angle is 154.3°, instead of 180° as suggested by the Mössbauer data. The Sn—O distances are very different (2.386 and 2.640 Å). ^{119}Sn NMR data also supported the formation of a 5-coordinate species[874,1016].



(90)

In $[Et_2SnCl_2L]$ {$L = dpeO_2$, *cis*-$Ph_2P(O)CH{=}CHP(O)Ph_2$}, the ligands are chelating with the ethyl groups in the *trans* positions of the octahedron[1014]. Similar behaviour was observed in $[Bu^n_2SnCl_2L]$ for $L =$ *cis*-$Ph_2P(O)CH{=}CHP(O)Ph_2$[1013], but the octahedral structure is highly distorted. For $[Pr^n_2SnCl_2L]$, the stereochemistry is basically 5-coordinate in the form of a distorted tetragonal pyramid. Here one oxygen of *cis*-$Ph_2P(O)CH{=}CHP(O)Ph_2$ is at a distance of 2.24 Å and the other at a distance of 2.58 Å[1013].

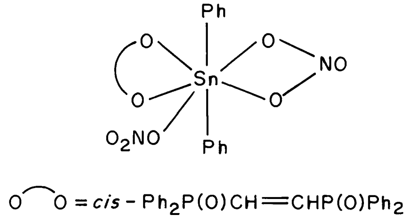
The complex $[(Ph_3SnCl)_2L]$ ($L = dpeO_2$) has a bridging L ligand with phenyl groups in the equatorial plane (**91**). The in-plane (114–127°) and axial angles (174.4°) reveal distortion in the geometry[1027,1028]. *cis*-$Ph_2P(O)CH{=}CHP(O)Ph_2$ was unidentate[1029,1030]. The unusual unidentate behaviour of this *cis* ligand is probably due to the tendency of Ph_3Sn unit to retain an equatorial disposition of the R groups. However, in $[Ph_2SnCl_2L]$ {$L =$ *cis*-$Ph_2P(O)CH{=}CHP(O)Ph_2$}, the ligand is chelating[1029].



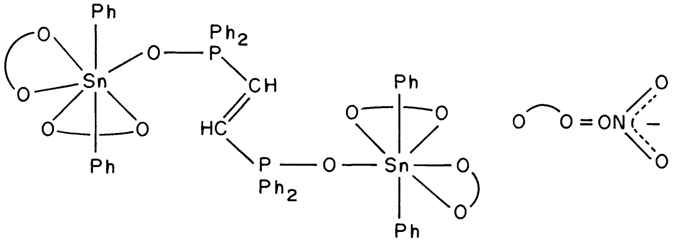
(91)

The structure of $[\{Ph_3Sn(ONO_2)\}_2L]$ ($L = dpeO_2$) is similar to that of $[(Ph_3SnCl)_2L]$[1031]. The complexes $[Ph_2Sn(NO_3)_2L]$ {$L =$ *cis*- and *trans*-$Ph_2P(O)CH{=}CHP(O)Ph_2$} have distorted pentagonal bipyramidal structures (**92**, **93**)[1032]. A structure similar to **85** was shown by $[Ph_2Sn(NO_3)_2L]$ ($L = dpmO_2$)[1033]. The complex $[\{Ph_3Sn\cdot$

$(ONO_2)\}_2$ (*trans*-$Ph_2P(O)CH{=}CHP(O)Ph_2$)] has a dimeric structure with the *trans* ligand acting as a bridge between two Ph_3Sn moieties. Each tin has a distorted trigonal bipyramidal geometry[1033].



(92)



(93)

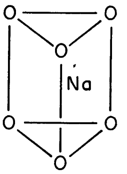
e. Complexes of phosphorus (VA). A few complexes of PF_5 with $Ph_2P(O)CH(X)\cdot P(O)Ph_2$ (X = H, Cl, Bu^n) have been reported (^{19}F NMR)[1034]. Species of the type $[PF_5L]$ (L acting as a monodentate) and $[PF_4L]^+$ (L = bidentate) were detected in all cases. An antimony(V) complex, $[(SbCl_5)_4L]$ ($L = C\{CH_2P(O)Ph_2\}_4$), has been reported[945a].

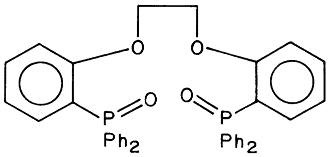
3. Alkali and alkaline earth elements

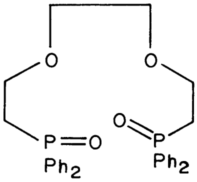
Alkali metal salts form complexes of the type (A) [MXL], (B) [ML)X, (C) $[ML_2I]$ {M = Li, Na, K, Cs; X = Cl, Br, I; L = $dpeO_2$, $R_2P(O)CH_2P(O)R'_2$; R = R′ = Ph, Bu^n, *p*-$MeOC_6H_4$; R = *p*-$MeOC_6H_4$, *p*-$CF_3C_6H_4$}[1035–1042], (D) $[NaL_3]Br\cdot 2H_2O$ and (E) $[NaL_3]I\cdot 2H_2O\cdot C_6H_6$ (L = $dpmO_2$)[1043,1044]. An alkali metal salt insoluble in MeCN or $CHCl_3$ became soluble in the presence of a phosphine oxide, indicating the formation of a complex species. An X-ray study of complexes D and E revealed a trigonal prismatic structure with the oxygen atoms of $dpmO_2$ occupying corners of the prism (**94**). The Na—O distances (2.434 Å) lay within the range typically observed for Na—O bonds (2.29–2.82 Å). Water and C_6H_6 were present in the crystal lattices.

Lithium and sodium salts of 2,4-dinitrophenolate formed stable complexes with podant ligands (**95**, **96**)[1045]. The complexing abilities of **95** and **96** exceed that of 18-crown-6 and dibenzo-18-crown-6; **95** exhibited higher Li/Na selectivity than **96**. Similarly, the alkali metal salts of 2,4-dinitrophenolates form complexes with several podant ligands such as $Me_2P(O)(CH_2OCH_2)_nP(O)Me_2$ ($n = 1,3$), $\{o\text{-}Ph_2P(O)CH_2C_6H_4OCH_2CH_2\}_2O$ and 1,2-$\{Ph_2P(O)CH_2OCH_2CH_2O\}_2C_6H_4$[1046,1047].

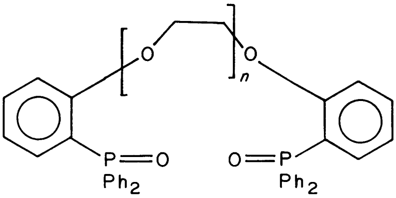
Studies on complexes of the alkaline earth metals are very limited[1048–1050]. Species of the type $[MgL]^{2+}$, $[CaL_2]^{2+}$, $[MgLI]^+$ and $[CaClL]^+$ (L = $dpmO_2$) were detected in solution by a conductivity method. Calcium chloride formed 1:1 and 1:2 complexes


(94)

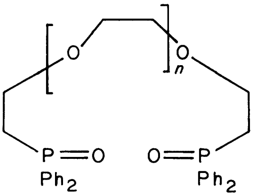

(95)


(96)

with podant ligands **97** and **98**[1050]. The stability constant of the 1:2 complex is larger than that of the 1:1 complex owing to a higher enthalpy contribution to the formation of the 1:1 adduct and a higher entropy contribution to the formation of the 1:2 complex.


$n = 1-5$

(97)


$n = 4,5$

(98)

III. TERTIARY PHOSPHINE SULPHIDES AND SELENIDES

Most of the coordination chemistry of the tertiary phosphine sulphides and selenides pertains to the d-block elements. Whereas there have been significant studies on Main Group elements, no complexes have been reported so far with s- or f-block elements. A recent attempt involving the reaction of $[(Me_5C_5)_2Yb]$ with Ph_3PE gave $[\{(Me_5C_5)_2Yb\}_2(\mu\text{-}E)]$ ($E = S, Se$) instead of the expected adduct[1051a].

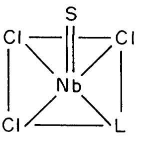
A. Transition Elements

1. *Complexes of the titanium and vanadium Groups(IVB and VB)*

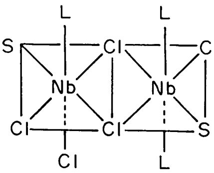
Titanium(IV) and vanadium(IV) and (V) form moisture-sensitive complexes of the type $[TiCl_4L_2]$, $[(TiCl_4)_2L]$, $[TiBr_4L]$ ($L = Ph_3PS$), $[TiX_4L']$ ($X = Cl$, Br) and $[VOCl_2L']$ $\{L' = Me_2P(S)NHP(S)Me_2\}$[1051b,1052–1056]. In the complexes $[(TiCl_4)_2L]$ and $[TiBr_4L]$ ($L = Ph_3PS$) halogen bridging and in the complexes $[TiX_4L']$ and $[VOCl_2L']$ chelation by L′ are suggested. Niobium(V) and titanium(V) complexes $[NbSCl_3(SPPh_3)]$, $[MX_5L]$ ($X = F$, Cl, Br; $L = Ph_3PS$, Ph_3PSe) and $[M_3Br_{15}L]$ ($L = dpeS_2$)[1056–1062] have been reported; they are also moisture sensitive.

An X-ray study has shown that $[NbSCl_3(SPPh_3)]$ exists as a mixture of a square-pyramidal monomer and a chloride-bridged dimer in the same unit cell (**99** and **100**)[1059,1060,1062]. The long Nb—Nb distance (4.240 Å) ruled out any possibility of metal—metal bonding in the dimer. Further Nb(V)–S interaction was weaker than that of Mo(V)–S[1063].

A solution-phase ^{19}F NMR study revealed the formation of species such as *cis*- and *trans*-$[TaF_4ClL]$, *trans*-$[TaF_3Cl_2L]$, *fac*-$[TaF_2Cl_3L]$, *trans–mer*-$[TaF_2Cl_3L]$ $\{L = (p\text{-}MeC_6H_4)_3PS\}$[1064] and $[TaF_5L]$ $\{L = (XC_6H_4)_3PS\}$[1061]. The donor ability of the ligands decreased in the order $X = p$-MeO > o-Me > p-Me > m-Me > p-Cl[1061].



(99)



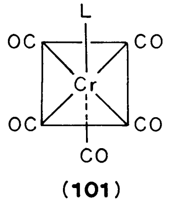
(100)

Organo-niobium(V) and -tantalum(V) complexes of stoichiometries $[MeMCl_4L]$, $[(MeMCl_4)_2L']$, $[(Me_2TaCl_3)_2L']$ and $[Me_2TaCl_3L]$ ($L = Ph_3PS$, $L' = dpeS_2$) have been reported[117]. The first two complexes have *cis* configurations whereas the latter two have *trans*-Me groups. Interestingly, $[Me_2NbCl_3]$ abstracted oxygen from Ph_3PO forming $[Me_2NbOCl_3(Ph_3P)]$, and there was no analogous reaction with Ph_3PS, demonstrating the relatively large Nb—O affinity as compared with the Nb—S bond[1065]. A substituted cyclopentadienyltantalum(V) complex, $[Ta(\eta^5\text{-}C_5Me_5)Cl_3(CH_2P(S)Ph_2)]$ with Ta—CH_2 bonding showed no Ta–S interaction[1066].

2. Complexes of the chromium Group(VIB)

Table 14 contains several complexes of Group VIB elements, which constitutes one of the most thoroughly studied Groups. The di-tertiary ligands $dpmS_2$, dpmPSe and $Ph_2P(Se)CH_2CH_2AsPh_2$ behaved as unidentate ligands in the complexes $[M(CO)_5L]$, coordinating via S, P and As donor groups, respectively. Chromium and tungsten complexes were stable in air in the solution phase unlike molybdenium complexes, which dissociated rapidly, demonstrating the high lability of the Mo—S bond. On bubbling CO through a benzene solution of $[M(CO)_5L]$ (M = Cr, W; $L = Me_2PhPE$), the original compound $[M(CO)_6]$ was obtained. This reveals a reversible binding tendency of the phosphine chalcogenides to Group VIB metals. The addition of MeI to $[M(CO)_5 \cdot (Me_2PhPS)]$ gave *S*-methylated ionic complexes, $\{Me_2PhPS(Me)\}[M(CO)_5I]$[1068,1091].

X-ray analysis of $[Cr(CO)_5(Me_3PS)]$ showed a nearly octahedral geometry (**101**) about the chromium atom[1069], which lies slightly above the square-plane towards Me_3PS. The Cr—C bond *trans* to Me_3PS was short (1.815 Å) compared with the *cis*-Cr—C bonds (1.889–1.916 Å). The normal Cr—S bond and short Cr—C distance (*trans* to Me_3PS) reveal the lack of any π-accepting ability of Me_3PS; a similar conclusion was reached from the appearance of high-energy ν(CO) peaks for the CO groups *trans* to the Me_3PS ligand.



(101)

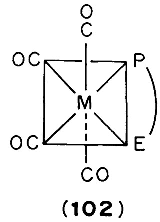
The reaction of $[M(CO)_6]$ with $Ph_2P(E)CH_2PR_1R_2$ gave the disubstituted *cis*-octahedral complexes $[M(CO)_4L]$-{complexes B(i)}[1072–1078], where the ligands chelate via the P and E donor atoms (**102**). Since the formation of the tungsten complexes required higher temperatures at which sulphur transfer from one phosphorus to another phosphorus becomes competitive with CO substitution, the tungsten derivatives were obtained indirectly by displacing norbornadiene from $[W(CO)_4(C_7H_8)]$ by Ph_2PCH_2-$P(S)R_2$. The ligands dpmPSe and $Ph_2P(S)CH_2CH_2AsPh_2$ did not react with

TABLE 14. Known complexes of the chromium and manganese groups

	Complex	L	Ref.
A	$[M(CO)_5L]$	(i) R_3PE[a], $dpmS_2$	1067–1071
	(M = Cr, Mo, W)	(ii) dpmPSe, $Ph_2P(Se)CH_2CH_2AsPh_2$	1072
B	(i) $[M(CO)_4L]$ (M = Cr, Mo, W)	$Ph_2P(E)CH_2PR_1R_2$[b]	1072–1078
	(ii) $[M(CO)_4L(pip)]$[c] (M = Mo, W)	$Ph_2P(Se)CH_2CH_2AsPh_2$	1072
	(iii) *cis*-$[M(CO)_4L_2]$ (M = Mo, W)	$Ph_2P(Se)CH_2CH_2AsPh_2$	1072
C	$[M(CO)_3(NO)L]$ (M = Mo, W)	dpmPSe	1079
D	(i) $[M(CO)_3LX_2]$ (M = Mo, W; X = Cl, Br)	dpmPSe, $Ph_2P(Se)CH_2CH_2AsPh_2$	1072
	(ii) $[M(CO)_nL_2Cl_2]$ ($n = 2,3$; M = Mo, W)	Ph_3PS	203
E	$[M(CO)_3L_2I_2]$ (M = Mo, W)	Ph_3PS	204
F	(i) $[W(CO)_2(NO)LI]$	dpmPSe, $Ph_2P(Se)CH_2CH_2AsPh_2$	1080
	(ii) $[W(CO)(NO)LL'I]$	See text	1080
G	$[(\eta^5\text{-cp})(CO)LM{-}M(CO)_3(\eta^5\text{-cp})]$ (M = Mo, W)	Ph_3PS	1081
H	$[MoOCl_3L]$	Ph_3PS, Ph_3PSe	164b, 1082–1085
I	(i) $WX_4(PPh_3)L$	Ph_3PS, Ph_3PSe	171, 1086
	(ii) $[Br_4W(\mu\text{-}L)_2WBr_4]$	Ph_3PS	171, 1086
	(iii) $[Cl_4W(\mu\text{-}L)_2WCl_4]Cl_2$	Ph_3PS, Ph_3PSe	171, 1086
J	$[WOClL_2](PF_6)$	$Me_2P(S)CH_2PMe_2$	1087
K	(i) $[M(CO)_3LX]$ (M = Mn, Re, X = Cl, Br)	dpmPE, $Ph_2P(E)CH_2CH_2AsPh_2$ (E = S, Se)	1088
	(ii) $[M(CO)_3LX]_2$ (X = Cl, Br, M = Mn)	$Ph_2P(E)CH_2CH_2AsPh_2$	1088
	(iii) $[M(CO)_3L_2X]$ (M = Mn, Re)	$Ph_2P(E)CH_2CH_2AsPh_2$	1088
L	$[MnL_2]$	$[Ph_2P(S)]_2N^-$	1089, 1090

[a] R_3, E = Me_3, Me_2Ph, $MePh_2$, Ph_3, Cy_3S; Me_2Ph, Ph_3, Cy_3, Se.
[b] R_1R_2, E = Ph_2; Ph, Pr^i; Ph, Me; Pr^i_2; Me_2, Bu^t_2, S; Ph_2, Se.
[c] pip = piperidine.

$[M(CO)_6]$ and hence its arsenic-bonded monosubstituted complexes $[M(CO)_5L)$ {A(ii) complexes} were obtained from the reaction of the anionic species $[M(CO)_5X]^-$ (X = Cl, Br; M = Mo, W) with the ligand in the presence of $AgNO_3$[1072]. Complexes B(ii) and B(iii) also contained arsenic-bonded monodentate ligands[1072].



(102)

The group VIB metal–chalcogen interaction decreases in the sequence W > Cr > Mo and for metal–PR_2 interaction in the sequence W > Mo > Cr, which is same as the decreasing trend of metal to ligand π-bonding from W to Cr. Further, the metal–PR_2 interaction is stronger than metal–EPR_2 interaction. It was also observed that phenyl groups on phosphorus enhanced ^{31}P–^{183}W coupling owing to π-interactions along the W–P bond[1078,1093].

Complexes $[M(CO)_3(NO)L]$, $[M(CO)_3LX_2]$ and $[W(CO)_2(NO)LI]$ {C, D(i), F(i) complexes} contain chelating ligands (Table 14). $[W(CO)(NO)LL'I]$ {L = dpmPSe, L′ = $Ph_2P(Se)CH_2CH_2AsPh_2$} has chelating L and unidentate arsenic-bonded L′[1080]. Complexes $[M(CO)_3LX_2]$ have been shown to exist as a mixture of isomers[1072] and their further reaction with dpmPSe gave incomplete formation of $[M(CO)_2L_2X_2]$ (one L is chelated whereas the second is P-bonded). A similar reaction of complex D(i) with $Ph_2P(Se)CH_2CH_2AsPh_2$ gave quantitative formation of $[M(CO)_2L_2X_2]$ (one L chelating and the second L binding via arsenic only). Bubbling of carbon monoxide through a solution of the latter complex gave $[M(CO)_3L_2X_2]$ (L monodentate, binding via arsenic only). Complex E is the first example of a 7-coordinate complex in metal phosphine chalcogenide chemistry[204].

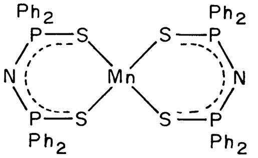
Reaction of $[(\eta^5\text{-cp})(CO)_2M{\equiv}M(CO)_2(\eta^5\text{-cp})]$ with Ph_3PS gave complex G (Table 14), which represents an unprecedented case of 1,1-addition of Ph_3PS to a metal–metal triple bond[1081]. The binding of Ph_3PS to molybdenum(V) in $[MoOCl_3L]$ is similar to that of Me_3PS and X-ray analysis showed a geometry intermediate between that of a square pyramid and trigonal bipyramid[1084], analogous to that of $[NbSCl_3(SPPh_3)]$[1060]. The behaviour of Ph_3PSe towards molybdenum(V) is similar; IR spectrometry showed a greater amount of electron density transfer to molybdenum(V) than in the case of Ph_3PS. The addition of Ph_3PS to $[MoOCl_3L]$ to form $[MoOCl_3L_2]$ showed that the 1:1 adduct predominates at equilibrium (ESR study)[203].

The μ values and IR data have supported ligand bridging in complexes I(ii and iii), where there is antiferromagnetic interaction ($\mu = 0.897$–1.118 BM) between the metal centres[1086]. An X-ray analysis of $[WOClL_2](PF_6)$ has shown that the ligand $Me_2P(S)CH_2PMe_2$ chelates to tungsten via P and S atoms[1087]. The chelate rings are so arranged as to give *cis*-S_2 and *cis*-P_2 coordination. A thermal study of $[M(CO)_nL_2Cl_2]$[203] (L = Ph_3PS) has shown that for $n = 3$, the complexes lose first two CO, then one CO and finally a Ph_3PS ligand is lost in a multi-step process. For $n = 2$, loss of one CO then two CO takes place followed by loss of the Ph_3PS ligands. Tungsten complexes were more thermally stable than molybdenum complexes.

3. Complexes of the manganese Group (VIIB)

Only a few complexes with Group VIIB elements are known (Table 14). The complexes $[M(CO)_3LX]$ {K(i)}[1088] resulted from a 1:1 reaction of $[M(CO)_5X)$ with L chelating via P, E or As, E donors. Complexes K(ii) have halogen bridging where $Ph_2As(CH_2)_2P(E)Ph_2$ bind to manganese via As only[1088]. $[M(CO)_3L_2X]$ {K(iii)}, obtained from a 1:2 reaction, also have M—As bonding.

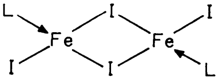
Complexes $[M(CO)_3LX]$ underwent electrochemical oxidation to form 17-electron cationic species, $[M(CO)_3LX]^+$, with unexpectedly large redox stability compared with species from analogous phosphine complexes, $[M(CO)_3L'X]$ (L′ = dpm, dpe)[1088]. The isolation of the cationic species was difficult owing to attack by solvents such as CH_3CN. $Ph_2P(S)NHP(S)Ph_2$ formed $[MnL_2]$ {L = $(Ph_2P(S))_2N^-$ with approximately tetrahedral geometry (**103**)[1089,1090].



(103)

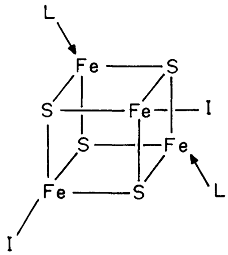
4. Complexes of the iron, cobalt and nickel Group (III)

a. Iron sub-Group. A mixed-ligand iron(0) carbonyl complex, $[Fe(CO)_2(Ph_3P)_2(Ph_3PS)]$, was obtained from $[Fe(CO)_2(Ph_3P)_2Br_2]$ by its reductive elimination and substitution reaction with Ph_3PS. A *cis*-trigonal bipyramidal geometry was suggested[1094–1097]. Iron(II) forms tetrahedral complexes, $[FeX_2L_2]$ (X = Cl, Br, I; L = p-Tol_3PS)[391] and $Fe(NO)_2XL$ (X = Br, CN; L = Ph_3PE)[1098]. A few poorly studied complexes include $[(FeCl_2)_nL]$, $[(FeCl_3)_nL]$ (n = 1, 1.5; L = Ph_3PS)[1056] and $[FeCl_3(Bu^n_3PS)]$.[1099] The iodide-bridged dimeric complexes $[L_2Fe(\mu\text{-}I)_2FeL_2]I_2$ (L = Ph_3PSe)[1102] and $[Fe_2I_4L_2]PhMe$ (L = Ph_3PS) have been reported[1103]. X-ray study of the latter complex showed a distorted tetrahedral geometry about each iron centre with a long Fe—Fe distance (3.397 Å) (**104**).



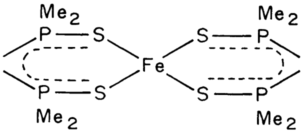
(104)

The cubane-type complex $[Fe_4S_4I_2L_2]$ (L = Ph_3PS) was obtained from the reaction of $[Fe(thf)_6]$ $[Fe_4S_4I_4]$, Ph_3PS and sulphur[1104]. It has a lower stability than $[Fe_4S_4I_2]^{2-}$ and thus decomposes readily in acetonitrile–thf. The core $Fe_4S_4{}^{2+}$ of the complex exhibits a slight tetragonal distortion. The Fe—$SPPh_3$ distances (2.316 and 2.321 Å) are longer than the terminal Fe–S bonds in RS^--coordinated $Fe_4S_4{}^{2+}$ clusters with cubane structure (**105**).



(105)

The anionic ligands $\{Ph_2P(E)\}_2CH^-$(L) and the isoelectronic $\{R_2P(S)\}_2N^-$ (R = Me, Ph) form highly air-sensitive complexes, $[FeL_2]$[950,1105]. The selenide complex decomposed rapidly in the air. An X-ray study of $[FeL_2]$ ($L = \{Me_2P(S)\}_2N^-$) showed a distorted tetrahedral structure (**106**)[1106].



(106)

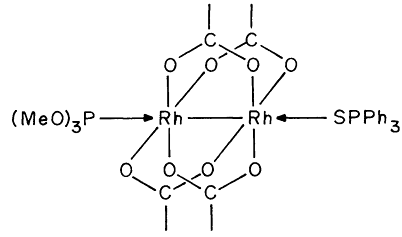
The cyclopentadienyl complexes $((\eta^5\text{-cp})Fe(CO)_2L]PF_6$ ($L = R_3PE$, R = Me, Me_2CH, Me_3C, Ph) were obtained from the reaction of $[(\eta^5\text{-cp})Fe(CO)_2(thf)](PF_6)$ with R_3PE[1107,1108]. In contrast, $[(\eta^5\text{-cp})Fe(CO)_2L]BF_4$ $\{L = Ph_2P(E)(CH_2)_nP(E)Ph_2{:}n = 1\text{–}3\}$ were formed by the oxidative cleavage of the Fe–Fe bond in the dimer $[(\eta^5\text{-cp})Fe(CO)_2]_2$ in the presence of L using $[cp_2Fe]BF_4$[1109]. Photolysis of a mixture of $[(\eta^5\text{-cp})Fe(CO)_2L]BF_4$ with $[Ni(NO)_4]$ gave a bimetallic complex, $[(\eta^5\text{-cp})Fe(CO)_2\cdot(\mu\text{-L})Ni(CO)_3]BF_4$. The formation of similar complexes with corresponding phosphines and phosphine oxides has also been reported. The electrochemical behaviour of $[(\eta^5\text{-cp})Fe(CO)_2L](PF_6)$ ($L = Me_3PS$, Ph_3PS) suggested that the products of the one-electron reduction are labile and lose the ligand L[1108]. Oxidation of the dimer $[(\eta^5\text{-cp})Fe(CO)_2]_2$ in the presence of ligands indicates the possibility of the electrochemical synthesis of the complexes $[(\eta^5\text{-cp})Fe(CO)_2L]$ (PF_6).

Only a few ruthenium(II) complexes of the type $[Ru(CO)_2L_2I_2]$ ($L = Ph_3PSe$)[1110–1111], $[RuCl_2LL']_2$ ($L = Ph_3PS$; $L' = CO$, Ph_3P)[1112,1113] and $[Ru(CO)_2L_2S]$[1112,1113] have been reported. *cis*-Octahedral geometry was inferred for the Ph_3PSe complex; the latter complexes involve chloride and sulphide bridging ligands, respectively.

b. Cobalt sub-Group. Cobalt(III) forms a number of complexes: (A) $[CoL_2X_2]$ (X = Cl, Br, I; $L = Me_3PE$)[1114,1115], (B) $[CoLX_2]$. *n*thf ($n = 0, \frac{1}{2}, \frac{3}{4}$; X = Cl, Br, I; $L = dpmS_2$, $dpmSe_2$)[1116], (C) $[CoL_4]$ $(ClO_4)_2$ ($L = Me_3PE$)[1114,1115], (D) $Co(NO)_2LX$ (X = Br, CN, $L = Ph_3PE$)[1098], (E) $[Co_2I_4L_2]$ ($L = Ph_3PS$)[1117], (F) $[CoLX_2]$ (X = Cl, Br, I, $L = \{Ph_2P(S)\}_2NH$[1118], (G) $[CoL_2]$ $(ClO_4)_2$ $[L = \{Ph_2P(S)\}_2CH_2$, $\{Ph_2P(S)\}_2\text{-}NH)$[1116,1118] and (H) $(CoL_2]$ ($L = \{Ph_2P(E)\}_2CH^-$, $\{R_2P(S)\}_2N^-$; R = Me, Ph)[950,1105,1116,1118,1119]. A cobalt(I) complex, $[CoLL'_{1/2}]$ $\{L = Ph_2P(S)CH_2P(S)Ph_2$; $HL' = HS_2CNHNHPh\}$, is also known[1120].

No X-ray studies have been reported for any of the complexes listed above. However, spectral and magnetic moment data support tetrahedral structures for complexes C and pseudo-tetrahedral for complexes A, B, D, F, G and H. The air-sensitive complexes H are similar to those of their nickel(II) analogues[1121]. The Co—S and Co—Se bonds have higher covalency than the Co—O bonds in Co(II)–OPR_3 complexes (based on β values)[1122,1123]. Further, the anionic bidentate ligands showed higher ligand field strengths[1124]. A homobimetallic complex, $[Co_2I_2(Ph_3PS)_2]$, is reported to possess ligand bridging with a weak Co···Co interaction[1117], but Ph_3PS is labile and can be readily displaced by Ph_3P or Ph_3PO.

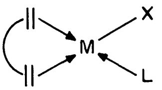
Rhodium(I) forms complexes of stoichiometry (A) $[RhCl(CO)$ $(Ph_3PS)_2]$[1112,1125], (B) $[Rh(CO)Cl(Ph_3P)_2(Ph_3PS)]$[1112,1125], (C) $[RhClL_2]_2$ ($L = Ph_3PS$)[372,1112,1125], (D) $[Rh(Ph_3PS)_3Cl]$[372], (E) $[Rh(CO)_2(Ph_3PS)Cl]$[372] and (F) $[RhL(\eta^2\text{-}S_2PCy_2)]$ $\{L = Ph_2P(S)$ $(CH_2)_3P(CMe_3)$ $(CH_2)_3PPh_2$[1126]. Monomeric square-planar, trigonal-bipyramidal and chloro-bridged dimeric square-planar structures have been suggested for complexes A, D and E, B and C, respectively. A dimeric adduct, $[Rh_2(O_2CMe)_4(Ph_3PS)(MeO)_3P]$, was detected in solution by ^{31}P NMR spectroscopy (**107**)[1127].



(**107**)

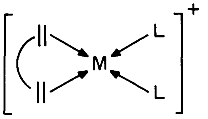
Several novel and air-stable organometallic complexes of rhodium(I) and iridium(I) with phosphine chalcogenides have been reported: (A) [(cod)(RhClL] (L = Me_3PS, Me_2PhPS, Me_2PhPSe), (B) $[(cod)RhL_n]X$ (X = ClO_4, Ph_4B; $n = 1$ for $dmpS_2$ and $dpmSe_2$ and 2 for Me_3PS, Me_2PhPS), (C) [(cod)IrClL) (L = Me_3PS, Me_2PhPS, $MePh_2PS$), (D) [(cod)IrL] (ClO_4) (L = $dpmS_2$, $dpmSe_2$), (E) $[(cod)Ir(X)Y_2L]$ (X = H, Cl; $Y_2 = Cl_2$, I_2; L = Me_3PS, $MePh_2PS$, Me_2PhPS)[1128], (F) $[M(dialkene)L_2]$ (ClO_4) [M = Rh, L = R_3PS, R = Ph, Me, Et, dialkene = cod, nbd; M = Ir, L = Ph_3PS, Me_3PS, dialkene-cod)[1129], (G) [M(dialkene) (Ph_3P)L] (ClO_4) (L = Ph_3PS, Me_3PS; dialkene = cod, nbd for Rh and cod for Ir][1129], (H) $[Rh(dialkene)(SePPh_3)_2]$ (ClO_4) [dialkene = cod, nbd, cyclooctatriene)[1130] and (I) $[M(cod)L_2]_n^{n+}$ and $[M(CO)_2L_2]_n^{n+}$ $n = 1$, 2; L = Me_3PS, Et_3PS, Ph_3PS)[1131].

Iridium(I) complexes C underwent oxidative addition reactions with HCl or I_2 forming complexes E. In contrast, the corresponding rhodium(I) couplexes showed no such activity, probably owing to the lower stability of rhodium(III) than iridium(III). The complexes [M(dialkene) $(Ph_3PS)_2$] (ClO_4) (M = Rh, Ir; dialkene = cod, nbd)[1129] were used as catalysts for the hydrogenation of hept-1-ene according to a pattern similar to the analogous complexes with alkyl sulphides used for hydrogenation of alkenes[1132]. In the present case, the iridium(I) complexes showed greater activity than the rhodium(I) complexes. All the complexes, except E, have square-planar geometry (**108**–**110**). The



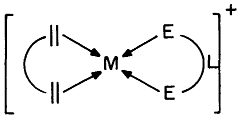
X = Cl, Ph_3P; L = R_3PS

(**108**)



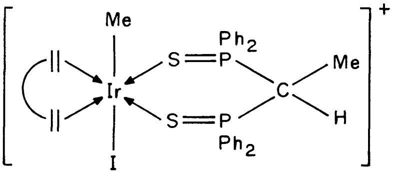
L = R_3PE

(**109**)



E⌒E = $dpmS_2$ or $dpmSe_2$

(**110**)

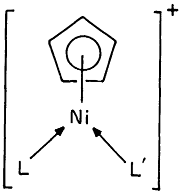


(**111**)

anionic ligand $\{Ph_2P(S)\}_2CH^-$ formed [Ir(L) (cod)]^{1133}, which on further reaction with MeI gave first [Ir($Ph_2P(S)CH(Me)P(S)Ph_2$) (cod)]I and subsequently [Ir(Me)I($Ph_2P(S)$-$CH(Me)P(S)Ph_2$) (cod)]I (**111**). Rhodium showed the reverse sequence Iridium formed the pentacoordinate complex [Ir(tfb)$_2$(Ph_3PS)] (ClO_4) with pentacoordination stabilized by tfb^{1134}.

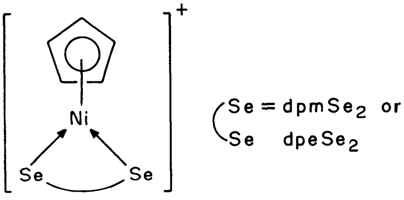
c. Nickel sub-Group. Nickel(II) forms complexes with various ligands of the type (A) [Ni(NO)L_2X] (X = Br, CN; L = Ph_3PE)^{1098}, (B) [NiLX_2].$^{1/2}$S (X = Br, I; L = dpmS_2; S = thf, CH_2Cl_2)^{1116}, (C) [NiL_n] $(ClO_4)_2$ ($n = 4$ for $Me_3PE^{1111,1115}$, 2 for dpm$S_2^{1116,1135,1136}$, (D) [NiL_2] (L = $\{Ph_2P(E)\}_2CH^-$, $\{R_2P(S)\}_2N^-$; R = Me, Ph^{950,1105,1137,1138}, (E) [(η^1-C_6F_5)Ni(Ph_3P)L] L = Ph_3PS)^{1139}, (F) [(η^5-cp)NiL_2] (BF_4) (L = Me_3PE, Ph_3PSe, $\frac{1}{2}$dpmSe$_2$, $\frac{1}{2}$dpeSe$_2$)^{1140,1141} and (G) [(η^5-cp)Ni(R_3P)L]BF_4 (R = Pr^i, Hex; L = Me_3PS)^{1142}. A few nickel(I) complexes, [NiLL′$\frac{1}{2}$] (L = dpmS_2; HL′ = HS_2CNRR'; NRR′ = Et_2N, PhNH, etc.) have also been reported^{1120}.

The spectral and magnetic moment data suggest distorted tetrahedral structures for the complexes A, B and C for $n = 2$), tetrahedral for the complexes C ($n = 4$) and D (L = $\{R_2P(S)\}_2N^-$) and square-planar for complexes D (L = $\{Ph_2P(E)\}_2CH^-$). Among the organonickel(II) complexes, E has square-planar geometry while the cations of the other complexes F and G may be represented as shown in **112** and **113**.



L, L′ = same or different

(**112**)

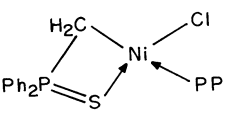


(**113**)

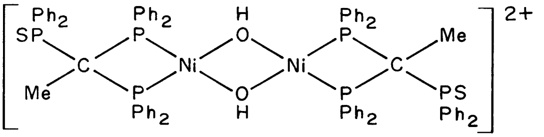
X-ray study of the complex [NiL_2] (L = $\{Me_2P(S)\}_2N^-$)^{1137} has confirmed the tetrahedral geometry about nickel. The S—Ni—S planes make a dihedral angle of 84.4°. There is no steric factor between the anionic ligands and hence a square-planar geometry should have been preferred. The reason for this apparent difference in adopting a tetrahedral rather than a square-planar structure is not clear. This complex with an NiS_4 core was the first example since all the other complexes with this core are diamagnetic with square-planar geometry$^{1143-1144}$.

Further comments on the complexes discussed above are that Ni—S and Ni—Se bonds have similar covalencies to those of cobalt(II) $^{1145-1148}$ and 10 *Dq* values for the phosphine chalcogenide complexes are similar. When L = $\{Ph_2P(E)\}_2CH^-$, (NiL_2] complexes are air-sensitive and diamagnetic. The selenide complex decomposes rapidly in solution and in the solid state, whereas the sulphide complexes decompose rapidly in solution but slowly in the solid state. In contrast, [NiL_2] (L = $\{R_2P(S)\}_2N^-$) are air-stable and paramagnetic ($\mu = 3.4$ BM)^{950,1137,1138,1149}. For R = Me, spin-state cross-over, tetrahedral$\rightleftharpoons$square planar, was observed.

A C,S-bonded nickel(II) complex (**114**) similar to [(Et_3P)ClPtCH(Ph_2PS)$_2$] has been reported^{462,1150}. Recently, a hydroxo-bridged dimeric cation, [(Ni(L)(μ-OH))$_2$] $(ClO_4)_2.Me_2CO$ (**115**) was obtained^{1151} from the reaction of [Ni(H_2O)$_6$]$(ClO_4)_2$ with $(Ph_3P)_3CMe$ and polysulphide, S_n^{2-}. The reaction of $(Ph_3P)_3CMe$ with S_n^{2-} oxidizes one arm of the ligand. X-ray measurements showed a square-planar geometry about each nickel atom. Interestingly, the $Ph_2P({=}S)CH_2$ arm of the ligand is uncoordinated.



(114)



(115)

Numerous air-stable complexes of palladium(II) and platinum(II) and some of palladium(IV) and platinum(IV) have been reported (Table 15). The complexes generally possess poor solubility, which may be responsible for the lack of NMR and other solution-phase studies.

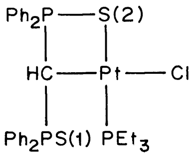
X-ray analyses of the complexes $[PdCl_2L_2]$ $\{L = PhEt_2P(S), Bu^i_3PS\}$ have been shown them to have *trans*-square-planar structures[1154–1155]. The short Pd—S distance for $L = Bu^i_3PS$ shows that it has a better σ-donor ability than $PhEt_2PS$ (2.334 versus 2.350 Å). It may be cautioned here that, on the basis of IR studies, *cis*-square-planar structures were suggested earlier[1155]. For other complexes (Table 15), square-planar, bromo- or sulphur-bridged square-planar dimeric and square-planar polymeric structures have been assigned for the complexes A, B, E(i) and (iv), G and H, C and F and D, E(ii) and (iii), respectively. The anionic ligand $\{Ph_2P(S)\}_2CH^-$ in $[PtCl(Et_3P)L]$ binds to platinum(II) via the methine carbon and one sulphur atom, forming a four-membered chelate ring (**116**)[462]. Owing to the lability of the Pt^{II}—S bond, three isomers (A, B and C) were identified (^{31}P NMR) (**116–118**). An X-ray study of isomer **116** showed nearly square-planar geometry about platinum(II)[462]. The Pt—S (bonded) distance (2.390 Å) is one of the longest reported for platinum(II) complexes, but is similar to that found in $Pt\text{-}SO_2$ complexes[1166–1169]; The Pt—S (non-bonded) distance is 3.70 Å. A slight rotation

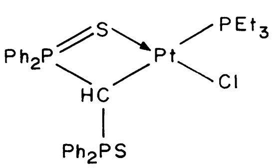
TABLE 15. Known complexes of palladium(II) and platinum(II)

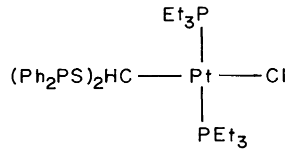
	Complex	L	Ref.
A	$MX_2L_2(M = Pd, Pt, X = Cl, Br)$	R_3PE[a]	18, 391, 1152–1156
B	$MX_2L(X = Cl, Br)$	$[Ph_2P(E)]_2CH_2$, $Ph_2P(S)CH_2P(S)Me_2$, $[Ph_2P(E)]_2(CH_2)_n$ ($n = 1$–4,6)	1116, 1152, 1157–1161
C	Pd_2Br_4L	Ph_3PE	1132
D	(i) $Pd_3X_6L_m$ ($X = Cl, Br, m = 2,4$)	$[Ph_2P(Se)]_2(CH_2)_n$ ($n = 2$–4,6)	1159, 1160
	(ii) $Pd_4X_8L_3(X = Cl, Br)$	$[Ph_2P(Se)]_2(CH_2)_n$ ($n = 4,6$)	1159
E	(i) $[Pt(CNS)_2L]_2$[b]	Ph_3PE	1162
	(ii) $M_3(CNS)_6L_2$[b]		
	(iii) $Pt_2(CNS)_4L$[b]		
	(iv) $ML(SCN)_2$[c]	$[Ph_2P(E)]_2CH_2$	1163
F	(i) $[PdL_2S]_2$	Ph_3PS	1164
	(ii) $[PdL(Ph_3P)S]_2$	Ph_3PS	1164
G	(i) $[PtCl(Et_3P)L]$	$[Ph_2P(S)]_2CH^-$	462
	(ii) ML_2	$[Ph_2P(S)]_2N^-$	1118
	(iii) $PdBr_2L$	$[Ph_2P(S)]_2NH$	1118
H	$[PhPt(PEt_3)_2L]^+$	Ph_3PS	1165
	(ii) $[(C_6F_5)Pt(Ph_3As)_2L]ClO_4$	Ph_3PS	423

[a] $R_3 = Ph_3$, *o*-, *m*- or *p*-Tol_3, Cy_3, Bu^i_3, $PhEt_2$.
[b] SCN-bridged polymer.
[c] M—SCN bonding.

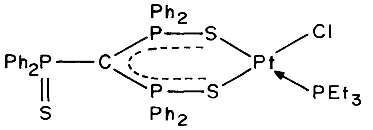
about the Pt—C bond would replace bonded S by non-bonded S. Isomer **118** is formed when excess of Et_3P is added to isomer **116**. ^{31}P NMR showed interchange of the P(S) groups in isomer **116**, probably owing to the higher *trans* effect of Et_3P. Isomer **117** was static as here Cl is *trans* to S.

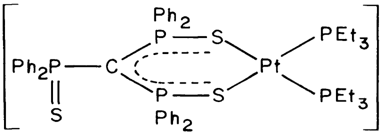

(116)


(117)

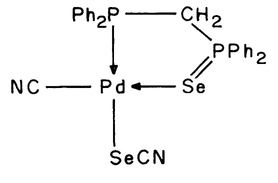

(118)

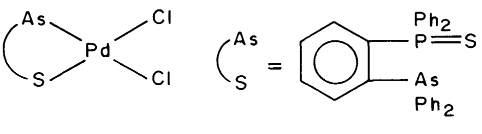
Reaction of the tripod ligand $\{Ph_2P(S)\}_3CH(HL)$ with $[Pt_2Cl_4(Et_3P)_2]$ $[Pt_2Cl_2(Et_3P)_4]$ $(BF_4)_2$ gave $[PtCl(Et_3P)L]$ (**119**) or $[Pt(Et_3P)_2L]$ (BF_4) (**120**), studied by NMR (^{13}C, ^{31}P and ^{195}Pt) and X-ray methods[1170]. ^{13}C NMR showed deprotonation of methine proton. The ^{31}P and ^{195}Pt NMR data showed a dynamic intramolecular exchange process involving the two PS groups in isomer **119** and all three PS groups in isomers **119** and **120**. The X-ray crystal structure of **119** has confirmed the binding of two PS groups to platinum(II) with a planar CP_3 chromophore (P—C—P angles 116.2–124.2°). The Pt—S bond *trans* to Et_3P was longer than that *trans* to the Pt—Cl bond[1171].


(119)


(120)

The reaction of $[Pd(SeCN)_4]^{2-}$ with dpm gave [PdL(CN)(SeCN)] (L = dpmPSe) (**121**) instead of the expected product. $[Pd(SeCN)_2L]$[1172]. Heating of $[Pd(SeCN)_2L]$ also gave **121** with the cyanide group *trans* to Se as shown by X-ray analysis. An S,As-bonded complex, $[PdX_2L]$ (**122**) (X = Cl, Br), has also been reported[1173].

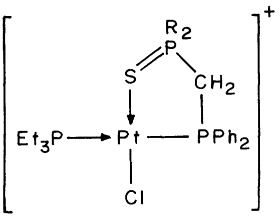

(121)


(122)

A platinum(II) complex, $[PtL_2]$ $(O_3SCF_3)_2$ underwent extrusion of selenium forming initially [PtLL′] $(O_3SCF_3)_2$ and finally $[PtL'_2]$ $(O_3SCF_3)_2$ $\{L = Ph_2P(Se)\ CH_2PPh_2;$ $L' = Ph_2P\text{-}(Se)CH_2P(Se)Ph_2\}$[1174]. Rearrangement of [PtLL″] $(O_3SCF_3)_2$ also gave the same product, $[PtL'_2]$ $(O_3SCF_3)_2$ {L′ is same as above, $L'' = Ph_2P\ CH_2PPh_2\}$[1174].

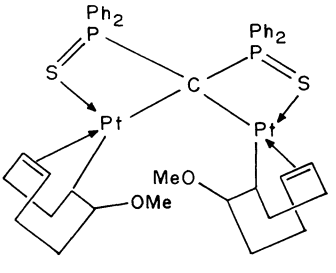
Reactions of $Ph_2PCH_2P(E)R_2$(E = S, Se; R = Ph, $CHMe_2$, CMe_3) with chlorobridged complex $[M_2Cl_4(PR_3)_2]$ (M = Pd, Pt, R = Et or Bu^n) in the presence of $NaClO_4$ or $NaBF_4$ gave *cis*- and *trans*-$[PtCl(PR_3)$ $\{Ph_2PCH_2P(E)R_2\}]X$ ($X = ClO_4$, BF_4)[425]. Here *cis*- and *trans*- refer to M–P bonds. Deprotonation of these complexes using NaH or using $Li^+[Ph_2PCHP(E)R_2]^-$ instead of the neutral ligand gave the corresponding *cis*- and *trans*-$PtCl(PR_3)$ $\{Ph_2PCH\text{-}P(E)R_2\}$]. The products were studied using ^{13}C, ^{31}P, ^{77}Se, ^{195}Pt NMR and X-ray data (one complex). The X-ray study of $[PtCl(PEt_3)$ $\{Ph_2PCH_2P(S)\text{-}(CMe_3)_2\}$ (ClO_4) showed *trans*-square planar structure (**123**).

An interesting platinum(II) complex, [PtL(MeOcod)] with the anionic ligand $\{Ph_2P(S)\}_2CH^-$(L), (**123**) has been reported[1133]. This showed both ligand and metal site reactivity in transforming to a novel dimer, $[Pt_2(Ph_2P(S)CP(S)Ph_2)$ $(MeOcod)_2]$ (**124**) containing a quaternary carbon bridge between platinum atoms (X-ray analysis).



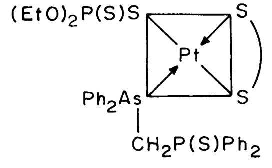
R = Me$_3$C

(**123**)

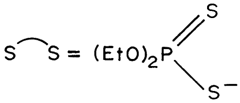


(**124**)

Interaction of $Pt[S_2P(OEt)_2]_2$ with $Ph_2PCH_2P(E)Ph_2$(L) gave (A) [LPtR]R $\{R = S_2P(OEt)_2\}$, (B) $[LPt(S_2P(O)OEt)]$ and (C) *cis*-and *trans*-$[PtL_2]R_2$ (*cis*, *trans* refer to M—P bonds linking L to M) [1175]. Compounds B are formed from A on slow reaction of the free anion R with A. The analogous ligand $Ph_2P(E)CH_2CH_2AsPh_2$(L′) also gave $[Pt(\eta^1\text{-}L')$ $(\eta^1\text{-}S_2P(OEt)_2)$ $(\eta^2\text{-}S_2P(OEt)_2]$. X-ray analysis for E = S showed a square-planar structure (**125**) with $Ph_2P(S)$ as a free dangling ligand end. Similarly, reactions of $Ph_2P(E)CH_2PPh_2$(L) with $[Pt(S_2CNEt_2)_2]$ gave a number of interesting products[1176], namely $[(\eta^1\text{-}L)Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)]$ and $[(\eta^2\text{-}L)Pt(\eta^2\text{-}S_2CNEt_2)]^+$. Owing to the higher Pt—Se lability, a number of side-products such as dpm and dpmSe$_2$ were also detected in the case of the selenium analogue (^{31}P, ^{77}Se and ^{195}Pt NMR).



(**125**)

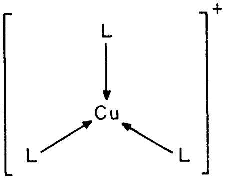


A small number of palladium(IV) and platinum(IV) complexes have been reported; (A) (Bu^n_4N) $[Pd(Ph_3PS)Cl_5]$[1177], (B) $[PtCl_4L_2]$ (L = *o*, *m*- and *p*-Tol_3PS)[1156], (C) $[PtCl_4L]$ $\{L = Ph_2P(S)\ (CH_2)_nP(S)Ph_2;\ n = 2\text{–}4\}$, (D) $[PtBr_4L]$ $\{L = Ph_2P(Se)\ (CH_2)_6P(Se)Ph_2\}$ and (E) $[PtBr_4L_2]$ $\{L = Ph_2P(E)\ (CH_2)_3P(E)Ph_2\}$[1160]. In complex E, L is unidentate, whereas in C and D, L are bidentate. The Pt^{IV}—Se bond is not stable as the ligand decomposes, as seen for Ph_3PSe and Ph_3AsS[1153]. Hence these complexes mentioned above were prepared at low temperature (20–25 °C) by slowly evaporating the reaction mixture.

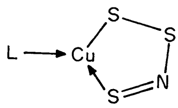
5. Complexes of the copper Group (IB)

Table 16 contains a number of copper(I) and some copper(II) complexes with mono- and di-tertiary phosphine chalcogenides. Owing to the tendency of copper(II) to undergo reduction to copper(I) in the presence of phosphine chalcogenides, only a small number of copper(II)–phosphine sulphide complexes have been isolated using Me_2CO as the solvent. Normally, copper(I) complexes were obtained after reducing copper(II) to copper(I) using ascorbic acid or hypophosphorous acid prior to its reaction with ligand.

An X-ray study of $[Cu(Me_3PS)_3]$ (ClO_4) showed nearly trigonal planar geometry (**126**)[1180]. The complexes, $[Cu(Me_3PS)_3]X$ and $[Cu(Ph_3PS)_3]$ X ($X = ClO_4$, BF_4) are isomorphic[1184]. The Cu—L bond strength was found to decrease in the order $Ph_3PS > PhMe_2PS > Me_3PS$ (IR)[1184]. A copper(I) complex, $[Cu(Ph_3PS)\,(NS_3)]$ (**127**), obtained from $[CuCl(Ph_3P)_3]$ and S_7NH, also possesses trigonal planar geometry about copper(I) (X-ray analysis)[1196].



(126)



(127)

Whereas the ionic complexes A were soluble in various organic solvents, the non-ionic complexes of the type $[CuLX]_n$ {B(i), (ii)} have poor solubility in common organic

TABLE 16. Known complexes of copper(I) and copper(II)

	Complex	L	Ref.
A	(i) $CuL_3]X^a$ ($X = ClO_4$, BF_4, NO_3)	R_3PE^b	1178–1185
	(ii) $[CuL_2]X^c$	$dpmS_2$, $dpmSe_2$, $dpseS_2$,	1157, 1158
	($X = ClO_4$, BF_4)	o-$(PSPh_2)(Ph_2As)C_6H_4$	1173
B	(i) $[CuLX]_n{}^d$ ($X = Cl$, Br, I, SCN)	R_3PS^e	1158, 1182, 1184, 1186–1188
	(ii) $[CuXL]_m{}^d$ ($X = Cl$, Br)	$dpmS_2$, $dpeS_2$	1157, 1158, 1173, 1189–1191
	(iii) $[CuClL]\cdot Me_2CO^a$	$dpmS_2$	1157, 1158, 1178
	(iv) $[(CuClL)_2\cdot 2(CuClL)]^f$	$dpmS_2$	1178
	(v) [CuBrL]	$Ph_2P(S)NHP(S)Ph_2$	1118
C	(i) $[CuCl_2L_2]^g$	Me_2PhPS, $MePh_2PS$	1157, 1158
	(ii) $[CuCl_2L]^g$	$dpmS_2$, $dpeS_2$, $dppS_2$	1157, 1158, 1189, 1192–1194
D	$[CuLL'](ClO_4)^h$	Ph_3PS	1195

[a] Trigonal planar.

[b] $R_3 = Me_3$, Et_3, Pr^i_3, Ph_3, Me_2Ph.

[c] Tetrahedral.

[d] Polymeric.

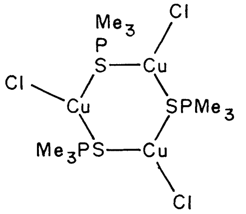
[e] $R_3 = Me_3$, Ph_3, Me_2Ph.

[f] Trigonal planar monomer and tetrahedral dimer.

[g] Distorted tetrahedral.

[h] L′ = 2,2′-bithiazole, trigonal planar.

solvents, suggesting polymeric structures. IR and X-ray measurements established the trimeric structure of $[Cu(Me_3PS)Cl]_3$ with a distorted trigonal planar geometry about each copper atom[1188,1197]. The angles about copper vary in the range 109.8–125.2°. Three Cu and three Cl atoms form a six-membered ring(**128**) which is very rarely observed in copper(I) chemistry.

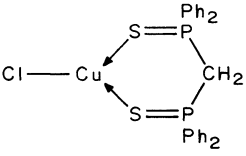


(128)

Polymeric $[Cu(Me_3PS)X]_n$ (X = Br, I) are isomorphic but different from $[Cu(Me_3PS)Cl]_3$. Similarly, in $[Cu(Ph_3PS)_3X]_n$, IR data rule out any ligand bridging[1187]. The difference may be attributed to the different electronic environments of Me_3PS (the better Lewis base) and Ph_3PS. $[Cu(Me_3PS)(SCN)]_\alpha$ is a long-chain polymer involving SCN^- bridging with terminal Me_3PS ligands [1184,1198]. The chains interact via SCN^- leading to pseudo-tetracoordination for some copper atoms.

The complex $[CuClL]Me_2CO$ {B(iii)} was obtained by reduction of a solution of $CuCl_2.2H_2O$ and $dpmS_2$ in Me_2CO using hypophosphorous acid, whereas the same reaction in EtOH gave $[(CuClL)_2.2(CuClL)]$ {B(iv)}[1157,1158,1178]. Heating the monomer $[CuClL]Me_2CO$ leads to loss of Me_2CO and formation of a dimer, $[CuClL]_2$, at temperatures > 140 °C.

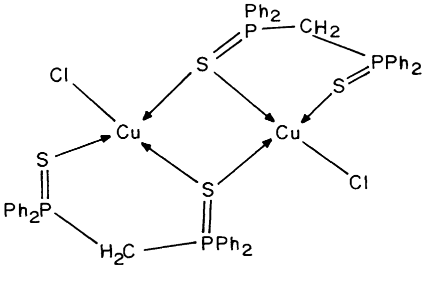
An X-ray study of $[CuClL]Me_2CO$)**129**) has shown that the geometry about copper is distorted trigonal-planar (S—Cu—S angles 113–123°)[1157,1158], the distortion being larger than that normally observed in mononuclear copper(I) complexes. The Me_2CO is unbonded.



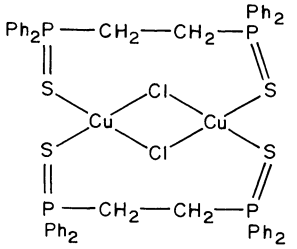
(129)

The X-ray structure of $[(CuClL)_2.2(CuClL)]$ {L = $Ph_2P(S)CH_2P(S)Ph_2$} shows that the monomer, CuClL, and dimer, $(CuClL)_2$, exist in the same unit cell[1178]. The monomer has the same geometry as above (**129**), whereas the dimer has each sulphur of the ligand acting as a bridge (**130**). The geometry about each copper is distorted tetrahedral. There was no evidence for Cu···Cu interaction. The reaction of $[CuClL]Me_2CO$ with Me_3PS gave $[Cu(Me_3PS)Cl]_3$, and this indicates the lability of the Cu—S bonds in the acetone complex. Treatment of the acetone complex with Cl_2 gave an orange solution due to $[CuCl_4]^{2-}$ [1199].

The complex [CuClL] (L = $dpeS_2$) also exists as a dimer (**131**)[1190]. The geometry about each copper is distorted tetrahedral. The Cu—S—P angles (109.9°, 106.6°) are larger than those found in the acetone complex (91.52°, 95.68°), from which it is concluded that when the ring strain is less, sulphur binds tetrahedrally[1188].



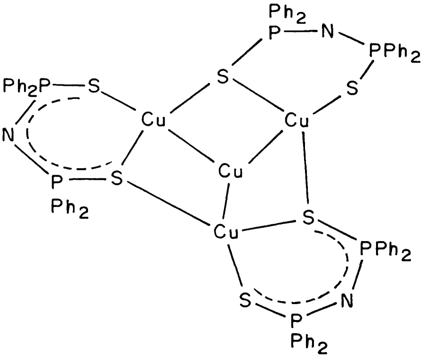
(130)



(131)

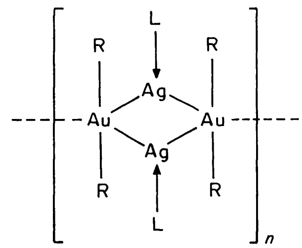
Reaction of $CuCl_2.2H_2O$ with the sodium salt of $Ph_2P(S)NHP(S)Ph_2$ in aqueous solution gave the dark purple compound, $[Cu_3L_4]$ (A). Purification of A in toluene–CCl_4 gave $[Cu_3L_3]$ or $[Cu_3L_3]$. $2.5CCl_4$ (B). Similarly, when A was worked up in CH_2Cl_2–CCl_4, a pink compound, $[Cu_4L_3][CuCl_2](CCl_4)$ (C) was obtained. When $[Cu(ClO_4)_2]$ solution in dmf was added to solution of A in toluene, the white compound $[Cu_4L_3](ClO_4)$ (D) was obtained. The compound $[CuL_2]$ (L = $\{Ph_2P(S)\}_2N^-$) (E) was obtained by the reaction of $\{Ph_2P(S)\}_2N^-K^+$ with $CuCl_2$ in methanol at − 78 °C[1090,1119,1200–1202].

An X-ray study of C showed that the copper(I) atoms in $[Cu_4L_3]^+$ are tetrahedral (**132**)[1202]. A has a μ value of 1.90 BM, suggesting the presence of one copper(II) site and two copper(I) sites. Other cluster compounds are diamagnetic. The blue copper(II) complex E has a pseudo-tetrahedral structure (ESR)[1203–1207]. A diamagnetic tetramer, $[CuL_4]$ (L = $\{Ph_2P(S)\}_2CH^-$), was obtained from organocopper(I), [ArCu], and $Ph_2P(S)CH_2P(S)Ph_2$[1208].

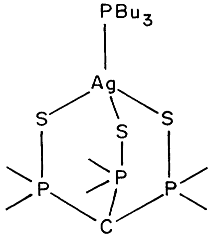


(132)

Only a few silver(I) complexes are known: (A) $[AgL_2]$ (ClO_4) (L = Ph_3PSe, $dpmS_2$, $dpmSe_2$, $dpeSe_2$)[1157,1158], (B) $[Ag(Cy_3PS)_2(NO_3)]$[1209] and (C) $[AgL(NO_3)].2H_2O$ (L = $dpmS_2$)[1157,1158]. The NO_3^- ions are in the coordination sphere, but their uni- or bi-dentate nature has not been established. The heterobimetallic complexes $[AuAgR_2(Ph_3PS)]_n$ (R = C_6F_5, $C_6H_2F_3$-2,4,6) (**133**)[1210] and a cage complex $[Ag(Bu_3P)L]$ (**134**) (L = $\{Ph_2P(S)\}_3C^-$[1211] have been reported. In **134**, silver has a tetrahedral geometry.



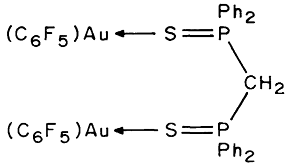
(133)



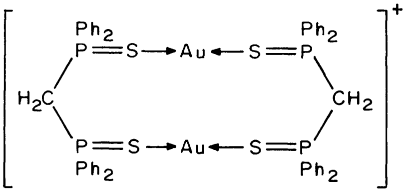
(134)

Gold forms a number of complexes (A) [AuClL] {L = Ph_3PE, *o*-$(Ph_2PS)(Ph_2As)C_6H_4$}, (B) $[Au(Ph_3PS)_2](PF_6)$ and (C) $[AuCl_3(Ph_3PS)]$[1153,1173,1181,1212–1217]. No adduct of gold(III) with Ph_3PSe or the related ligands Ph_3AsS and Ph_3SbS could be isolated on account of ligand decomposition on reaction with a gold(III) salt[1153,1215]. An X-ray study of [AuClL] (L = Ph_3PE) has shown a nearly linear geometry about gold(I)[1212,1218]. B has a similar geometry. In [AuClL] {L = *o*-$(PSPh_2)(Ph_2As)C_6H_4$}, the P=S group is uncoordinated and only Ph_2As binds to gold(I)[1173].

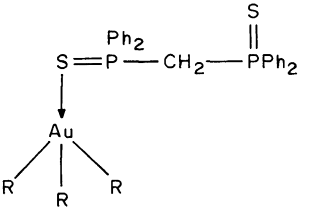
Reactions of $dpmS_2(L)$ with $[(C_6F_5)Au(tht)]$, $[Au(tht)_2](ClO_4)$, $[(C_6F_5)_3Au(OEt_2)]$ and $[(C_6F_5)_2Au(tht)_2](ClO_4)$ gave the air- and moisture-stable products $[(C_6F_5)_2Au_2L]$ (**135**), $[Au_2L_2](ClO_4)_2$ (**136**), $[(C_6F_5)_3AuL]$ (**137**) and $[(C_6F_5)_2AuL](ClO_4)$ (**138**), respectively. They were studied by ^1H, ^{19}F and ^{31}P NMR spectroscopy[1219]. Reaction of **138** with NaH gave $[(C_6F_5)_2AuL]$ (L = $\{Ph_2P(S)\}_2CH^-$) (**139**), involving C,S-bonding similar to a platinum(II) complex[462]. Reaction of **139** with [RAu(tht)], $[Au(tht)_2](ClO_4)$ or $AgClO_4$ gave bi- or tri-nuclear complexes (**140** and **141**). A binuclear complex, $[Au_2L_2]$ (L = $\{Ph_2P(S)\}_2N^-$) (**142**) was obtained from the reaction of $Ph_2P(S)$-$NHP(S)Ph_2(LH)$ with either [Au(tht)Cl] or $[(C_6F_5)_2Au(tht)]$[1219]. Similarly, $[R_2AuL]$ (**143**) was obtained from LH and $[R_2AuCl]_2$.



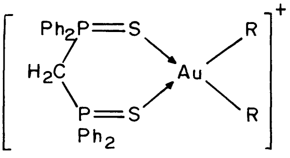
(135)



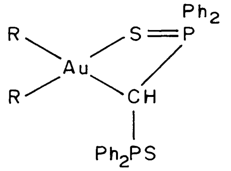
(136)



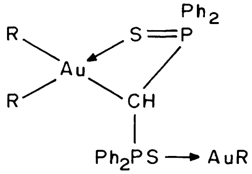
(137)



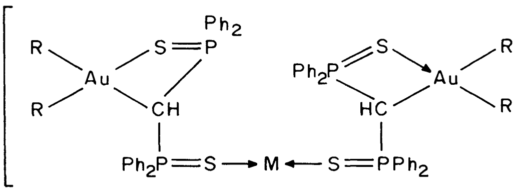
(138)



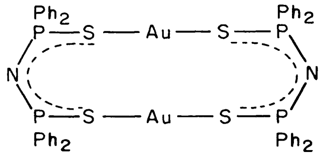
(**139**)



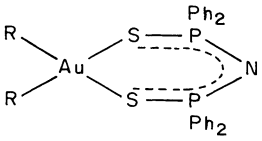
(**140**)



(**141**, M = Ag, Au)



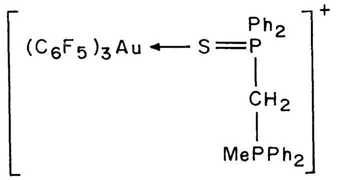
(**142**)



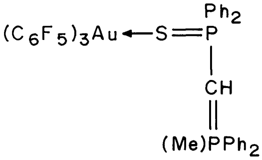
(**143**)

The unsymmetrical bis(phosphine) ligand dpmPS, on reaction with $[(C_6F_5)_2Au(tht)]^+$, forms $[(C_6F_5)_2AuL]^+$, which on treatment with NaH loses a CH_2 proton forming $[(C_6F_5)_2Au(Ph_2PCHP(S)Ph_2)]$[1220]. The anionic ligand chelates via P and S. Expectedly, the P—C bond length was shorter than that in a complex in which dpm acts as a chelating agent.

$[Au(C_6F_5)_3(Ph_2P(S)CH_2PPh_2Me)](ClO_4)$ (**144**) was obtained from the reaction of $[Au(C_6F_5)_3(OEt_2)]$ with $(Ph_2P(S)CH_2PPh_2Me)$ (ClO_4)[1221]. Compound (**144**) is air and moisture stable. Reaction of **144** with NaH gave the neutral methanide complex $[Au(C_6F_5)_3(Ph_2P(S)CHPPh_2Me)]$ (**145**). Reaction of **145** with $[Au(C_6F_5)$ (tht)] (1:2) gave $[Au(C_6F_5)\{Ph_2P(S)CH[Au(C_6F_5)]$ $PPh_2Me\}]$ (**146**). Reaction of **145** with [AuCl(tht)] gave the mixed-valence binuclear complex $[Au(C_6F_5)_3\{Ph_2P(S)CH(AuCl)$-$PPh_2Me\}]$ (**147**). Compound **147** reacted with $\{N(PPh_3)_2\}Cl$ and $\{NBu_4\}Br$ to form $[AuX(Ph_2P(S)CHPPh_2Me)]_2$ (X = Cl, Br) (**148** and **149**). Compound **148** reacted with $AgClO_4$ to give the cationic complex $[Au(Ph_2P(S)CHPPh_2Me]_2(ClO_4)_2$ (**150**), and **150** reacted with Cl_2 to give the gold(II) complex $[AuCl(Ph_2P(S)CHPPh_2Me)]_2(ClO_4)_2$ (**151**).

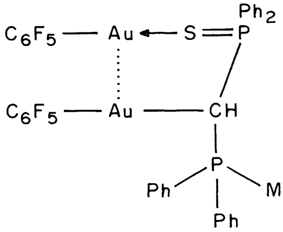


(**144**)

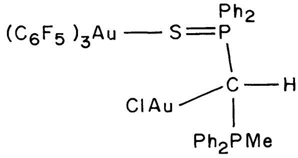


(**145**)

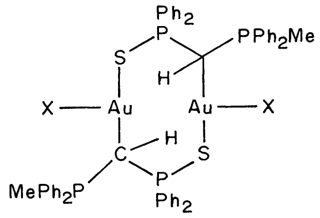
Compound **145** reacted with $[Ag(OClO_3)(PPh_3)]$ (1:1) to afford a mixture of $[Ag(Ph_2P(S)CHPPh_2Me)]_2(ClO_4)_2$ (**152**). $[Ag(Ph_2P(S)CH_2PPh_2Me)](ClO_4)_2$ was obtained from $AgClO_4$ and $[Ph_2P(S)CH_2PPh_2Me\}(ClO_4)$. An X-ray study of **146** showed that the structure involved an Au ··· Au interaction (3.224 Å). Further compounds of gold(III) have also been reported[1222]: $[Au(C_6F_5)Cl\{Ph_2P(S)CH_2PPh_2(CH_2R)\}(ClO_4)$ (R = H, Ph), $[(C_6F_5)_2ClAu\{Ph_2P(S)CHPPh_2(CH_2R)\}]$ and $[(C_6F_5)_2ClAu\{Ph_2P(S)CH(AuX)PPh_2Me\}]$ (X = C_6F_5, Cl).



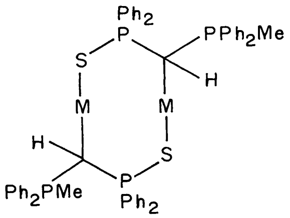
(**146**)



(**147**)

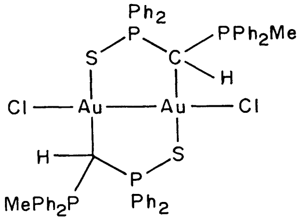


(**148** and **149**)



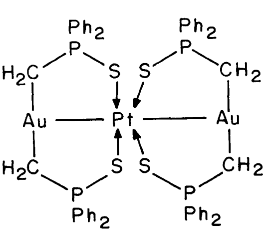
M = Ag, Au

(**150** and **152**)

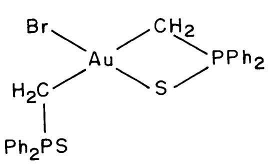


(**151**)

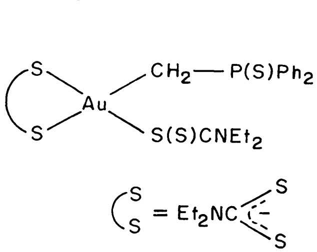
Reaction of the lithium salt $LiCH_2P(S)Ph_2$ with $[Au(C_4H_8S)Cl]$ in a 2:1 ratio gave $Li[Au\{CH_2P(S)Ph_2\}_2$, characterized as $\{(Ph_3P)_2N\}[Au\{CH_2P(S)Ph_2\}_2]$ (A)[1223,1224]. Reaction of A with *cis*-$[PtCl_2(SEt_2)_2]$ in a 2:1 ratio gave the neutral, linear trinuclear complex $[Au_2Pt\{CH_2P(S)Ph_2\}_4]$ (B). Treatment of A with $K_2[PtCl_4]$ gave $[Au_2Pt\{CH_2P(S)Ph_2\}_4Cl_2]$ (C). Oxidation of B with Cl_2 in CCl_4 or reaction of B with $PhICl_2$ also gave C. A, B and C have been characterized by X-ray measurements. A contains a C—Au—C linkage; B contains an Au—Pt—Au unit with $—CH_2P(S)Ph_2$ acting as the bridge (**153**). In C, Cl is bound to the terminal gold atoms, the remainder of bonding being the same. Similarly, SO_2 adds to the gold atoms forming $[Au_2Pt\{\mu\text{-}C, S\text{-}CH_2P(S)Ph_2\}_4(SO_2)]$[1224]. The oxidation of A with Br_2 in CH_2Cl_2 gave



(**153**)



(**154**)



(**155**)

$[Au\{CH_2P(S)Ph_2\}_2Br]$ (**154**)[1225], exhibiting a dynamic rearrangement involving CH_2 resonances (NMR). Reaction of $[Au\{CH_2P(S)Ph_2\}_2Cl]$ with [Au(tht)Cl] gave a mixed valence complex, $[Au^IAu^{III}\{CH_2P(S)Ph_2\}_2Cl_2]$ and a dimer, $[Au^{II}\{CH_2P(S)Ph_2\}Cl]_2$. Similarly, reaction of tetraethylthiuram disulphide with $[Au\{CH_2P(S)Ph_2\}]_2$ cleaves the dimer, forming $[Au\{CH_2P(S)Ph_2\}(S_2CNEt_2)_2]$ (**155**).

6. Complexes of the zinc Group (IIB)

Several complexes of Group IIB elements are given in Table 17. Except for the mercury(I) complexes J, all the other mercury(II) complexes are stable to air and moisture. Owing to the low solubility of the complexes, X-ray data have only been obtained for a few of the compounds listed. However, as discussed below, a large number of solution-phase investigations using NMR spectroscopy have been reported.

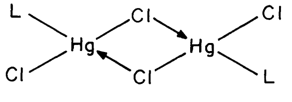
An X-ray study of $\{HgCl_2(Ph_3PSe)]$ showed that it has a dimeric structure (**156**)[1232]. It may be mentioned that $[HgCl_2(Ph_3AsO)]$, an analogous complex, has an oxygen-bridged dimeric structure[1242]. For $[HgCl_2(Ph_3PS)]$, a structure similar to that of

TABLE 17. Known complexes of zinc(II), cadmium(II) and mercury(II)

	Complex	L	Ref.
A	$[MX_2L_2]$[a] (M = Zn, Cd, Hg; X = Cl, Br, I, NO_3)	R_3PE[b]	1115, 1154, 1227–1230
B	$[MX_2L]$ (Zn, Cd, Hg; X = Cl, Br, I, NO_3, SCN)	(i) R_3PE[c,d]	1056, 1153, 1154, 1156, 1187, 1209, 1227, 1229, 1231, 1232
		(ii) $[Ph_2P(S)_2]CH_2$[a], $Ph_2P(S)CH_2P(S)Me_2$[a], $[Ph_2P(E)]_2(CH_2)_n$[a] (n = 2–4,6) $Ph_2P(Se)CH_2PPh_2$[a]	1075, 1157, 1158, 1161, 1227, 1233–1236
		(iii) $[Ph_2P(S)]_2NH$[a]	1118, 1193, 1237–1239
C	$[M_2X_4L]$[c] (M = Cd, Hg; X = Cl, Br, I)	$[Ph_2P(E)]_2(CH_2)_n$ (n = 4,6)	1234, 1235
D	$[CdBr_2L_3]$[e]	p-Tol_3PSe	1227
E	(i) $[Hg_3(NO_3)_6L_4]$[f]	Ph_3PSe	1227
	(ii) $[Hg_3X_6L_2]$ (X = Cl, I)	$[Ph_2P(E)]_2(CH_2)_3$	1233, 1234
F	$[Hg_4X_8L_3]$ (X = Cl, Br, I)	$[Ph_2P(E)]_2(CH_2)_n$ (n = 2,4)	1234
G	$[ZnL_4](ClO_4)_2$[a]	Me_3PE	1115, 1179, 1226, 1240
H	$[ML_2]X_2$[a] (M = Zn, Cd, Hg; X = NO_3, ClO_4)	$[Ph_2P(S)]_2CH_2$	1157, 1158, 1193
I	(i) $[ML_2]$[a] (M = Cd, Hg)	$[Ph_2P(S)]_2N^-$	1118, 1138
	(ii) [HgClL]	$[Ph_2P(S)]_2NH$	1118
J	$[Hg_2(AsF_6)_2L]$	Ph_3PE, p-Tol_3PS	1241

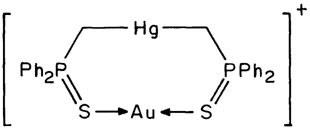
[a] Tetrahedral.
[b] R = Ph, Me, Bu^n, $(CNCH_2CH_2)$.
[c] Halogen-bridged dimer.
[d] R = Ph, Cy, o-, m-, p-Tol, $(CNCH_2CH_2)$.
[e] Octahedral dimer.
[f] Polymeric tetrahedral.

$[HgCl_2(Ph_3PSe)]$ is suggested[1232]. In a study by Lobana and Sandhu[1243], the formation of $[HgBr_2(1.5)Ph_3PS]$, which is probably a mixture of the 1:1 and 1:2 (M:L) adducts, and $[HgBr_2(Ph_3PSe)_2]$ were reported. It was also reported that the previous reports on the formation of $[HgCl_2(Ph_3PS)_2]$[1228] and $[(HgX_2)_2Ph_3PSe]$ ($X = Cl$, Br)[1244] were incorrect.

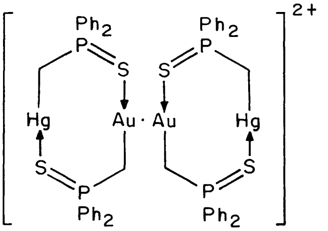


(156)

A number of investigations of cadmium(II) and mercury(II) have been reported recently using unsymmetrical phosphine chalcogenides, anionic ligands, tridentate ligands and some related ligands. A 2,2-dimethyl-2-silabut-3-enyldiphenylphosphine chalcogenide, $Ph_2P(E)CH_2SiMe_2(CH{=}CH_2)$, reacted with $HgCl_2$ to form pseudo-tetrahedral dimeric complexes $[HgCl_2L]_2$[1245]. Reaction of $Li\{CH_2P(S)Ph_2\}$ with $HgCl_2$ in thf gave a ylide complex, $[Hg\{CH_2P(S)Ph_2\}_2]$[1246], which on further reaction with [Au(tht)Cl] in CH_2Cl_2 in the presence of $TlPF_6$ formed $[HgAu\{CH_2P(S)Ph_2\}_2](PF_6)$ (**157**). Similarly, reaction of $[Au\{CH_2P(S)Ph_2\}_2]$ with $HgCl_2$ in the presence of $TlPF_6$ formed **158**. Compounds **157** and **158** have been studied by X-ray methods. These compounds do not interconvert on heating in thf.

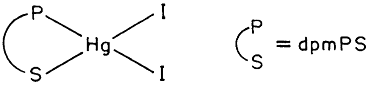


(157)

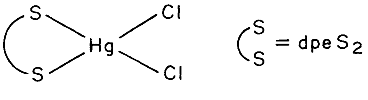


(158)

Reaction of HgX_2 with unsymmetrical phosphine chalcogenides formed a series of complexes of the type (A) $[HgX_2L]$ $\{X, L = Cl$, Br, I, $Ph_2P(E)CH_2PPh_2$; Cl, $Ph_2P(S)(CH_2)_2PPh_2$; Cl, Br, I, $Ph_2P(Se)(CH_2)_2PPh_2$; Cl, Br, I, $Ph_2P(S)(CH_2)_nP(Se)Ph_2$, $n = 1,2\}$ and (B) $[Hg_3X_6L_2]$ $\{X = Br, I; L = Ph_2P(S)(CH_2)_2PPh_2\}$[1100,1101]. Tetrahedral structures were suggested. An X-ray study of $[HgI_2L]$ ($L =$ dpm PS) has confirmed a tetrahedral geometry about mercury[1247a] (**159**). The Hg—S distance was 2.760 Å, which was longer than that (2.559 Å) in another phosphine sulphide complex, $[HgCl_2L]$ ($L = dpeS_2$)[1247a] (**160**). The ligand $dpeS_2$ forms a seven-membered chelate ring which represents the first example in tertiary phosphine chalcogenide chemistry. Recently, X-ray analysis of $[HgCl_2(dpmS_2)]$ has confirmed six-membered ring formation about mercury with tetrahedral geometry[1247b].

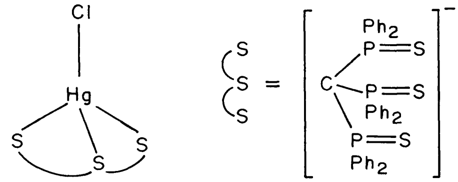


(159)



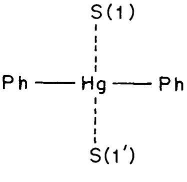
(160)

The complexes $[HgL_2]$ ($L =$ dpmPS, dpmPSe) (A)[1248] were obtained from the reaction of $Li(Ph_2P(E)CHPPh_2)$ with $HgCl_2$ and these represent rare examples of deprotonated dpmPE (E = S, Se). The product A contains P,E-bonded chelates (^{31}P, ^{199}Hg NMR study). Tripod ligands, $\{Ph_2P(S)\}_3CH(LH)$ and $(Ph_2PS](Me_2PS)_2CH(LH)$ reacted with HgX_2 (X = Cl, Br, I) to form the complexes [HgXL] ($L = \{Ph_2PS\}_3C^-$ and $(Ph_2PS)(Me_2PSC^-)$). [CdXL] complexes were obtained in a similar manner[20,1249,1250]. In the case of the cadmium(II) complexes, the presence of Et_3N as the base was essential. All these were studied using ^1H, ^{13}C, ^{31}P and ^{199}Hg NMR and X-ray diffraction methods. ^1H and ^{13}C NMR data confirmed the deprotonation of CH proton. The X-ray study of [HgClL] $\{L = Ph_2P(S)\ (Me_2PS)_2C^-\}$ has shown tetrahedral geometry about mercury (**161**). The Hg—$SPPh_2$ bond was longer than the Hg—$SPMe_2$ bond (2.710 Å versus 2.536 Å). The non-bonding Hg—C distance was 3.437 Å).



(161)

Recently a series of organomercury complexes have been reported: (A) [PhHgXL] [X, L = CH_3COO^-, Ph_3PS[1251], Cl_3CCOO^-, Ph_3PSe[1251], Ph_3PS[1252]), (B) $[Ph_2HgL]$ $\{L = Ph_2P(S)(CH_2)_2P(S)Ph_2\}$[1253], (C) [RHgClL] $\{R = m\text{-}NO_2C_6H_4$ or $p\text{-}ClC_6H_4$; $L = (Ph_2PSe)_2(CH_2)_n$, $n = 1, 2$; $R = m\text{-}NO_2C_6H_4$, $L = (Ph_2PS)_2CH_2\}$[1254] and (D) $[(RHgCl)_2L]$ $\{L = (Ph_2PS)_2CH_2, (Ph_2PSe)_2(CH_2)_3\}$[1254]. They were studied by IR, ^{31}P, ^{77}Se and ^{199}Hg NMR and X-ray methods (for complex B). The interaction of $PhHg^{II}$ with S or Se was weak and could only be established from ^{77}Se and ^{199}Hg NMR measurements[1251]. X-ray analysis of $[Ph_2HgL]$ ($L = dpeS_2$)[1253] showed an Hg···S distance of 3.913 Å. Hence this complex may be labelled as a weak molecular adduct (**162**). Only sulphur atoms from the two L molecules passing above and below the plane containing Ph_2Hg moiety are shown. Complexes C and D were shown by IR study to have stronger RHg···E interaction, although this interaction was weaker than that found in HgX_2–phosphine chalcogenide complexes.



(162)

In the following text, solution-phase interactions of zinc(II), cadmium(II) and mercury(II) with tertiary phosphine chalcogenides studied by ^{31}P, ^{113}Cd, ^{77}Se and ^{199}Hg NMR spectroscopy are discussed. The anions in the case of zinc(II) and cadmium(II) were generally the bulky AsF_6^- or SbF_6^- ions, which have little interaction with the metal centres, whereas for mercury(II) halides or SCN were used. Table 18 contains various complexes that have been detected which have coordination numbers ranging from 2 to 4. The metal to ligand ratios are varied in order to obtain the desired predominant species. At room temperature, there was generally exchange between the free and the coordinated ligands. It may be mentioned that cadmium(II) formed $[Cd(Ph_3PO)_4]^{2+}$ and

TABLE 18. Complexes of Group IIB (studied by NMR)

	Complex	L	Ref.
A	$[ZnL_n]^{2+}$ ($n = 3,4$)	R_3PE^a	998
B	$[ZnL_2]^{2+}$	(i) R_3PE^b	998
		(ii) $dpmS_2$	998
C	$[ML_nL'_{4-n}]^{2+}$ (M = Zn, Cd; $n = 1$–3)	$L = Cy_3PSe$; $L' = Cy_3PS$	998, 1000
D	$[ML]^{2+}$ (M = Zn, Cd)	$[Ph_2P(E)CH_2CH_2]_2P(E)Ph^c$	998
E	$[ML_2]^{2+}$ (M = Zn, Cd)	$[Ph_2P(E)CH_2]_3CMe^d$	998
F	$[CdL_n]^{2+}$ ($n = 3,4$)	R_3PE^e	999, 1000, 1255
G	$[CdL_2]^{2+}$	(i) $dpmSe_2$, $dpeSe_2$, $dppSe_2$	999, 1255
		(ii) o-Tol_3PE	1000
	$[CdL_nL'_{4-n}]^{2+}$ ($n = 1$–3)	$L = Cy_3PS$; $L' = Cy_3PSe$	1000
H	(i) $[HgX_2L_2]$ (X = Cl, Br, I, SCN)	Bu^n_3PE, Bu^n_2PhPSe, Bu^nPh_2PSe	1256–1259
	(ii) $[Hg_2X_4L_2]$ (X = Cl, Br)	Bu^n_3PSe	1258
	(iii) $[HgX_2(Bu^n_3P)L]$	Bu^n_3PSe	1259

[a] $R_3 = Ph_3$, o-Tol_3, Cy_3.
[b] $R_3 = o$-Tol_3, Cy_3.
[c] Tridentate.
[d] Bidentate.
[e] $R_3 = Ph_3$, $Ph_2(o$-$Tol)$, $Ph(o$-$Tol)_2$, p-Tol_3, Cy_3, Bu^t_3.

$[Cd(Ph_3PO)_6]^{2+}$ species against only four-coordinate cadmium(II)–phosphine chalcogenide species. Moreover, whereas Cd—E (E = S, Se) bonds are labile, Cd^{II}—O bonds are comparatively inert. Hence it may be concluded that phosphine chalcogenides cannot compete with phosphine oxides for coordination to cadmium(II).

From ^{113}Cd NMR, it was observed that for $[Cd(R_3PE)_4]^{2+}$, the shielding of cadmium(II) decreased in the order $E = O \gg Se > S$. Owing to the higher affinity of cadmium(II) for oxygen, any attempt to prepare mixed-ligand species of the type $[Cd(Cy_3PO)_x(Cy_3PS)_{4-x}]^{2+}$ instead gave $[Cd(Cy_3PO)_4]^{2+}$ and $[Cd(Cy_3PS)_4]^{2+}$ [1000,1260]. It was further noted that interaction of MX_2 (M = Cd, Hg) with the ligands decreased in the sequence $Cl > Br > I$[1256,1257].

The unsymmetrical phosphine chalcogenides $Ph_2P(E)CH_2PPh_2(L)$ reacted with Cd^{2+} to form $[CdL_2](ClO_4)_2$, $[CdL_2(dmso)_x](CF_3SO_3)_2$ ($x = 1,2$) and $[Cd(\eta^2\text{-}L)(\eta^1\text{-}L)(dmso)_x]^{2+}$ ($x = 1$–3)[1261]. Similarly, $[CdL'_2]X_2$ $\{L' = Ph_2P(E)CH_2P(E)Ph_2;\ X = ClO_4, CF_3SO_3\}$ were formed (^{31}P, ^{77}Se and ^{113}Cd NMR)[1261]. It was observed that the Cd—P bond was weaker than either Cd—S or Cd—Se bonds when the interaction of Ph_3P was compared with that of Ph_3PSe. From cyclic voltametric studies, it was found that both $[CdL_2]^{2+}$ and $[CdL'_2]^{2+}$ complexes undergo two-electron reversible processes at a mercury electrode. Similarly, the ligands mentioned above formed $[HgL_2]^{2+}$ and $[HgL'_2]^{2+}$, as shown by ^{31}P, ^{77}Se and ^{199}Hg NMR studies[1262]. Competitive exchange studies revealed that mercury(II) prefers to bind $Ph_2P(E)CH_2PPh_2(L)$ more than $Ph_2P(E)CH_2P(E)Ph_2(L')$. The electrochemical reduction of both $[HgL_2]^{2+}$ and $[HgL'_2]^{2+}$ at a mercury electrode occurs via a mercury(I) intermediate:

$$HgL_2^{2+} + Hg \rightleftharpoons 2[HgL]^+ \xrightleftharpoons{+2e^-} 2Hg + L$$

$\{L = Ph_2P(E)CH_2PPh_2;\ L' = Ph_2P(E)CH_2P(E)Ph_2;\ E = S, Se\}$. Whereas the complexes with L showed both chemical electrochemical reversibility, the complexes with L′ showed chemical reversibility, but electrochemical irreversibility.

B. Main Group Elements

1. Complexes of boron, aluminium, indium and thallium(IIIA)

Boron(III) halides form moisture-sensitive adducts, $[BX_3L]$ (X = Cl, Br, I; L = R_3PE, R = Me, Cy, Ph; E = S, Se)$^{1263-1265}$. The B(III)—E bond strengths decreased as shown by IR and ^1H NMR data in the order $BI_3 > BBr_3 > BCl_3 > BF_3$^{740,1263}. Ligand exchange was slow in the BI_3L complexes but fast with other adducts. An adduct with diborane, $\frac{1}{2}B_2H_6{\cdot}R_3PS$ (R = Me, Ph) has been reported^{747}.

A few aluminium(III) adducts of composition $[(AlCl_3)_n(Ph_3PS)]$ ($n = 1-3$) and $[AlBr_3(Ph_3PS)]$ have been reported^{1056,1266}. Reaction of $dpmS_2$ with dissobutylaluminium hydride gave $[(AlCH_2CHMe_2)_2\{Ph_2P(S)CPPh_2(S)\}_2\ \{Al(CH_2CHMe_2)_2\}_2]^{1267}$. X-ray study of this complex has shown an unusual S_4Al_4 core.

Indium(III) forms $[InX_3(Me_3PS)_2]$ complexes (X = Cl or Br)^{1268}. An X-ray analysis for X = Cl showed a distorted trigonal bipyramidal geometry with the thio ligands in the apical positions. Thallium(III) also forms complexes of the type $[TlCl_3L]$ (L = Ph_3PE) and $[PhTl(O_2CCF_3)_2(Ph_3PS)]^{1269-1271}$.

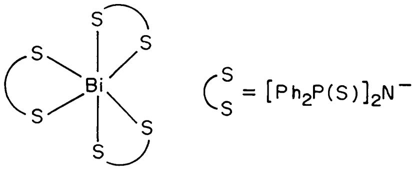
2. Complexes of Tin(II, IV) and lead(II) (IVA)

The interaction of $[Sn(SbF_6)_2]$ and $[Pb(SbF_6)_2]$ with tertiary phosphine chalcogenides has been studied using ^{31}P, ^{119}Sn and ^{207}Pb NMR spectroscopy^{1272}. The formation of $[ML_3]^{2+}$ (L = Cy_3PE; M = Sn, Pb), $[M(Cy_3PS)\ (Cy_3PSe)_2]^{2+}$ and $[M(Cy_3PS)_2(Cy_3PSe)]^{2+}$ was established. In contrast, Cy_3PO formed both $[M(Cy_3PO)_2]^{2+}$ and $[M(Cy_3PO)_3]^{2+}$. From ^{207}Pb NMR studies it was concluded that δ(Pb) values decrease in the sequence Se > S > O$^{1273-1277}$. For the complexes $[ML_3]^{2+}$, trigonal pyramidal geometry with a stereochemically active lone pair has been suggested.

Tin(IV) forms a number of complexes: (A) $[SnCl_4L_2]$ (L = Ph_3PS)^{1056}, (B) $[SnX_4L_2)$ (X = Cl, Br, I; L = Ph_3PE)^{18,1278}, (C) $[SnCl_4L_2]$ $\{L = (p\text{-}RC_6H_4)_3PS$, R = Me_2N, H, MeO, Me, Cl$\}^{1279}$, (D) $[SnX_4L_2]$ (X = Cl, Br; L = R_3PS; R_3 = Me_3, Et_3, Pr^n_3, Bu^n_3, Me_2P)^{1280}, (E) $[SnCl_4L_m]$ (m = 1, 2; L = Bu^n_3PE)^{1281}, (F) $[SnCl_4L]$ [L = $dpeS_2$]^{1193,1278} and (G) $[Ph_3SnXL]$ (X = NCS, NCO, N_3; L = Ph_3PS)^{866,1282,1283}. X-ray data are not available for any of these complexes.

3. Complexes of antimony(V) and bismuth(III) (VA)

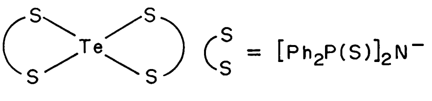
A few antimony(V) and bismuth(III) complexes are known: $[SbCl_5L]$, $[SbCl_3Br_2L]$ (L = Ph_3PS)^{1056,1284}, $[(SbCl_5)_2L]$ (L = Bu_3PS, Bu_3PSe)^{894} and $[BiL_3]$ (L = $\{Ph_2P(S)\}_2N^-$)^{1285}. The 2:1 antimony complexes dissociate in CH_2Cl_2 to form $[SbCl_4L][SbCl_6]$ ion pairs. The geometry about bismuth in $[BiL_3]$ is distorted octahedral (**163**). This is the first example of a complex of a Main Group element with $\{Ph_2P(S)\}_2N^-$ whose X-ray structure has been reported.



(163)

4. Complexes of tellurium (II, IV) (VIA)

Tellurium(II) forms a complex $[TeL_2]$ (L = $\{Ph_2P(S)\}_2N^-$), for which X-ray studies showed a square-planar geometry (**164**)^{1286}. A series of tellurium(IV) and organotellurium(IV) complexes have been reported: (A) [$TeCl_4L_n$], (B) [$RTeCl_3L_n$] ($n = 1, 2$; L = Ph_3PE, R = Ph, 4-$MeOC_6H_4$, 4-BrC_6H_4)[1287], (C) [R_2TeCl_2L] (R = Ph, *p*-$MeOC_6H_4$; L = R'_3PSe; R' = Ph, *p*-MeC_6H_4, Bu^n, $dpeSe_2$)[1287,1288]. For C a distorted octahedral geometry with one site occupied by a lone pair has been suggested ($dpeSe_2$ coordinates via one selenium only).



(164)

IV. TERTIARY PHOSPHINE TELLURIDES

In comparison with tertiary phosphine oxides, sulphides and selenides, very little work has been reported on the coordination chemistry of tertiary phosphine tellurides. The difference is attributed to the lower stability of P=Te bond versus P=O, P=S or P=Se bonds. Before discussing the coordination chemistry of phosphine tellurides, it may be appropriate to give a brief account of the synthesis, stability and reactivity of the phosphine tellurides, which will be useful in understanding the poor reports on their coordination chemistry.

Tributylphosphine telluride (Bu^n_3PSe) was prepared by the reaction of Bu^n_3P with tellurium in a large excess of toluene by refluxing for 21 h under a methane atmosphere (m.p. 35.0 °C)[1289]. The ligand decomposes on storage. Other papers have dealt with the synthesis of ligands of the R_3PTe type (R = alkyl or alkylaryl)[32,1290,1291].

Tellurium in tertiary phosphine tellurides is labile, as evidenced by various studies. R_3P makes nucleophilically attacks on tellurium in R_3PTe. It has been suggested that linear intermediates of the type R_3PTePR_3 are fomed (R = Me_3C, Me_2N)[1292]. Rapid transfer of tellurium between $(Me_3C)_3P$ and $(Me_3C)_3PTe$ was observed by NMR spectroscopy[1291]. The P—Te bond length is 2.368 Å, indicating a bond order of 1.5[1293].

An X-ray study of $Ph_3PTePPh_3$ (obtained by the reaction of $Ph_4As^+TeCN^-$ with excess of Ph_3P in MeCN containing $LiClO_4$) has shown a linear P—Te—P moiety[1294]. There is a normal bond between one P and Te, while the interaction between Te and the other P is weak. The IR spectra of Oct^n_3PTe in CCl_4 showed a hydrogen-bond interaction with MeOH and MeCN[1295]. ^{31}P and ^{125}Te NMR showed that the two nuclei couple in RR'R″ PTe (R groups chosen from Bu, Me, Me_2N, Et, EtO, NEt_2)[1296].

Tellurophosphoranes (R_3PTe) react with MeI to form $R_3P^+TeMeI^-$ (R = Me, Me_2CH, Bu^n, Me_3C, Me_2N)[1297]. A thin film of CdTe was deposited cathodically on titanium in a photoelectrochemical cell using Bu^n_3PTe and a propylene carbonate solution of cadmium(II)[1298]. Cyclic voltametry revealed the formation of a cadmium(II) complex with Bu^n_3PTe so that electron transfer can be effective. R_3PTe (R = Me, Et) reacted with HgR_2 (R = Et, Ph) at 115 °C to form mercury telluride (HgTe) as the sole solid-state product[1299]. In the case of Ph_2Hg, it was observed that Ph_2Te and Ph_2Te_2 are the major organic products.

The reaction of Et_3PTe with [$Mn_2(CO)_{10}$] under mild conditions gave [$(Et_3P)_2(CO)_3MnTe]_2$ (A)[1300]. A has a structure similar to that of RTeTeR with the $(Et_3P)_2(CO)_3Mn$ moiety replacing the R groups. Pyrolysis of A at 300 °C gave crystalline MnTe. A similar reaction of Et_3PTe with [$cp_2Fe_2(CO)_4$] in the presence of Et_3P gave [$cp(Et_3P)(CO)Fe]_2Te$ and [$cp(Et_3P)(CO)FeTe]_2$[1301].

Dications of the type [$R_3PTeTePR_3]^{2+}$ were obtained when R_3PTe (R = Me_3C, Me_2CH) was oxidized by ferricinium salts[1302]. The compounds [$(Me_3P)_3CoTe_2Co(PMe_3)_3$] (B) (similar to A) were obtained when [$CoX(PMe_3)_3$] (X = Cl, PMe_3, etc.), Li[$CoL(PMe_3)_3$] (L = ethene), [$CoCl_2(PMe_3)_3$] and [$Co(CO)_2(PMe_3)_2]_2$ were oxidized by tellurium[1303]. The reaction of B with CO gave [$\{(Me_3P)_2(CO)_2Co\}_2Te_2$].

Extrusion of tellurium from Bu_3PTe takes place when it reacts with (i) $[(MeC_5H_4)_3U]$·thf and (ii) $[(Me_5C_5)_2Yb]$. Tellurium-bridged complexes, $[(MeC_5H_4)_3U]_2$-Te[1304] and $[(Me_5C_5)_2Yb]_2Te$[1051a] are formed. Whereas extrusion of sulphur and selenium from Ph_3PS and Bu_3PSe respecitvely, was observed, no extrusion of oxygen from Ph_3PO took place. Instead $[(MeC_5H_4)_3UPh_3PO]$ was formed[1304].

The first stable tellurophosphorane complexes $[M(CO)_5(R_3PTe)]$ ($M = Cr$, Mo, W; $R = Me_3C$) (A) were reported by Kuhn *et al.*[19] in 1985. The photolysis of $[M(CO)_6]$ in thf in the presence of R_3PTe for 12 h gave monosubstituted products (A) in quantitative yield. An X-ray analysis of $[W(CO)_5(Bu^t_3PTe)]$ showed octahedral geometry with W—Te bonding.

Reaction of $[(\eta\text{-cp})Fe(CO)_2(thf)]^+$ with R_3PTe gave $[(\pi\text{-cp})Fe(CO)_2(R_3PTe)]^+$ ($R = Me$, Me_2CH, Me_3C, Me_2N, morpholino)[1305]. NMR data reveal Fe—Te π-bonding. Reaction of $Li(Ph_2P(Te)CHPPh_2)$ {prepared from Te and $(Ph_2P)_2CHLi$} with $HgCl_2$ gave $[Hg(Ph_2P(Te)CHPPh_2)_2]$ containing P and Te bonds with Hg (^{31}P and ^{199}Hg NMR)[1248].

V. APPLICATIONS

The applications covered in this section are analytical and catalytic applications. Among the analytical applications, liquid–liquid extraction of metal ions constitutes one of the most extensively studied areas, other areas including reversed-phase chromatography and ion-selective electrodes.

A. Analytical Applications

In this section, the separation and determination of metals using various types of phosphine oxides and chalcogenides are described. Broadly, the following areas are covered: (1) liquid–liquid extraction; (2) reversed-phase chromatography (liquid–solid extraction system); (3) ion-selective electrodes; (4) miscellaneous applications; (4.1) extractive and direct determination of metals; and (4.2) Fluorimetric determination and related applications.

Section 1 contains a number of systems which relate to the quantitative separation and determination of metals, whereas Section 4 describes only such systems not covered in Sections 1–3.

1. Liquid–liquid extraction

The ligands used for extraction studies can be divided into three types: (a) mono-tertiary phosphine oxide; (b) di-tertiary phosphine oxides; (c) Poly-tertiary phosphine oxides; and (d) Mono- and di-tertiary phosphine sulphides or selenides.

a. Extraction with mono-tertiary phosphine oxides. There have been numerous investigations on the use of mono-tertiary phosphine oxides (R_3PO), either alone or together with β-diketones, pyrazolones, etc., for the extraction of metals. The d- and f-block elements have been studied to much greater extent than the s- and p-block elements. When these ligands are used together with other reagents, they generally act synergistically. Thus, the most interesting work on liquid–liquid extraction chemistry deals with the use of these ligands as synergists. The phenomenon of synergism may be attributed to the formation of a mixed-ligand complex or an adduct complex which has a higher solubility in the organic phase than that of the simple chelate[1306]. In the adduct complex, coordinated water is replaced by an organophosphorus reagent. The synergistic extraction of the metal ions has various advantages: enhanced extractability, widening of the optimum pH range, stabilization of an extracted species by forming an adduct and a favourable kinetic effect[1307]. In the kinetic effect, equilibrium is reaced in a shorter time on the addition of the adduct molecules such as the organosphosphorus reagents. The addition of alcohols, esters, ketones, etc., also leads to enhanced extraction[1308].

Among mono-tertiary phosphine oxides, tri-*n*-octylphosphine oxide (topo) is the most extensively used ligand, probably owing to its high donor property, low toxicity and vapour pressure and poor miscibility with water. Two other ligands used extensively are tri-*n*-butylphosphine oxide (Bu^n_3PO) and triphenylphosphine oxide (Ph_3PO). Some other phosphine oxides have been used and are described. In the synergistic systems, β-diketones, pyrazolones, di(2-ethylhexyl)phosphoric acid and a few others are the reagents used for extraction, with phosphine oxides acting as the synergists. There are a few other cases with different synergistic combinations.

i. Elements of Groups IA and IIA. Topo (in benzene) extracts alkali metal iodides (MI, M = Li, Na, K, Cs) from the aqueous phase[1309]. Alkali metal chlorides or bromides are not extracted. The difference is attributed to the lower solvation energy and higher metal–iodide covalency, which promote extraction of the alkali metal iodides. The extraction ability of topo is higher than that of tbp or diisoamyl methylphosphonate; the latter possess more electronegative RO groups bonded to phosphorus, which lowers their basicity. Also, tbp and related analogues have higher miscibilities with water, which lowers the effective reagent concentration.

The extraction of alkali metals (Li, Na, K, Cs) from basic media (pH > 9) with the synergistic pairs $HA–R_3PO$ (HA = Htta, Hdbm; R = *n*-octyl, Ph, Bu^nO) in benzene followed the trend Li > Na > K > Cs[1310,1311]. The separation factors, for example for Li/Na, varied as ~2000 (Hdbm–topo), 1000 (Hdbm–tbp), 100 (Hdbm–Ph_3PO) and ~10 (Hdbm). The extracted species had the composition [MAL_2] and the order of extraction was topo > tbp > Ph_3PO (e.g. for Li, $\log\beta = 7.55$, 4.42 and 3.95, respectively). The larger size of Ph_3PO relative to the smaller Li^+ appears to be responsible for this sequence, but the incomplete data on Ph_3PO prohibit comments on the other metals.

The fluorinated β-diketones $RC(O)CH_2C(O)R'$ ($R = CF_3$, C_2F_5, C_3F_7; $R' = CMe_3$) and topo in benzene also showed selective extraction of lithium over the other alkali metals from neutral solutions; the selectivity of Li over Mg, Ca and Sr was poor[1312]. For the $C_3F_7C(O)CH_2C(O)CMe_3$–topo pair, the separation factors were as follows:

Li/M:	1300	3800	3700	2500	0.019	0.067	1
M:	Na	K	Rb	Cs	Mg	Ca	Sr

These Li/M values vary directly with the variation in the ionic radii. The extracted species was [Li(A)(topo)$_n$] [$n = 1, 2$; A = anion of a β-diketone). A change of solvent affected the extraction sequence in the order: dodecane > xylene > CCl_4 > benzene ($K_{ex} = 315$, 125, 93 and 55, respectively). Interestingly, a 94% recovery of the lithium present in a brine sample (Li 0.080, Na 145, K 29 gl^{-1}) was readily obtained. Another β-diketone, nonyltrifluoroacetone, and topo (or Ph_3PO) in benzene extracted Li, Na, K and Cs synergistically[1313].

The combinations α-acetyl-*m*-dodecylacetophenone (LIX 54)–topo and α-perfluoroalkanoyl-*m*-dodecylacetophenone (LIX 51)–topo extracted Li^+ synergistically[1314]. The extracted species were [Li(A)(topo)$_{1.3}$] (HA = LIX 51 or LIX 54). The extraction performance of LIX 51–topo is 4.65×10^4 times higher than that of LIX 51 alone or LIX 54–topo. Only LIX 51–topo extracted Na^+ {[NaA(topo)$_{1.3}$]} and the extractability of Na^+ was much less than that of Li^+.

The 4-acyl-5-pyrazolones with bulky substituents and topo are able to extract lithium quantitatively[1315]. As the general trend shows, Ph_3PO caused much less enhancement in the extraction. Similarly, the extraction of Na^+ is enhanced by a mixture of the reagents, although the overall extraction is less than that of lithium. Topo caused an increase in the extraction of Li^+ (or K^+) by dibenzo-18-crown ether or 18-crown-6 ethers[1316].

Only a few studies have been reported for the alkaline earth metals. Topo (in kerosene) showed poor extraction of Ca^{2+} from nitrate media[1317] {as $[Ca(NO_3)_2topo]$, $K_{ex} = 0.61$} and also extraction from an HCl medium using Htta and topo {as $[Ca(tta)_2(topo)_2]$} was even less ($K_{ex} = 1.1 \times 10^{-2}$)[1318,1319]. The same appears to be true for Ph_3PO[1320]. Significantly, *N*-phenylthioacetohydroxamic acid (HA) (in cyclohexane) showed no extraction of Ca^{2+}, but in the presence of topo the extraction was quantitative[1321]. The stability constant for the extracted species {as $[CaA_2(topo)_2]$} is 5.8×10^{11}, which explains the reason for the quantitative extraction of calcium. The pair 1-phenyl-3-methyl-4-stearoyl pyrazol-5-one and topo (in benzene) extracted Ca^{2+} and Sr^{2+} from a citrate medium (pH 9)[1322]. This method was applied to the extraction and determination of strontium in solar salt samples.

Topo and a series of crown ethers, e.g. 12-crown-4, 15-crown-5 and benzo-15-crown-5, synergistically extracted calcium, rubidium and caesium as their picrates, $[M^{n}(ether)\cdot(topo)](picrate)_n$ ($n = 1,2$)[1323]. The extractability of the rubidium complex was higher than that of the caesium complex.

ii. Elements of Group IIIA. No extraction of aluminium has been reported. However, gallium(III) was extracted from chloride or HCl solution using topo, Ph_3PO and $Bz(p\text{-}MeC_6H_4)_2PO$ in an organic solvent and the extracted species was $[GaCl_3L]$[1324–1327]. Indium(III) was extracted from HCl solutions with topo, Bu_3PO or tbp (in benzene and other solvents) and extraction followed the sequence topo > Bu_3PO > tbp[1328]. It is surprising that Ph_3PO showed no extraction of indium[1328]. Formation of $[InCl_3L_2]$ as the species was observed from $\leqslant 6$ M HCl, whereas $H[InCl_4L_2]$ was formed from concentrated HCl solutions.

From the chloride medium, the extraction of indium(III) with different ligands varied in the order $R_3PO > R_2(R'O)PO > R(R'O)_2PO > (R'O)_3PO$ (R and R' = alkyl)[1329,1330]. The species extracted, $[InCl_3L_2(H_2O)]$, was the same as that observed from HCl solution. The synergistic extraction of indium(III) was noted from ClO_4^- medium with a bipyrazolone, viz. 4,4′-sebacoylbis(2,5-diphenyl-2*H*-pyrazol-3-one) and topo (in toluene)[1331]. However, no synergism was observed when 1-phenyl-3-methyl-4-acylpyrazol-5-one (acyl = benzoyl, thenoyl, lauroyl) and topo in toluene were used[1332]. This observation can be regarded as an exception. Among the pyrazolones alone, benzoylpyrazolone was described as the best extractant. Another synergistic system for the extraction of indium(III) from sulphate medium is the combination of versatic 10 acid and topo (in benzene)[1333].

The only investigation of thallium(III) is its extraction with Bu_3PO from $HCl\text{–}H_2SO_4$ solutions, where the extracted species was $H[TlCl_4L_3(H_2O)]$[1334].

iii. Elements of Groups IVA–VIA. Topo (in CCl_4) extracted tin(II) as $[SnCl_2(topo)_2]$ from HCl solution[1335] and it was observed that on varying the organic solvents, the extraction decreases on decreasing the polarity of the solvent:

Solvent:	$PhNO_2 >$	$PhMe >$	$o\text{-}C_6H_4Me_2 >$	$C_6H_6 >$	CCl_4
D	10.12	5.98	5.65	5.52	2.22

The solvents *m*-cresol and $CHCl_3$ showed very poor extraction ($D = 0.08$ and 0.12 respectively). The extraction of tin(IV) from chloride media with Bu_3PO (in cyclohexane) involved the species $[SnCl_4L_m]$ ($m = 1,2$)[1336]. In contrast, tbp-type ligands showed poor extraction. Bis(2,4,4-trimethylpentyl)-*n*-octylphosphine oxide and tris-(2,4,4-trimethylpentyl)phosphine oxide[1337] were found to be more selective than topo for the separation of Sn^{4+} from Zn^{2+}, Cu^{2+}, Pb^{2+}, Fe^{2+} and Fe^{3+}.

Lead(II) was extracted with topo from NO_3^- media[1338]. Topo also acted as a synergist in the extraction of lead(II) using Hpmtfp in cyclohexane (from NO_3^- medium)[1339]; 1,1,1-trifluoro-5-methyl hexane-2,4-dione in xylene (from $NaClO_4$ medium)[1340] and htta in *n*-hexane (from NaSCN–$NaClO_4$ medium)[1341]. The topo–Hpmtfp combination[1339] gave >98% extraction; Ca, Sr and Ba ions caused no interference in the extraction. In the topo–Htta system[1341], several species, $[Pb(ClO_4)_2L_4]$, $[Pb(ClO_4)(SCN)L_n]$ ($n = 3,4$) and $[Pb(SCN)_2L_3]$ (L = topo), were detected in the organic phase. The extraction of NaSCN alone was poor, but $[Pb(ClO_4)_2]$ has a high extractibility and thus the mixed species $[Pb(ClO_4)(SCN)]$ were readily formed. Significantly, $[Pb(ClO_4)(SCN)L_3]$ and $[Pb(SCN)_2L_3]$ showed similar extraction ($K_{ex} = 6.96$ and 7.48, respectively). This indicates the instability of $[Pb(SCN)_2]$, making it prone to acquire a high solvation number ($n = 3$). It is well known that stable MX_2 species form $[MX_2L_2]$-type compounds[1342].

Antimony(III) was extracted from 1–10 M HCl using Bu_3PO, topo or Ph_3PO (in benzene)[1328]. The species extracted were $[SbCl_3L]$ from ⩾6 M HCl and $H[SbCl_4L_m]$ ($m = 1,2$) from 4–8 M HCl. There are reports of the extraction of bismuth(III) (from NO_3^- medium) with topo (neat)[1338] and selenium(IV) and tellurium(IV) (from Cl^- medium) with Ph_3PO[1320].

iv. Elements of Group IIIB. Topo–Hacac (in benzene or CCl_4) extracted scandium(III) present in trace amounts from aqueous $NaClO_4$ solution; it transferred to the organic layer as $[Sc(acac)(ClO_4)_2(topo)]$[1343]. A series of organophosphorus reagents extracted scandium(III) and yttrium(III) from $NaNO_3$ solution as $[M(NO_3)_3L_2]$ (L = R_3PO, etc.; R = alkyl)[1344]. The replacement of R by R′O successively reduced the extraction, as noted earlier. Topo and Ph_3PO both extracted scandium(III) as $[Sc(tta)_3L_2]$[49].

The ligands Bu_3PO, topo or R_3PO (R is a group containing C_7–C_9 carbon atoms) and Ph_3PO extracted yttrium(III) from HNO_3 solutions as $[Y(NO_3)_3L_m]$ $m = 1$ or 3)[1345–1347]. Synergistic combinations Bu_3PO–Htta and topo–Hpmbp (in benzene) extracted yttrium(III) as $[Y(tta)_3(Bu_3PO)_2]$ (from NO_3^- medium)[1348] or $[Y(pmbp)_3\cdot(topo)]$[1349]. The species extracted was$[Y(pmtfp)_3L_m]$ ($m = 1,2$) when topo–Hpmfp in benzene (from $HClO_4$ medium) was used[1350]. Calorimetric and temperature-dependent studies of extraction methods showed that the synergistic effect was attributed to the replacement of coordinated H_2O by the topo molecule[1351]. A mixture of tbp and triisoalkylphosphine oxide or diisooctyl methylphosphonate and triisoalkylphosphine oxide also extracted yttrium(III) from Cl^-–SCN^- medium[1352]. Bis(2-ethylhexyl)ethylphosphine oxide[1353] or a mixture of R_3PO (R = *n*-Hex) and topo (60:40)[1354] in kerosene is able to separate yttrium(III) quantitatively from aqueous nitrate solutions of rare earths. Here yttrium(III) is left in the aqueous phase.

v. Elements of Group IVB. Bu_3PO (in cyclohexane) is reported to extract titanium(IV) from Cl^- medium (as $[TiCl_4L_m]$; $m = 1,2$)[1336], but extraction from HCl or H_2SO_4 solutions with topo was greatly enhanced by the addition of NH_4SCN and the method could be used to determine titanium spectrophotometrically[1355,1356]. The intense yellow species $[Ti(SCN)_4L]$ (L = topo) absorbed at $\lambda_{max} = 432$ nm. A number of metal ions tested {iron(III), uranium(VI), cerium(III), platinum(IV), etc.} did not interfere. The presence of NO_3^- ions was detrimental to the system as it decomposed the thiocyanate complex. Topo (in kerosene) can extract titanium from ore leach[1357]. The extraction is carried out after treatment of the acid leach of Ti–Fe ore with a chloride of Na, K, Mg or NH_4.

Topo (in cyclohexane) ensured the quantitative separation of zirconium(IV) from uranium(VI) and iron(II) and iron(III)[1358] (from SCN^- medium). Titanium, as expected, interfered. Uranium(VI), which is normally extracted from 7 M HCl, was suppressed in the presence of SCN^- ions. For separating zirconium from hafnium by this method, the addition of H_2SO_4 to the aqueous phase enhanced the separation[1359,1360]. Zirconium forms stronger complexes with $SO_4{}^{2-}$ ions than hafnium does, whereas for hafnium the order is the reverse with SCN^- or OH^- ions. Further, the addition of HCl inhibited the separation, as the chloro complexes of both were extracted equally by the organic layer.

Topo (in cyclohexane) could be used to determine zirconium(IV) in Cl^- medium by an extractive spectrophotometric method involving addition of pyrocatechol (ethanol) direct to the organic extract[1358] ($\lambda_{max} = 655$ nm; sensitivity $= 1 \times 10^{-6}$ g ml^{-1} zirconium). The method is useful even in the presence of large amounts of Al, U, V, Fe, Cr and Th (moderate). However, Ti, Hf and Mo interferred. $PO_4{}^{3-}$ and $SO_4{}^{2-}$ in low concentrations do not interfere; in the presence of $NO_3{}^-$, U, Th and Hf interfere.

Using topo in cyclohexane, the D value for zirconium was 1000 (from 7 M HCl), 478 (from 7 M HNO_3) and 10 (from 1 M HCl or HNO_3 solutions)[1361–1362]. An enhancement in extraction occurred on addition of Cl^- or $NO_3{}^-$ salts of uni-, bi- or tri-valent metals. The extracted species were $[ZrCl_4L_2]$ and $[Zr(NO_3)_4L_2]$ with $>99\%$ extraction. It was possible to separate zirconium from hafnium and niobium[1363]. The extraction from $HClO_4$ solutions was less and was also low from H_2SO_4 or HF solutions. Whereas interference from tartrate was small, EDTA in sufficient amount prevented extraction[1362,1364]. The behaviour of Bu_3PO was similar[1365]. At >8 M HNO_3 concentration, the species $[Zr(NO_3)_4(L)_2]xHNO_3 \cdot yH_2O$ was formed. The topo–Htta pair probably formed [Zr(tta)$_4$(topo)] species in the extraction of zirconium(IV) from HNO_3 medium[1361]. On variation of the substituents in $R_2R'PO$ in the system $R_2R'PO$–HNO_3($R,R' =$ Me to C_8H_{17} and Ph)[1366], the distribution coefficient increases with decreasing B (where $B = \Sigma H/\Sigma C$, ΣH and ΣC being the sums of the number of H and C atoms, respectively, in the extractant) until R and R′ are C_8H_{17}. Branching of the chain decreases D, although the reverse effect would be expected on the basis of electrophilicity and solubility considerations.

In the extraction of hafnium(IV) from a mixture of acids ($\geqslant 3$ M $HClO_4 + HNO_3$ or 5 M $HClO_4 + HCl$) using Htta, Hpmbp or *N*-benzoyl-*N*-phenylhydroxylamine in benzene, $CHCl_3$ or *n*-octane, Ph_3PO, topo and tbp acted as synergists[1367,1368]. The order of synergistic effect was topo $>$ Ph_3PO $>$ tbp. Bu_3PO, however caused no synergism. Hafnium forms mixed complexes and $HClO_4$ has a considerable salting-out effect. No synergism occurred when a mixture of $HClO_4$ and H_2SO_4 was used.

vi. Elements of Group VB. The pairs R_3PO–Htta (in cyclohexane) and R_3PO–dithizone (H_2dz) (in benzene) (R = *n*-butyl and *n*-octyl) extracted vanadium(IV,V) from aqueous solutions (pH ≈ 4.1)[1369–1372]. Various species were identified [VO_2(tta)L], [VO(tta)$_2$L], [VO_2(Hdz)(tbpo)] (A) and [VOOH(Hdz)(topo)] (B). A was stable for 1 h whereas the colour of B faded during the standing time, probably owing to the dimerization

$$2\mathrm{VOOH(Hdz)(topo)} \rightleftharpoons \mathrm{(Hdz)VO(topo)(\mu\text{-}OH)_2V(O)(Hdz)(topo)}$$

H_2dz alone showed poor extraction. In the R_3PO–H_2dz system, topo gave a higher extraction than Bu^n_3PO ($K_{ex} = 10^{2.5}$ for topo, 3×10^2 for Bu^n_3PO). Topo–Hpmtfp (in cyclohexane) showed incomplete extraction of $VO_2{}^+$ from aqueous solution (pH 1.5–2.8)[1339]. A mixture of trialkylphosphine oxides (R_3PO) in kerosene extracted vanadium(IV) or vanadium(V) from low pH (1.0–2.5) solutions[1373]. On increasing the concentration of vanadium in the solution, the extraction maximum shifted to the low pH range and metavanadic acid, $[HVO_3(R_3PO)_2]$, transferred to the organic layer.

Topo (in cyclohexane) separated tantalum(V) from aqueous HCl solution and this separation was more complete than that of zirconium from hafnium[1363]. Similarly, niobium(V) was separated from $Ti(SO_4)_2$ solution[1374]. For high niobium extraction, the addition of HCl or HF was necessary. Topo and $R_2R'PO$(R,R' = Me to C_8H_{17} and Ph) have been used to extract Nb and Ta from different media: HNO_3[1366], $HF-H_2SO_4$[1375] and HCl, HF, $HClO_4$[1364].

vii. Elements of Group VIB. The extraction of these metals has been possible only when present in their hexavalent state, although a recent report reveals that the extraction of chromium(III) can be achieved by a cooperative action of light (photoreduction) and topo on chromium(VI) species[1376]. The back-extraction of chromium(III) was also promoted by photoirradiation. Except for this, all other studies require oxidation of the metal to its hexavalent state prior to extraction. For example, while extracting chromium(III) from concentrated NaCl or KCl solutions using topo (in benzene)[1377], it was oxidized to the chromium(VI) state with silver oxide solution in H_2SO_4 (or bromine water when HCl is present). By this procedure, the extraction is feasible at the microgram level (diphenylcarbazide in ethanol was added to the organic layer for the determination of chromium).

Chromium(VI) has been extracted from different solutions (1M MX; M = H, Na; X = Cl, ClO_4, NO_3)[1378] by forming hydrogen-bonded species $H_2[CrO_4L_2]$, $H_2[CrO_4(HX)L_m]$ and $H_2[CrO_4(HX)_2L_m]$ ($n = 2$ for ClO_4^-, NO_3^- and 3 for Cl^- ions; L = topo). The greatest extraction was obtained from the ClO_4^- medium: $ClO_4^- > Cl^- \approx NO_3^- > SO_4^{2-}$. It was demonstrated that Ph_3PO could separate chromium(VI) from solutions of iron(III), yttrium(III), gold(III) and molybdenum(VI) in mineral acids[1345].

A series of organophosphorus reagents, R_3PO (R = octyl, isopentyl and Ph), extracted molybdenum(VI) from mineral acid solutions[1345,1379,1380]. The species, for instance, from aqueous HCl was $[MoO_2Cl_2L_2]$. High separation factors from Cr, Au and Fe were observed with Ph_3PO[1345]. Topo showed significant synergism when molybdenum(VI) was extracted from various mineral acids using H_2dehp[1381]. The greatest extraction ($D > 1000$) was observed from 3.5 M HCl solutions (HCl > H_2SO_4 > HNO_3). Bu_3PO–H_2dehp selectively extracted molybdenum when present as an impurity in tungsten produced from impure scheelite and related ores[1382].

Using topo (in kerosene) tungsten(VI) was extracted from mineral acids in the sequence HCl > H_2SO_4 > NO_3 ($D > 250$, ≈ 50, low, respectively[1383]. Topo–Adogen-381 and tricaprylmethylammonium chloride in xylene quantitatively separated $[WO_4]^{2-}$ from $[ReO_4]^-$ when present in mineral acids[1384].

viii. Elements of Group VIIB. Topo–Hpmtfp (in cyclohexane) extracted manganese(II) quantitatively (>98%) from aqueous solutions (pH 1.5–2.8)[1339]. The extraction of manganese(II) with a series of reagents, Topo–β-diketones (Hacac, Htfa, Hhfa, Hba and Hbfa) in CCl_4 from ClO_4^- solutions was poor for various practical purposes except with Hba[1385]. Topo–Htta extracted manganese(II) as $[Mn(tta)_2topo]$[1386]. A less common non-aqueous system involves the extraction of manganese(II) from ethylene glycol with topo (in cyclohexane or toluene) in the presence of 10^{-3}–10^{-2} M HCl[1387]. The addition of LiCl had a salting-out effect.

Technetium(VII) was extracted from $(NH_4)[TcO_4]$–HCl solution with a series of phosphine oxides (in benzene or cyclohexane) in the sequence R_3PO > tbp > Ph_3PO (R = *n*-butyl, *n*-octyl, *n*-hexyl, *n*-decyl, 2-ethylhexyl)[1326,1388,1389]. The highest percentage extraction was 85% with R_3PO. The hydrogen-bonded (L)$HTcO_4$ appears to be the extracted species and Ph_3PO shows the weakest hydrogen bonding.

Rhenium(IV) was quantitatively extracted from aqueous 3–4 M HCl (HBr) using Bu_3PO (in CCl_4) and the formation of $(Bu_3PO)_3(H_3O)_2[ReX_6]$ was established[1390]. A similar species, $(R_3PO)_2(H_3O)[ReO_4]$ was suggested when rhenium(VII) was extracted from aqueous HCl using topo (in C_6H_6, CCl_4, etc.)[1391–1993]. As expected, the extraction with phosphine sulphides and selenides was poor ($R_3PO > R_3PS > R_3PSe$; R = *n*-octyl).

A method for the quantitative separation of $[ReO_4]^-$ from $[WO_4]^{2-}$ was mentioned in the previous section[1384]. Pure $(NH_4)_2[ReO_4]$ was obtained from H_2SO_4 solution containing molybdate ions using topo and by varying the basicity of the amines[1394]. $[ReO_4]^{2-}$ and $[MoO_4]^{2-}$ were stripped stepwise by adjustment of the pH of NH_4^+-containing solutions.

ix. Elements of Group VIII. *Iron sub-group.* Topo extracted iron(III) from 4 M HCl (or 1 M HCl + 3 M NaCl)[1395] and SCN^--HNO_3[294] quantitatively. The nature of the species was probably $[FeX_3L_n]$ ($n = 1, 3$; X = Cl, NCS). Other investigations have involved the extraction of trace Fe[1396], the removal of iron from organic leaches[1399] and the separation of iron from aluminium and zinc[1398] (Table 19). Synergistic combinations of topo–Hdbm (in benzene)[1405] or topo–Hpmtfp (in cyclohexane)[1339] quantitatively extracted iron(II) from aqueous solutions of pH 6–7 and 1.5–2.8, respectively. The topo–Hdbm system was used for the determination of iron(II) in spring water (sensitivity 0.0047 μg cm^{-3} of iron). The complex extracted, $[Fe(dbm)_2(topo)_2]$, absorbed at λ_{max} 408 nm. Zinc(II), lead(II), chromium(III), tin(II), PO_4^{3-}, CN^- and citrate all interferred; $S_2O_3^{2-}$, F^- and tartrate were used to mask the interference of copper(II), aluminium(III) and manganese(II), respectively.

Similarly, Hacac–topo (in cyclohexane)(I)[1406], topo–Htta (in benzene)(II)[1407–1409] topo–H_2dehp (in kerosene)(III)[1410] and Ph_3PO–Hacac (in $CHCl_3$)(IV)[1411] extracted iron(III) from perchlorate, chloride, sulphate and thiocyanate solutions, respectively. In system I, the presence of ClO_4^- was necessary to produce synergism and the presence of NO_3^- or SO_4^{2-} showed poor extraction. The extracted species was $[Fe(acac)_2(topo)_2]$-(ClO_4). In system II, maximum extraction occurred at pH 2.63 and at higher pH the extraction decreased. Also, it was observed that with Htta in benzene alone, the extraction

TABLE 19. Extraction of iron(III) using tertiary phosphine oxides

	System	Comments and extracted species	Ref.
1	topo–NaSCN	Extraction of trace Fe, but extraction non-quantitative	1396
2	topo–C_6H_6–(HCl + H_2SO_4)	Simultaneous removal of Fe (2.43%), Cu(0.4%), Cd(7.65%) and Zn(74.2%) from a leached powdered residue from zinc smelting	1399, 1400
3	topo–CCl_4 (or C_6H_{12})–$NaClO_4$ (or $NaClO_4$ + NaX, X = Cl, Br)	Extraction is increased with added X^- ions and was pH dependent $[Fe(topo)_4(ClO_4)_3]$	1402, 1403
4	topo–amines–(octan-2-ol)–SO_4^{2-} (pH 1–2)	Separation was possible even in the presence of Al and Zn	1397
5	topo (or $R_2R'PO$, R = *n*-hexyl, R′ = n-octyl)–Acid	Iron ($\geqslant 1$ g l^{-1}) was removed from organic leaches obtained from phosphate minerals containing uranium(VI)	1396
6	Ph_3PO–C_6H_6–mineral acids	Iron separation from chromium(VI), molybdenum(VI), yttrium(III) and gold(III)	1320, 1345
		H-bonded species, $(Ph_3PO{\cdot}H)[FeCl_4]$ suggested	1404
7	R_3PO–xylene–NaCl (R = Ph, alkyl)	Phenyl substituent on P showed lower extraction than alkyl substituent. Species $FeCl_3(R_3PO)_2{\cdot}H_2O$ was formed	1329, 1330

rate was very slow[1408,1409] and the addition of topo enhanced both the rate and the extent of extraction. In system III, the extraction was quantitative (>98%). In system IV[1411], the extraction was quantitative and selective in the presence of the ions tested, chromium(III), manganese(II), cobalt(II), nickel(II), zinc(II), CH_3COO^-, Cl^-, $SO_4{}^{2-}$ and $NO_3{}^-$; however, copper(II) interferred. Multiple extractions were needed for chromium, nickel and zinc when Cl^- was the anion, whereas in all other cases a single extraction was sufficient to remove iron quantitatively from the aqueous SCN^- medium (pH 2.7–2.8). The synergistic species identified was $[Fe(NCS)(acac)_2(Ph_3PO)]$. Extraction with Ph_3PO alone was poor. The method was suitable for the extractive determination of iron in steel samples[1411b].

Ruthenium(III) was extracted with topo or Oct^i_3PO in *n*-hexane from an acidic solution of the nitroso complex, $Na_2[Ru(NO)(NO_2)_4(OH)]$[1412], but the extraction was lower than that of the chlororuthenium complexes[1413]. In extracting ruthenium(III) from 2 M HCl with topo or Bu_3PO in $CHCl_3$, the addition of *n*-octanol or cyclohexanol lowered the extraction on account of their hydrogen-bonded interaction with R_3PO, thus lowering the effective concentration of the reagents[1414].

Osmium(III) was extracted from HCl or HBr media using topo, tbp, etc., as their halide complexes[1415], and higher extraction was achieved from HBr over HCl and with topo in place of other reagents.

Cobalt sub-group. The alkyl ligand Bu^n_3PO extracted cobalt(II) from a mixture of aqueous HCl, LiCl and $CaCl_2$ solutions and the extraction follows a hydration–solvation mechanism, forming $[(M^{x+}\cdot mH_2O)_{2/x}\cdot n'Bu_3PO][CoCl_4]$ (where $x = 1$ for HCl and LiCl and 2 for $CaCl_2$, and m and n' are hydration and solvation numbers, respectively[1416]. Similarly, topo extracted cobalt(II) from LiCl, KSCN, HCl and HNCS solutions. It showed higher extraction than Alamine 336-S from acid-deficient systems, but lower extraction from acid-rich solutions[1326,1417]. Extraction of cobalt(II) with tris(2,6-dimethylphenyl)phosphine oxide perchlorate ($R_3POH^+ClO_4{}^-$) in $CHCl_3$ was poor[1418].

Topo–Hpmbp (in benzene)[1419] and topo–Hpmtfp (in hexane)[1339] extracted cobalt(II) quantitatively (>98%) from acidic media (pH 4.9–6.0 and 1.5–2.8, respectively). A series of other β-diketone–R_3PO systems which extract cobalt(II) under different conditions are topo–Htta (in different organic solvents; pH 5.1)[1420] and R_3PO–Htta (or Hhfa, Hpvta, Hbfa, Hacac, Hba and Htfa) (R = *n*-butyl, *n*-octyl or phenyl) (in benzene[1421,1422], CCl_4[1423], cyclohexane[1424a] or $ClO_4{}^-$ medium). The extracted species was generally $[CoA_2L]$[1420–1423] (A = anion of chelating ligand; L = organophosphorus reagent), although the formation of $[CoA_2L_2]$ (HA = Htfa, Hbfa, Hhfa) in CCl_4[1424] has also been reported. Some other conclusions drawn are: (a) the stabilities of the cobalt(II) adducts decrease in the sequence topo > Bu_3PO > tbp > *n*-hexanol, which corresponds to the order of basicity of the Lewis bases[1421]; (b) the sequence of the extraction constants and adduct formation constants is Htta > Hhfa > Hpvta[1422]; and (c) Topo–Hbfa (in cyclohexane)[1424a] could be used for the extractive–spectrophotometric microdetermination of cobalt(II) ($\leqslant$ 20 ppm) ($\lambda_{max} = 380$ nm for $[Co(bfa)_2topo]$). Copper(II), nickel(II), iron(III), manganese(II), EDTA, citric acid and larger amounts of lead(II), strontium(II), chromium(III) and bismuth(III) interfere in the determination, however.

Recently, Hpmbp and topo (or $dpmO_2$, $dpeO_2$) extracted synergistically cobalt(II), nickel(II), zinc(II) and cadmium(II), forming $[M(pmbp)_2(topo)_n]$ ($n = 2$ for Co, Ni and 1 for Zn) and $[M(pmbp)_2L]$ (L = $dpmO_2$ or $dpeO_2$)[1424b]. Other synergistic systems studied are R_3PO–quinolin-8-ol[1425] (R = *n*-butyl or octyl), topo-4-methyl-*N*-8-quinolinylbenzenesulphonamide[1426], topo–resacetophenone oxime[1427] and R_3PO–phosphinic acid (R = alkyl)[1428]. The species identified is $[CoA_2L]$; the order of extraction in the quinolin-8-ol system is topo > Bu_3PO > tbp[1425]. In the phosphinic acid system, the addition of R_3PO enhanced the separation of cobalt and nickel[1428].

A mixture of quinolin-8-ol (HQ) and triphenylphosphine oxide (Ph_3PO) showed synergism of 10–12% in the extraction of cobalt(II) compared with the use of HQ alone[1429]. At the synergic point, cobalt(II) was separated from its binary mixtures with chromium(III), silver(I), mercury(II), magnesium(II) or aluminium(III) with a recovery of over 97%. Mercury(II) and silver(I) were transferred to the organic layer together with cobalt(II) and zinc(II) and this was sorted out by stripping the organic layer with concentrated HCl, which released cobalt(II) to the aqueous layer. Further stripping of the organic layer with concentrated. HNO_3 facilitated the release of mercury(II) or silver(I) to the aqueous layer. The extraction was at a maximum in the pH range 4.0–10.0 and poor at pH 2.0. In cobalt(II) extraction with *S-tert*-dodecylthioglycolic acid (HA), topo or tbp inhibited the extraction; this represents the only example where no synergism was observed[1430]. Hydrogen-bonded interaction of HA with R_3PO, which would lower the concentration of HA, might be responsible for the observed difference.

Investigations with rhodium and iridium are few: topo–trichloroacetic acid (or pentadecafluorooctanoic acid) in benzene quantitatively and rapidly extracted rhodium(III) as $[Rh(A)_3(topo)_4]$ (A = anion of the acid)[1431–1432]. H_2dehp showed a similar extraction, but topo caused no enhancement[1431]. R_3PO–C_6H_6 (R = alkyl) was employed for the extraction of rhodium and iridium from 4 M HCl solution prior to the determination of the micro amounts of rhodium present in large amounts of iridium in an anodic stripping voltammetric method[1433].

Nickel sub-group. Topo–hexane extracted nickel(II) from aqueous SCN^-–ClO_4^- medium[1434], although the extraction was less than that of cobalt(II) from solutions with high concentrations of SCN^- ions. From ClO_4^- alone, the extraction of both metals was similar. The formation of various species in the organic phase, namely $[Ni(ClO_4)_2L_4]$, $(Ni(NCS)(ClO_4)L_4]$ and $[Ni(NCS)_2L_4]$ for nickel(II) and $[Co(ClO_4)_2L_3]$, $[Co(NCS)(ClO_4)L_3]$, $[Co(NCS)_2L_2]$ and $Na[Co(NCS)_3(topo)_3]$ for cobalt(II), was established[1435]. Other extraction studies have been made with topo[1338] and Ph_3PO[1320] from aqueous chloride media.

The quantitative extraction of nickel(II) was achieved with topo–Hpmtfp in cyclohexane from aqueous solution (pH 1.5–2.8)[1339]. Other synergistic systems used for the extraction of nickel(II) include topo–[4-(2-pyridylazo)resorcinol][1436], topo–(Kelex 100 and 8-sulphonamidoquinolines) in chlorobenzene[1437] and topo–β-diketones (Htta, Hacac, Hba, Htfa, Hbfa or Hhfa) in CCl_4 from perchlorate medium[1435,1438–1443]. Table 20 gives a summary of the extraction data for nickel(II), cobalt(II) and copper(II). The extraction of cobalt(II) and nickel(II) with Hacac or Hacac–topo was poor; likewise, extraction with Htfa and Hhfa was poor, but the addition of topo enhanced the extraction to a measurable extent. From Table 20, a number of conclusions may be drawn: (a) the stability constants of nickel(II) chelates in the aqueous phase are generally higher than those of cobalt(II) chelates but lower than those of copper(II) chelates; (b) the partition constants of nickel(II) chelates are one tenth to one thirtieth of those of cobalt(II) chelates and much lower than those of copper(II) chelates; and (c) the adduct formation constants are similar. The higher hydration of nickel(II) and cobalt(II) is responsible for their low partition coefficients.

Topo–cyclohexane (in $CHCl_3$, mibk or 2,2′-dichlorodiethyl ether) mixtures are useful in the mutual separation of palladium, platinum and gold from aqueous HX (X = Cl, Br)[1444]. Other reagents used for extraction studies are topo–R_3PO (in toluene or decanol)[1445,1446] for palladium and platinum from HCl (I), topo–molten diphenyl for palladium and platinum from HCl (or HNO_3)[1447] (II), topo–R_3PO for palladium from HNO_3 (III)[1448] and topo–toluene for platinum from HCl(IV)[1449a]. For system I, maximum extraction (as $[MCl_2L_2]$) was observed at 5 M HCl, and an increase in the length of the hydrocarbon chain of the alkyl substituent increased the extraction[1445]. Significantly, topo showed lower extraction than the corresponding phosphine sulphides. When > 20% of topo with decanol was used, the extraction was same as that when topo

TABLE 20. Summary of data for extraction of cobalt(II), nickel(II) and β-diketone–topo system[a]

Reagent	M	Log β_1 (aq.)	Log β_2 (aq.)	Log D	Log β_1 (org.)	Log β_2 (org.)
Hacac	Co	—	—	−0.94	1.46	NC[b]
	Ni	—	—	−2.25	2	NC
	Cu	7.81	14.22	0.83	1.28	NC
Hba	Co	4.55	8.14	1.37	3.44	NC
	Ni	4.41	9.86	−0.14	3.50	NC
Htfa	Co	3.50	5.60	−2.14	5.36	7.76
	Ni	3.74	6.68	−3.25	5	8
	Cu	4.80	9.14	1.40	2.96	NC
Hbfa	Co	3.40	5.24	2.06	6.15	9.34
	Ni	3.60	6.68	0.76	5.19	8.98
Hhfa	Co	1.56	2.32	−1.02	5.19	10.58
	Ni	1.90	3.10	−2.1	5.80	10.50
	Cu	2.25	3.20	1.39	5.63	9.36

[a] Data from refs. 1438–1441.
[b] No complex.

alone was used[1446]. Hence for the lower topo concentration, decanol had a synergistic effect. In system II, the D value was nearly same for palladium and platinum from HCl (Pd 126, Pt 123), but from HNO_3, D was higher for platinum(II) (107) than palladium(II) (6.7)[1447]. There was no extraction from H_2SO_4 medium. System III showed a higher extraction for palladium with phosphine oxides over phosphonates or phosphates [1448]. Various species identified were $[Pd(NO_3)_2L_2]\cdot nH_2O$ ($n = 0, 2, 4$). System IV showed a high extraction of platinum(IV), probably because the extraction steps involve a solvating mechanism ($K_{ex} = 2.6 \times 10^3\,dm^3\,mol^{-1}$); in contrast, rhodium(III) showed poor extraction.

x. Elements of Group IB. Extraction studies for copper(II) with phosphine oxides alone are scarce. Thus, although topo showed extraction of copper(II) from Cl^- medium[1338], there was no extraction from HCl, H_2SO_4 or HNO_3[1447]. As a result, phosphine oxides are mainly used as synergists in the extraction of copper(II) with different reagents. Various synergistic systems used for the extraction of copper(II) include topo–β-diketones (Htta, Htfa, Hhfa, Hacac or Htfma) in benzene[1449b,1450–1453], n-hexane[449] or xylene(I)[1340], topo–Hpmap in benzene and other solvents (II)[1454] and topo (or Ph_3PO)–benzeneazo-2-naphthol(HA) from NaOAc–HOAc (pH, 5.5)[1455] (III) (no synergism). From system I, the order of extraction efficiency of the β-diketones was inferred from D values to be Htta > Hhfa > Htfa > Hacac[449,1449b]. The lower D value for Hhfa than for Htta is attributed to the solubility of $[Cu(HFA)_2\cdot 2H_2O$ in water[1450]. Topo–Hacac showed no synergism, probably owing to the low stability of the adduct[1451]. Interestingly, the formation constants for

$$CuA_2 + TOPO \overset{K}{\rightleftharpoons} CuA_2(TOPO)$$

in benzene[1452] supported the above sequence [HA, K ($l\,mol^{-1}$): Htta, 1700; Htfa, 940; Hacac, 45). For the Htta–topo system[1450], it was observed that copper(II) showed a higher value for the equilibrium constant for the reaction

$$M^{2+} + 2HTTA + TOPO \overset{K}{\rightleftharpoons} M(TTA)_2(TOPO)^+ + 2H^+$$

than zinc(II) (K: Cu, 1800; Zn, 0.1).

Another observation for system I(topo–Htta–C_6H_6)[1453] is that higher topo concentrations destroyed the synergism owing to (Htta.topo) adduct formation and to increased TOPO $\cdots$ H_2O interaction, which increases the amount of H_2O in the organic layer, which in turn would compete with TOPO for adduct formation with $[Cu(tta)_2]$. For system II, it was observed that the extraction constant increases monotonously with a decrease in temperature (37–7 °C)[1454]. For system III, the decrease in the formation constants of $[CuA_2]$ with increasing solubility of H_2O in the solvent indicates the lack of any H_2O in the coordination sphere of the extracted complex[1455]. This explains the lack of synergism when topo or Ph_3PO was added to benzeneazo-2-naphthol solution for extraction. The species extracted were generally of the type $[CuA_2L]$ (A = anion of the chelating ligand; L = organophosphorus reagent).

Recently, silver(I) was extracted using Ph_3PO in $CHCl_3$ from the aqueous phase (pH 6, HoAc–NaOH buffer)[1456]. A number of ions tested (Mn, Co, Ni, Cu, Zn, Cd, Sn, Pb, Mg, Al, Cr, Fe, NO_3^-, CH_3COO^-, SO_4^{2-}) did not interfere, but mercury(II) did interfere. The extracted species was established as $[Ag(Ph_3PO)_n(NO_3)]$ ($n = 1$, 3 depending on Ph_3PO concentration). Silver(I) was synergistically extracted with dibenzo-18-crown-6–topo[1457] and the species was $[Ag(E)(topo)]^+$ $(picrate)^-$ (E = crown ether).

Unlike copper(II), there have been several investigations of gold(III) extraction with tertiary phosphine oxides, namely topo in C_6H_6 (or $CHCl_3$, CCl_4, PhMe, C_6H_{12} or isooctane) from HCl solutions[1391,1392,1445], topo in CCl_4 from hydrohalic acids (gold present in traces)[1460], topo in molten diphenyl[1447] from HCl, H_2SO_4 or HNO_3 and Ph_3PO in C_6H_6[1345,1458,1459]. From these studies, it was concluded that (a) gold was generally extracted as a hydrogen-bonded ion-pair species, $(R_3PO)_nHAuCl_4$ ($n = 1$, 2)[1391,1392,1445], or $H_3O^+{\cdot}3R_3PO{\cdot}yH_2O \cdots [AuX_4]^-$ ($0 \leqslant y \leqslant 3$) (R = Ph, *n*-octyl; X = Cl, Br)[1459,1460]; (b) the separation factors for Au, Mo, Cr and Fe are fairly good for mutual separations[1345]; (c) the maximum *D* was at 4 M acid concentration and its value increased from 3.53 to 10.32 on changing trihexylphosphine oxide to topo; *D* was also at a maximum when the number of carbons atoms in the extractant was between 23 and 24; the introduction of an electron-withdrawing group lowered the value of *D*[1445]; in contrast, the tertiary phosphine sulphides were found to be better extractants than the phosphine oxides; and (d) the extraction of gold(III) from HCl or H_2SO_4 with topo in the diphenyl system[1447] was higher than that from HNO_3 ($D > 10^3$ versus 86.4). The tendency of HNO_3 to be extracted with R_3PO appears to be responsible for this apparent difference. Significantly, the topo–diphenyl pair showed no extraction of silver(I)[1447].

Bis(2-ethylhexyl)dithiophosphate and topo in toluene extracted silver and gold simultaneously from copper- or bismuth-containing materials prior to their determination by atomic absorption spectrometry[1461].

xi. Elements of Group IIB. Topo in C_6H_{12} extracted zinc(II) from NaX–$NaClO_4$ (X = Cl, Br, I) solutions[1342]. A variety of extracted species such as $[Zn(ClO_4)_2(topo)_4]$, ZnX $(ClO_4)(topo)_3]$ and $[ZnX_2\ (topo)_2]$ were identified, and the extraction decreased in the sequence $I^- > Br^- > Cl^-$ ($K_{ex} = 6.12$, 4.51 and 3.64, respectively). The higher covalent bonding character of iodide and its hydrophobic nature increased the extraction of ZnI_2 complexes over other zinc(II) halide complexes. From SCN^- media, zinc(II) showed enhanced extraction as $[Zn(NCS)_2\ (topo)_2]$[1462]. The difference is attributed to the greater stability of $Zn(NCS)_2$ species over ZnX_2 in the aqueous phase.

The extraction of zinc(II) from molten KSCN at 195 °C with R_3PO in phenanthroline decreased in the order topo $> Ph_3PO > (Me_2N)_3PO >$ bipy ($K_{ex} = 3.80$, 3.20, 2.0 and 1.60, respectively), the extracted species being $[ZnL_n(NCS)_2]$$\{n = 2$ for topo, $(Me_2N)_3PO$, 3 for Ph_3PO and 1 for bipy$\}$[1463].

Using tertiary phosphine oxides, other extraction systems for zinc(II) are topo in PhMe from HCl or Cl^- medium[1326,1338,1464,1465], topo in C_6H_6 from 3 M HCl + 1 M

H_2SO_4[1466] or 4 M H_2SO_4 (I)[1467], R_3PO–xylene from Cl^- media (II)[1329,1330] and topo in toluene or decalin from glycol or MeOH–H_2O phases containing Cl^- and ClO_4^- ions (III)[1468,1469]. System I showed a higher recovery of zinc(II) over cadmium(II) (79.5% versus 2.6%). Here water was used as the stripping agent instead of the acids or bases commonly employed. Similarly, system II showed excellent selectivity for zinc(II) over iron(II), copper(II) and lead(II) and moderately good selectivity over iron(III); as usual the extraction decreased in the sequence $R_3PO > R_2(R'O)PO > R(R'O)_2PO > (R'O)_3PO$. System III showed an extraction order for the glycols of propylene glycol > ethylene glycol > ethylene glycol–water.

Topo–Htta (or Hhfa) extracted zinc(II) from $HClO_4$ solution as $[ZnA_2(topo)_n]$ (^{65}Zn tracer study) ($n = 1$ for Htta and 1, 2 for Hhfa)[449,1450]. The extraction constants (K_{ex}) followed the sequence $[Zn(Hfa)_2(topo)] > [Zn(tta)_2(topo)] > [Zn(tta)_2(topo)] > [Zn(tta)_2]$ ($K_{ex} = 1000, 12, 0.1$ and 8.5×10^{-10}, respectively). The excess of topo destroyed the synergism in the case of Hhfa system, which was avoided when the aqueous phase was buffered with acetate (pH 5). The fluorinated β-diketones showed a higher extraction of zinc(II) owing to the increased stability of topo adducts with zinc(II) chelates[1470]. As expected, a CF_3 group in β-diketones increases the Lewis acidity of the zinc(II) chelates.

Distribution studies on $[Zn(tta)_2(topo)]$[1471] revealed that the order of extraction in a series of organic solvents(S) decreased in the order hexane > cyclohexane > CCl_4 > C_6H_6 > $CHCl_3$ ($D = 0.175, 0.135, 0.051, 0.028$ and 0.0003, respectively). The addition of water to the Zn^{II}–Htta–topo system lowers the extraction as topo is replaced from $[Zn(tta)_2(topo)]$ by H_2O forming $[Zn(tta)_2(2H_2O)]$. Addition of topo increases the extraction again. Other β-diketone–R_3PO systems for zinc(II) extraction are topo (or Ph_3PO)–Hbfa (or Hpvta) in C_6H_6 from ClO_4 medium[1472,1473] (I), topo (or Bu_3PO)–Hbfa (or thiobenzoyltrifluoroacetone) in C_6H_6 from ClO_4^- medium(II)[1421,1474] and topo–Hbfa–Hba in CCl_4(III)[1475]. System I revealed that topo gave better extractions than Ph_3PO or even $dpmO_2$ or $dpeO_2$[1473]. In system II, Htbfa gave a higher extraction than Hbfa in the absence of topo, whereas in the presence of topo it gave a lower extraction ($\log K_{ex} = 5.04$ for Htbfa–topo and 5.72 for Hbfa–topo). Additionally, Htbfa alone showed gave a extraction than topo or Bu_3PO. Species of the type $[ZnA_2L]$ were formed in systems I and II, whereas in the ternary system III species of the type $[Zn(bfa)(ba)(topo)]$, $[Zn(bfa)_2(topo)]$ and $[Zn(ba)_2(topo)]$ were detected[1475].

Pyrazolone–R_3PO and other combinations that have been used for the extraction of zinc(II) are topo–Hpmsp in C_6H_6 (I)[1476], topo–Hpmbp in different organic solvents[1477], topo–Hpmtp in C_6H_{12} (II)[1339], topo–H_2dehp(III)[1478,1479], topo–NaD (NaD = sodium dinonylnaphthalenesulphonate, a liquid cation exchanger) in C_6H_6 from $HClO_4$ (IV)[1480] and topo–(4-methyl-*N*-8-quinolinylbenzenesulphonamide) in toluene(V)[1481]. System I was most effective for the separation[1476] of zinc(II) from cadmium(II) at pH 4.5. An amount as low as 20 μg of zinc in 20 mg of cadmium (1:1000 ratio) could be separated. In system II, quantitative extraction (> 98%)[1339] of zinc(II) was achieved from aqueous solutions of pH 1.5–2.8. System III showed a lower extraction than those shown by topo–β-diketones[1478,1479], probably owing to the steric hindrance in the former. Addition of more topo reduced the extraction (antisynergism) owing to H_2dehp–topo hydrogen-bonded adduct formation, which lowered the effective concentration of H_2dehp. Similarly, system IV showed[1480] lower synergism than topo–Htta. However, the extraction was quantitative ($K_{ex} = 6.1 \times 10^4$). Significantly, NaD alone showed a greater extraction than Htta by a factor of 10^3. The use of HD–topo in place of NaD–topo lowered the extraction due to HD·topo adduct formation. The extracted species was suggested to be $[ZnD_2(topo)_n]$ ($n = 1, 2$). System V also extracted zinc(II) quantitatively from 0.1 M HNO_3 solution. Quinoline-8-ol and Ph_3PO synergistically extracted zinc(II) in a manner similar to that of cobalt(II) as described earlier[1429].

TOPO has been used to extract cadmium(II) from NO_3^- or Na(X, ClO_4) (X = Cl, Br,

I) media[1326,1338,1482], but efficient extractions occur when topo is combined with other chelating agents. For instance, extraction of cadmium(II) with topo–Hbfa in C_6H_6[1483,1484] was efficient, whereas topo or Hbfa alone showed negligible extraction. The extracted species was established to be $[Cd(bfa)_2(topo)_2]$. Other effective combinations topo–$F_3CC(O)CH_2C(O)C_2H_5$ in xylene from perchlorate medium[1340] and topo–Hpmtp in C_6H_{12} showed quantitative extraction[1339]. Extraction with topo–H_2dehp in tetradecane has also been reported[1485].

Topo in molten diphenyl[1447] showed a higher extraction of mercury(II) from HCl ($D = 61.3$) and lower from HNO_3 or H_2SO_4 ($D = 0.1$–0.6), suggesting a higher extractability of $[HgCl_2(TOPO)_n]$ ($n = 1, 2$) type of species over corresponding nitrate or sulphate species. In comparison, the extractions of gold, palladium and platinum were high. Triisopentylphosphine oxide in various solvents extracted mercury(II) as $[HgCl_2L]$ and $[HgCl_2L_2]$[1486].

xii. f-Block elements. This group of elements has attracted considerable interest in extraction science on account of both the separation difficulties posed by these elements and their importance in the generation of nuclear energy and in radiochemistry.

Lanthanides. For convenience, the extraction studies are divided into different sections based on the nature of the reagent used.

Extraction of lanthanides with R_3PO alone. Table 21 contains various metals extracted with tertiary phosphine oxides (R_3PO). It can be seen that the most commonly extracted species is $[MX_3L_3]$ (X = anion) and the coordination number varies depending on the coordinating ability of the anion; NO_3^- generally acts as a chelate and thus 8- or 9-coordinate species are formed. Some important comments on the systems may be made as follows. In system I, the addition of $Na_2H_2edta{\cdot}2H_2O$ promoted extraction, but the mechanism involved is not known[1487]. In system II, the extraction increased in the order topo > Bu^n_3PO ≫ tbp[537]. For a given reagent, $\log K_{ex}$ was found generally to increase with decrease in the metal ion radius (e.g. for topo, the $\log K_{ex}$ values are 8.35 for La and 9.39 for Cu).

In system III, topo showed a lower extraction[1488] than tbp, which is probably the only case of reversal of the general trend, followed by R_3PO, namely, topo > Bu^n_3PO > Ph_3PO > tbp. In system IV, maximum extraction of cerium(III) was noted at 2 M topo[1489]. Similarly, system V showed a maximum value of D at 0.3–0.5 M HNO_3[1346]. System VI showed[1491] that K_{ex} is not necessarily higher for smaller ionic radii (K_{ex}:M = Nd, 5.8×10^7; Er, 1.5×10^6; Gd, 5.3×10^4) and can follow a complicated trend depending on the system. System VII showed a case of the salting-out effect[1492], where the presence of NH_4NO_3 was necessary for extraction.

From systems IX and X, it was observed that the replacement of an R group by an alkoxy group (RO) lowered the extraction[1344,1352], obviously owing to decreased Lewis basicity of $(RO)_3PO$ and also to enhanced $H_2O \cdots (RO)_3PO$ interaction. A decreasing trend in extraction of the type $R_3PO > R_2(RO)PO > R(RO)_2PO > (RO)_3PO$ is followed. Interestingly, system XI (at ⩾0.25 M topo) is the most selective[1494] for lanthanide separations to date. It also represents the first report of the extraction of lanthanides as their hydroxides. System XII involves the extraction of the rare earths[1495] from several geosamples. Here Sc, Fe, Cr, U and Th are also removed. The use of mixed R_3PO ligands did not show any improvement in extraction over the use of individual ligands (XIII)[1496].

Europium(III) showed a higher extraction from LiCl than HCl media (XIV)[1497] and it may be attributed to the lowered effective concentration of topo due to topo···HCl interaction. System XV is very useful for separating europium from americium and curium[1498–1499]. System XVI shows the effect of temperature (20–60 °C) on the extraction of europium(III)[1500]. It was found that $-\Delta H$ values were higher for R_3PO than for tbp, although the trend was the reverse for $-\Delta S$ values. Hence the extraction was enthalpy driven.

TABLE 21. Extraction of lanthanides with tertiary phosphine oxides

System	Metal extracted	Reagent and medium	Species extracted	Ref.
I	La	topo; ClO_4^-	$[La(ClO_4)_3L_n]$	1487
II	La, Eu, Lu	R_3PO–xylene (R = *n*-octyl, Bu^n); SCN^-	$[M(NCS)_3L_n]$($n = 3, 4$)	537
III	Ce	topo–PhMe; HNO_3 or $LiNO_3$	$[Ce(NO_3)_3L_3]$	1488
IV	Ce	topo; NH_4SCN	$[Ce(NCS)_3L_3]$	1489
V	La, Sm, Pr, Gd, Dy, Ho	R_3PO–kerosene ($R = C_nH_{2n+1}$, $n = 7$–9); NO_3^-	$[M(NO_3)_3L]$	1346, 1490
VI	Nd, Gd, Er	topo–polyphenyl; $LiNO_3$–KNO_3 (molten)	$[M(NO_3)_3L_n]$($n = 2, 3$)	1491
VII	Nd	topo–kerosene; NH_4NO_3	$[Nd(NO_3)_3L_n]$	1492
VIII	Ln	R_3PO (R = Ph; *n*-octyl); HNO_3	$[M(NO_3)_3L_3]$	1493
IX	Ln (except Pm)	R_3PO; NO_3^-	$[M(NO_3)_3L_2]$	1344
X	Ln	R_3PO (R = isoalkyl, etc.); Cl^-, SCN^-	$[M(NCS)_3L_n]$(?)	1352
XI	La, Pr, Eu, Tb, Ho, Yb	topo–$CHCl_3$; Cl^-	$[M(OH)_3L_n]$	1494
XII	Ln	topo–C_6H_{12}; acidic solutions	—	1495
XIII	Ln	topo–Bu^n_3PO–PhMe; NO_3^-	$[M(NO_3)_3L_3]$ (L = topo, Bu^n_3PO) and $M(NO_3)_3(topo)(Bu^n_3PO)$	1496
XIV	Eu	topo–*p*-xylene; HCl (or LiCl)	$[EuCl_3L]$	1497
XV	Eu	topo–*p*-xylene; NH_4NO_3	$[Eu(NO_3)_3L_3]$	1498–1499
XVI	Eu	R_3PO (R = mixed alkyl groups); HNO_3 (or NH_4NO_3)	—	500

TABLE 22. Extraction of lanthanides with tertiary phosphine oxides–β-diketones

System	Metals extracted	Reagent and medium	Species extracted	Ref.
I	Ce	(a) topo–Htta; lactic acid	$[Ce(tta)_3L_2]$	1501
		(b) R_3PO–HA (HA = naphthoyltrifluoroacetone; R = Ph, *n*-octyl); acidic	$[CeA_3L_2]$	1502, 1503
II	La, Nd, Eu, Tb, Lu	topo–Hbfa; acidic	$[M(bfa)_3L_n](n = 1, 2)$	533a
III	Nd, Ho, Er	(a) topo–Htta–C_6H_6; acidic	$[M(tta)_3L_n](n = 1, 2)$	1504, 1505
		(b) topo–Htta–PhMe; CH_3COO^-		
IV	Nd, Ho, Er	topo–Htta; X^- ($X = ClO_4$, NCS, NO_3, Cl)	$[M(tta)_3L_2]$	1506
V	Sm, Pm, Tm	R_3PO–Htta–C_6H_6 (R = Ph, *n*-octyl); HCl	$[M(tta)_3L_n](n = 1, 2)$	1318–1319, 1507
VI	Ho, Er	topo–Htta; ClO_4^-	$[M(tta)_2L_5](ClO_4)$	1509
VII	Tb	Ph_3PO–Htta–bipy; $LiNO_3$–NH_4NO_3 (molten)	—	1508
VIII	Ln (except La, Ce, Pm)	Bu^n_3PO–Htta	$[M(tta)_3L_n](n = 2–4)$	1348
IX	Ln (except Pm, Lu)	Ph_3PO–Htta–C_6H_6; ClO_4^-	$[M(tta)_3L_2]$	1510
X	Ln	topo–high mol. wt β-diketones (LIX 51, LIX 54) or Hdbm (HA)–kerosene; acidic	$[MA_3L_n](n = 1, 2)$	1511
XI	Nd	topo (or Ph_3PO)–Htta; acidic	$[Nd(tta)_3L_2]$	49
XII	Eu	(a) R_3PO–Hbfa–C_6H_6 (or $CHCl_3$, CCl_4) (R = Ph, *n*-octyl); ClO_4^-	$[Eu(bfa)_3L_n](n = 1, 2)$	1473, 1512, 1513
		(b) Bu^n_3PO–Htta–C_6H_{12}; NO_3^-	$[Eu(tta)_2(NO_3)L_2]$ and $[Eu(tta)_3]$	1514
		(c) topo–Htta–C_6H_{12}; Cl^-	$[Eu(tta)_3L_2]$	1515
		(d) topo (or Bu^n_3PO)–ASCN–xylene–NH_4SCN	See text	1516
		(e) topo–Htta–different solvents (see text); acidic	$[Eu(tta)_3L_n](n = 2, 3)$	1517
		(f) Ph_3PO–Htta–$CHCl_3$; ClO_4^-	$[Eu(tta)_3L_2]$	1518[a]
XIII	Lu	(a) topo–(Hba + Hdbm)–C_6H_6; acidic	See text	1519
		(b) topo–(Hba + Hbfa)–C_6H_6; acidic		
XIV	Lu	topo–β-diketones–C_6H_6; acidic	$[LuA_3L]$	1520

[a] Ph_3AsO, an analogous ligand, showed a higher extraction than that with Ph_3PO.

Synergic extractions of lanthanides with R_3PO–β-diketones. Table 22 lists various metals studied using β-diketones with R_3PO as the synergists. Europium(III) is the most studied element and is therefore discussed in detail. The extracted species are generally of the $[MA_3L_2]$ type, having 8-coordination. Species with different numbers of A^- and L ligands attached to M have also been detected. Topo again is a superior synergist to Bu^n_3PO, Ph_3PO and tbp, in that sequence.

Some comments may be made on the systems shown in Table 22. System Ib shows more efficient extraction of cerium(III) than system Ia, although both showed better extraction than with either β-diketone or R_3PO alone[1501–1503]. A separation factor of 4.0 for Ce/Am was achieved in system Ia; the separation factors for other elements are (Ce/Eu, 4.3, Ce/Pm, 6.7). From system II, based on stability constant data[533a], it was concluded that the stability of an adduct increases with increase in the ionic radius: Lu > Tb > Eu > Nb > La. However, system VIII shows that the stability constants[1348] increase with increasing atomic number of the lanthanides and this difference may be attributed to the different set of reagents used.

From system IV, the extraction was found to vary with the anions in the sequence, for example, for Ho[1506] $ClO_4 > NCS > NO_3 > Cl$. Also, the nature of species varied from $[M(tta)_3L_2]$ at low metal concentration to $[M(tta)_2XL_5]$ at high metal concentrations.

The variation in the nature of the solvents[1318,1319,1507,1509] affected the *D* values in the sequences (V, VI): (a) cyclohexane > *n*-hexane > CCl_4 > C_6H_6 > $CHCl_3$[1318,1319] and (b) 1,2-$C_2H_4Cl_2$ > CH_2Cl_2 > C_6H_5Cl > $Cl_2C{=}CHCl$ > C_6H_6[1509]. These orders represent the decreasing sequence of their dielectric constants. From system V, it was further observed that samarium(III) extraction[1507] was quantitative with topo or Ph_3PO (topo, $\beta = 3.9 \times 10^{13}$; Ph_3PO, $\beta = 8.2 \times 10^{10}$), which provides an efficient method for samarium(III) extraction, but the effect of interferents is not known.

The use of high-molecular-weight β-diketones (system X)[1511] did not show any improvement in the separation factors between neighbouring metals (separation factors are 2.33 for Hdbm and 1.97 for LIX 51 and 1.72 for LIX 54). From system XIIa, it was concluded that the stability of an adduct increased in the order topo > Ph_3PO > tbp > quinoline[1473,1512,1513] and also that higher $\log \beta_2$ values were observed in CCl_4 than in $CHCl_3$[1512]. A significant observation from system XIIc is that the stability constants were higher for topo than for bis(*n*-hexylphosphinyl)alkanes[1515] discussed later.

In the Eu^{III}–Htta–topo system[1513,1521], it was established that the synergistic reactions in the organic phase are predominantly enthalpy stabilized, whereas complex formation reactions with the trivalent lanthanides in the aqueous phase are invariably entropy stabilized[1521]. The increased electrostatic interactions between the metal chelate and the donor molecules in the organic phase of low polarity increase the enthalpy values. Further, the energy required to remove H_2O from the hydrated metal chelate in the organic phase is small because only a small number of H_2O molecules are attached in the organic phase, which lowers the entropy.

In the extraction of europium(III) with topo (or Bu^n_3PO) and ASCN (XIIId)[1516] (where ASCN is the thiocyanate form of Aliquat 336-S, a quaternary ammonium chloride liquid anion exchanger), the extracted species were: $[Eu(NCS)_4{\cdot}A{\cdot}(topo)_n]$ ($n = 2, 3$) and $[Eu(NCS)_4{\cdot}A{\cdot}(Bu^n_3PO)_4]$. The species with R_3PO alone were $[Eu(NCS)_3(topo)_n]$ ($n = 3, 4$) and $[Eu(NCS)_3\ (Bu^n_3PO)_4]$. The mechanism of synergistic extraction appears to be the replacement of R_3PO by ASCN molecules and the preferential extraction of the bulky ammonium-like species $[M(NCS)_4(topo)_3]^-$ by the cation of the quaternary amine. Equilibrium constants for the synergistic extraction vary in the sequence topo < Bu^n_3PO ≪ tbp. The strongly basic topo is replaced with more difficulty than the weakly basic tbp. Thus, topo showed antisynergism with ASCN, Bu^n_3PO caused no change and tbp showed synergism. The synergism appears to be solvent dependent and thus no synergism was observed in *n*-hexane.

The extraction data for system XIIe[1517] as a function of effect of solvents is shown in Table 23. The adduct formation constants $K_{S,m}$ are strongly dependent on the diluent, e.g. $K_{S,2} = 15.08$ in pentane and 7.68 in $CHCl_3$. The solubility parameter, δ_{org}, of the diluent and log $K_{S,m}$ are correlated by a linear equation:

$$\log K_{S,m} = 2B\delta_{org} + \text{constant}$$

where B is a negative constant obtained as the slope of the plot of log $K_{S,m}$ vs δ_{org}. The extraction constant, $K_{ex,S}$, varies in proportion to $K_{S,m}$ in each diluent and a similar relationship,

$$\log K_{ex,S} = 2B\delta_{org} + \text{constant}$$

can be written. Generally, $K_{S,m}$ and $K_{ex,S}$ decrease with increasing solubility of the adduct in a solvent, with a few exceptions. The values increase in the order aliphatic diluents > CCl_4 > benzene and its derivatives > some halogenated diluents. From similar studies on the uranyl system, which forms $[UO_2(tta)_2(topo)]$[1522], log $K_{ex,S}$ decreases to a lesser extent with increasing δ_{org} and thus separation from europium(III) is difficult in aliphatic diluents, but it is very easy in diluents with large solubility parameters. Hence the choice of solvent is very important not only for synergism but also for separation from other components.

The shift reagent $[Eu(tta)_3]$ has been used to study the synergistic extraction of rare earths[1523] by analysing the NMR shifts in the phenylortho-protons of Ph_3PO by its interaction with $[Eu(tta)_3]$. The concentration dependence of the induced shifts gives the stoichiometry and the stability constant of the adduct, $[Eu(tta)_3L_2]$ ($L = Ph_3PO$).

TABLE 23. Adduct formation and synergistic extraction constants for the Eu–Htta–topo system (25 °C)[a,b]

Diluent	S_{org}	Log $K_{S,2}$	Log $K_{ex,S}$
Pentane	7.05	15.08	7.02
Hexane	7.3	14.96	6.85
Heptane	7.4	14.76	6.71
Cyclohexane	8.2	14.46	6.54
Isopropylbenzene	8.5	13.04	4.92
Carbon tetrachloride	8.6	12.88	4.43
Toluene	8.9	12.02	4.01
Benzene	9.15	11.78	4.10
Chloroform	9.3	7.68	−0.74
Chlorobenzene	9.5	11.34	3.00
Dichloromethane	9.7	10.14	1.87
o-Dichlorobenzene	10.0	11.66	3.39
Bromoform	10.5	9.04	0.53

[a] From ref. 1577.

[b] Equations:

$$[Eu(tta)_3] + mS \xrightleftharpoons{K_{S,m}} [Eu(tta)_3S_m]$$

org. org. org.

$$Eu^{3+} + 3Htta + mS \xrightleftharpoons{K_{ex,S}} [Eu(tta)_3S_m] + 3H^+$$

aq. org. org. org. aq.

TABLE 24. Extraction data for the lutetium(III)–β-diketone–topo systems[a]

$R^1C(O)CH_2C(O)R^2$			
R^1	R^2	Log *K*	Log β_1
Me	Me	—	4.35
Et	Et	−16.57	4.35
Pr^i	Pr^i	−16.57	4.80
Me	Bu^t	−16.90	4.80
Bu^t	Bu^t	−18.37	4.80
Me	Ph	−15.21	5.25
Me	Naphthalene	−15.06	5.45
Ph	Ph	−15.16	6.15
Me	CF_3	—	6.25
Ph	CF_3	−7.69	7.50
$2\text{-}C_4H_3S$[b]	CF_3	−6.50	7.25
$2\text{-}C_4H_3O$[c]	CF_3	−6.78	7.15
CF_3	CF_3	—	6.25

[a] All data from ref. 1520.
[b] 2-Thiophenyl.
[c] 2-Furyl.

Ph_3PO interacts with $[Eu(tta)_3]$ in $CDCl_3$ in two steps, 1:1 and 1:2 ($\log\beta_1 = 7.93$, $\log\beta_2 = 9.67$).

The ternary system XIII revealed that the stability of an adduct of the mixed chelate varies in the order[1519] $[Lu(ba)(bfa)_2] > [Lu(ba)_2(bfa)] > [Lu(ba)(dbm)_2] \approx [Lu(ba)_2(dbm)]$. A detailed study of the extraction of lutetium(III) with a series of β-diketones reveals a number of interesting observations (system XIV, Tables 22 and 24)[1520]: (a) β-diketones with a CF_3 group can extract lutetium(III) from a lower pH region owing to the enhanced acidity of the OH groups; (b) β-diketones with bulky groups such as benzoyl, thenoyl and pivaloyl showed high extractability, attributed to the hydrophobic structure of the chelating molecule; and (c) the stability of the topo adducts ($\log\beta$) increase with increase in $\log K$, indicating that there is no steric hindrance by the terminal groups.

Extraction of lanthanides with R_3PO–pyrazolones and other reagents. Like β-diketones, pyrazolones also constitute an important class of reagents, although they have attracted less attention. Table 25 gives the synergistic systems used for the extraction of lanthanides together with the various types of species extracted. From systems I–VI, it was concluded that (a) the extraction constants showed a maximum at europium or holmium and the change was monotonic with increasing atomic number[1524,1525]; (b) Hpmop is more selective than Hpmbp (the separation factors with Hpmop were, Pr/Eu 1.33 and Eu/Tb 2.02)[1526]; (c) the synergism is attributable to expansion of the coordination sphere and not to replacement of H_2O by topo[1349,1351]; (d) Hpmbup–topo showed a higher synergic effect than Hpmbp–Bu_3PO (system V)[1532]; (e) the ternary systems also show synergism, e.g. for terbium(III) (system IV)[1528] N-503 enhanced the extraction significantly ($\log\beta = 4.01$ versus 1.45 when no N-503 was used); and (f) the pyrazolonethione ligand alone gave no detectable extraction in the ranges studied, but the addition of topo resulted in synergistic extraction (system VI)[1529].

When R_3PO-substituted phosphoric acid combinations were used (systems VII–X), the following conclusions were made: (a) in the case of cerium(III) extraction, a large Ce/Am separation factor of 150 was achieved in system VII(a)[1501]; (b) an antagonistic effect was observed in the extraction of dysprosium(III) (VIIb) when excess of topo was

TABLE 25. Extraction of lanthanides with tertiary phosphine oxides–pyrazolones and other synergistic systems

System	Metals extracted	Reagent and medium	Species extracted[a]	Ref.
I	La, Pr, Eu, Ho, Yb	topo (or cmpo)[b]–Hpmtfp–$CHCl_3$; ClO_4^-	$[MA_3L_2]$	1524, 1525
II	Pr, Eu, Yb	topo–Hpmop–$CHCl_3$; acidic	$[MA_3L]$	1526
III	Nd	(a) topo–Hpmbp; acidic	$[NdA_3L]$	1349, 1351
		(b) Bu^n_3PO–Hpmbp–PhMe; $HClO_4$	—	1527
IV	Tb	topo–Hpmbp–N 503[c]–PhMe	$[TbA(N\,503)_2L_3]$	1528
V	Yb	Bu^n_3PO–Hpmbup–PhMe	$[YbA_3L_n]$ ($n = 1, 2$)	1532
VI	Eu	topo–HA[d]–C_6H_6; $HClO_4$	$[EuA_2(HA)L_2(ClO_4)]$	1529
VII	Ce	topo–H2dehp; lactic acid	$[CeA_3L_2]$	1501
	Dy	topo–H2dehp–kerosene; HCl	—	1530
VIII	Ln	R_3PO–H2dehp; NO_3^- (R = 1-methylheptyl)	$[MA_3]$, $[M(NO_3)_3L_3]$	1531
IX	Tm	topo–HA–PhMe; HCl (HA = mono-2-ethylhexyl-phosphoric acid)	—	1533
X	Ln	topo–HA[e]; Cl^-	$[MA_3(HA)(topo)]$	1534
XI	La, Pr, Eu, Yb	topo–HA–CCl_4[f]	$[M(OH)A_2L_2]$	1535
XII	La, Pr, Eu, Yb	topo–HA–CCl_4[g]; Cl^-	$[MClA_2L_3]$	1536
XIII	Eu	(a) topo–HA–$CHCl_3$[h]	$[EuA_3L_2]$	1537
		(b) topo–HA–$CHCl_3$[i]	$[EuA_2(HA)L_n]$	1538
XIV	Ln	R_3PO–nta–deta[j] (R = isoamyl)	—	1539
XV	Pm	topo–HA–$CHCl_3$[i]	$[PmA_{1.5}(HA)_{1.5}L_n]$	1538
XVI	Eu	Ph_3PO–H_2Sal–C_6H_6 (or n-hexane)[k]	$[Eu(HSal)_3L_2]$	1540

[a] HA represents pyrazolones or other similar reagents.

[b] cmpo = octylphenyl (*N*,*N*-diisobutylcarbamoylmethyl)phosphine oxide.

[c] N 503 = *N*, *N*-dimethylheptylacetamide.

[d] HA = 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-thione.

[e] HA = bis(2,4,4-trimethylpentyl)phosphoric acid.

[f] HA = 2-(3,5-dibromo-2-pyridylazo)-5-diethylaminophenol.

[g] HA = 2-(2-pyridylazo)-4-nonylphenol.

[h] HA = 1-nitroso-2-naphthol.

[i] HA = *N*-benzol-*N*-phenylhydroxylamine.

[j] NTA = nitriloacetic acid; deta = diethylenetriaminepentaacetic acid.

[k] H_2Sal = salicylic acid.

used[1530]; (c) system VIII showed a lack of mixed chelates, an observation against the normal trend[1531]; and (d) system IX promises[1533] interesting mutual and group separations of f-block elements as the trend in their extraction shows: $Tm > Y \gg Eu > Am$. Extraction with substituted phenols suggests that the separation factors for the heavier lanthanide elements become large; they are the highest to date (system XII)[1536]. Additionally, the species are different to those normally observed. System XIIIb revealed that extraction decreases in the order topo < tbp > bipy, a behaviour against the common trend[1538]. Similarly, system XIV shows that an amine reagent can be suitable for the separation of the cerium sub-group[1539]. The extraction of europium(III) from nitrate solutions with trioctylammonium nitrate, $\{Oct_3NH\}(NO_3)$[1541], forms the species

$\{R_3NH\}[Eu(NO_3)_4]$, which reacts with R_3PO (R = Ph, *n*-octyl) in benzene to form $[Eu(NO_3)_4L]^-$. However, the exact nature of the species requires further investigations.

Actinides. Most of the extraction studies reported for the actinides deal with Th, U, Pu and TPE elements. Only a few investigations on the other actinide elements have been reported. Uranium is the single most studied element among f-block elements, with europium and americium occupying second and third positions respectively.

Actinium. Actinium(III) was extracted from 8 M LiCl with topo as $Li_2[AcCl_5L_2]$ and the recovery was more than 95%[1542].

Thorium. Topo (in cyclohexane) extracted thorium(IV) from HCl, HNO_3[1543] or Cl^- solutions[1337]. A single extraction quantitatively removed thorium(IV) from 1 M HNO_3 or 7 M HCl; extractions from acids at other concentrations were low. Extraction from H_2SO_4 or H_3PO_4 solutions was poor and in the case of $HClO_4$ solution two immiscible phases formed, complicating the recovery of thorium. This method (topo–C_6H_{12}) was useful in the quantitative recovery of thorium from monazite and other raw materials after their leaching with H_2SO_4 or H_3PO_4. Rare earths do not interfere, but zirconium(IV) is co-extracted with thorium(IV). The nature of the extracted species depended on the anion, being $[ThX_4L_3]$ for X = Cl, NO_3[1543,1544] and $[ThX_4L]$ for X = Br[1545], but was independent of the organic solvent (PhMe, Me_2CO, etc.) Interestingly, from bromide solutions, the separation of thorium from uranium was facile. Other studies of the extraction of thorium include topo in dodecane from aqueous $LiNO_3$ solution[1546] and R_3PO (R = isopentyl, etc.) in C_6H_6, CCl_4, $CHCl_3$ or heptane[1547,1548]. The species extracted were of the type $[Th(NO_3)_4L_n]$ ($n = 1$–4).

Topo–Htta in different organic solvents (e.g. hexane)[49,1318,1319,1505,1549] synergistically extracted thorium from HCl as $[Th(tta)_4L]$. Whereas topo enhanced extraction, the addition of other oxygen donors such as ethanol and isobutanol lowered synergism due to the replacement of coordinated topo by these alcohols. The Htta-Bu^n_3PO (or Ph_3PO) also synergically extracted thorium forming the species: $[Th(tta)_4(Ph_3PO)]$, $[Th(tta)(NO_3)_3]$[49,1550]. With Bu^n_3PO, the synergism was attributed to the tendency of thorium to acquire 8-coordination and not to the replacement of H_2O by Bu^n_3PO. Whereas topo–Hdbm in C_6H_6 showed no synergism[1310], topo–LIX 54 (a β-diketone, HA) in C_6H_6 showed quantitative extraction of thorium (as ThA_4L) from acidic solutions (pH 2.8)[1551].

Thermodynamic studies on the extraction of thorium[1349,1351] by topo–Hpmbp suggested that synergism was associated with the replacement of solvate water by an adduct molecule with no change in the coordination number. Other extraction systems are topo–benzoic acid in CCl_4[1552] and topo–quinolin-8-ol[1553]. The topo-benzoic acid system offers an easy method for the separation of Th from La, Gd, Y or Tb.

Protactinium. Ph_3PO in $CHCl_3$ separated protactinium(V) from thorium(IV) in HNO_3 solution[1554]. An analogous arsenic ligand, Ph_3AsO, could also be used. Another study described the extraction of protactinium(V) from a variety of acids such as HF, $HClO_4$, oxalic or tartaric acid; extraction was highest from $HClO_4$[1364].

Uranium. Uranium extraction occurs essentially in the hexavalent state and only a few studies have dealt with the tetravalent state. The work reported is split into various parts. A separate section describes the recovery of uranium from wet-process phosphoric acid solutions and ores.

Extraction of uranium with R_3PO alone. In a number of investigations the use of R_3PO alone for the extraction of uranium(VI) from various media was studied. Topo has been most commonly used for the extraction of uranium(VI). It was observed that the nature of the extracted species remained more or less the same when the aqueous phase contained different anions (Cl^-, NO_3^-, etc). The most common species was $[UO_2X_2(R_3PO)_2]$ (X = Cl, NO_3, ClO_4, $\frac{1}{2}SO_4$; R = *n*-octyl, *n*-butyl, etc.) and the organic solvents commonly used were cyclohexane, toluene, benzene, $CHCl_3$ or CCl_4[1326,1338,1356,1548,1555–1561].

The formation of species of the type $[UO_2(NO_3)$ (ClO_4) (Bu^n_3PO)[1560], $[UO_2(NO_3)_2$ $(topo)]$[1564], $[UO_2(SO_4)L_2]\cdot H_2SO_4$ (L = topo, Bu^n_3PO)[1557] has also been observed.

Some other conclusions on and applications of the use of R_3PO for the extraction of uranium(VI) are as follows: (a) topo in cyclohexane[1562] or topo in molten naphthalene (at 80 °C)[1563] quantitatively separated uranium from several elements present in HNO_3 solutions[1563]; (b) topo in toluene separated uranium, present in urine, with 90.5% recovery; Na, K, Ca, Mg and Fe did not interfere[1564]; (c) recovery of uranium from aquatic sediments[1565] and that of uranium and thorium (in traces from rare earths[1566]) using topo in cyclohexane; (d) recovery of uranium from uranium liquors with R_3PO (R = *n*-butyl, *n*-octyl) or Ph_3PO[1567]; (e) separation of uranium(VI) from bismuth (1 : 10 000 ratio) with tris(2-ethylhexyl)phosphine oxide in cyclohexane from $NaNO_3$ solution (pH 2.5–3.0[1568], (f) separation of uranium(VI) from rare earths dissolved in a fused NaSCN–KSCN eutectic with topo–tetralene[1569]; (g) topo in toluene extracted $U^{234,238}$ from a sample of Ra^{226} in $HClO_4$ solution[1570]; (h) extraction was high from HNO_3 or HCl and poor from H_2SO_4 or H_3PO_4[1556]; (i) the extractability of uranium(VI) from HNO_3–H_2SO_4 with R_2MePO (R = $HOCH_2$—) in benzene was much higher than that with tbp[1571]; however, thorium is co-extracted; and (j) UO_2^{2+} was synergistically extracted when Oct_3N was added to topo for extraction from aqueous $(NH_4)_2SO_4$[1572]; the extracted species was identified as $(R_3NH)_2[UO_2(SO_4)_2$ (topo)].

The only investigation into the extraction of uranium(IV) with phosphine oxides is its extraction from HCl with topo in cyclohexane[1573]. It was observed that an increase in temperature (10–45 °C) led to a higher transfer of UCl_4 from the aqueous to the organic layer. The activation energy was 45.2 kJ mol^{-1} for topo and 38.5 kJ mol^{-1} for tbp.

Extraction of uranium with R_3PO–β-diketones. Only R_3PO–Htta (R = Bu^n, *n*-octyl, Ph) combinations have been used for the synergistic extraction of uranium. The extraction of uranium with R_3PO–Htta in benzene, $CHCl_3$, etc., from HCl or HNO_3 formed $[UO_2(tta)_2L_n]$(L = topo, Bu^n_3PO or Ph_3PO; $n = 1$–3)[49,449,1318,1319,1504,1574–1576] in the organic layer. The extraction with Htta alone was poor and addition of R_3PO enhanced the extraction[1575,1576] by a factor of 10^4. The K_{ex} values for the extraction of uranium(VI) from HCl with R_3PO–Htta varied in the order topo $\gg$ Bu^n_3PO $>$ tbp ($K_{ex} = 4.1 \times 10^8$, 3.5×10^3 and 3.0×10^2, respectively)[1318,1319]. Further, the highest extraction was observed when the organic solvent was cyclohexane. Studies on the effect of temperature[1578] on extraction from HCl with Htta–topo revealed that a 10° C rise in temperature lowered the extraction by 20–30% whereas it remained unaffected with Htta alone. The extraction of uranium(IV) with Htta–Ph_3PO has been reported and the species $[U(tta)_4L]$ was formed[1577]. The formation constants of 1.24×10^4 and 2.67×10^5 for $[U(tta)_4L]$ and $[UO_2(tta)_2L]$, respectively, revealed a higher extraction of uranium(VI) than uranium(IV).

Extraction of uranium with R_3PO–pyrazolones. A series of combinations of pyrazolones and topo in the usual solvents were used for the extraction of uranium(VI). The extracted species was $[UO_2A_2L]$ (HA = Hpmbp[1349,1351,1574,1579]; Hpmcbp = 1-phenyl-3-methyl-4-(2′-chlorobenzoyl)pyrazol-5-one[1580]; HPMTFP[1581]; Hbmppt = 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-thione[1582]]. Some conclusions that may be drawn from these studies include (a) the synergism was attributed to the replacement of solvate water by the added ligand[1349,1351]; (b) adduct formation was enthalpy and entropy stabilized[1579,1581]; (c) Hpmcbp–topo showed higher extraction than Hpmbp–topo[1580]; (d) the extraction properties of Hpmtfp–topo were similar to those of Hpmap[1581]; and (e) the extraction could be followed by a computer-controlled flow-injection system[1582].

A ternary system, Hpmbp–Htta–topo, extracted UO_2^{2+} as $[UO_2(pmbp)(tta)\cdot(topo)]$[1574]. This ternary complex is stable, but no improvement in extraction over

Hpmbp–topo was achieved although it showed a higher extraction than Htta–topo. Uranium(IV) was extracted as [UA$_3$ClL] from HCl with Hpmbp–topo in CHCl$_3$[1583].

Extraction of uranium with $R_3PO–H_2dehp$ (and related compounds). The synergistic extraction of uranium(VI) was carried out using H$_2$dehp (or related compounds) and R$_3$PO combinations (R = Bu^n, *n*-octyl, Ph, isoamyl) as follows: topo–H$_2$dehp (HA) from HNO$_3$–H$_2$SO$_4$ solution[1584], R$_3$PO–H$_2$dehp (R = Bu^n, Ph, isoamyl) from sulphate medium[1585–1588] and R$_3$PO–(R'O)$_2$P(O) (OH) (R = *n*-butyl,*n*-octyl; R' = *n*-butyl)[1563,1589,1590] from H$_2$SO$_4$ solution and topo–(*n*-OctO) (Bu^{n}O)P(O)(OH)[1591a]. The extracted species were normally [UO$_2$A$_2$(HA)$_2$(R$_3$PO)][1584,1586,1590] and [UO$_2$A$_2$(R$_3$PO)][1563,1589] {HA = H$_2$dehp or (R'O)$_2$P(O)OH, etc.}. Some other comments are: (a) H$_2$dehp also extracts HNO$_3$ to some extent[1584]; (b) the order of synergistic enhancement appears to be topo > (isoamyl)$_3$PO > Bu$^n_3$PO > Ph$_3$PO > tbp[1563,1585,1587–1589]; (c) Bu$^n_3$PO–H$_2$dehp was demonstrated as suitable for the recovery of uranium(VI) from low-grade uranium liquors[1588]; (d) in CCl$_4$, synergism was higher than that in *n*-hexane[1563,1589]; and (e) the synergistic extraction was attributed to an adduct formation and not to the replacement of HA molecules[1590].

Extraction of uranium with R_3PO–organic acids. Topo–fatty acids/aromatic acids have also been used for the extraction of metals. Here the acids act as synergists, although antisynergism was also observed under certain experimental conditions. For instance, in the extraction of uranium(VI) with topo in CCl$_4$ from aqueous perchlorate medium[1591b], benzoic acid acted as a synergist up to a certain acid concentration (0.01 M), but at higher acid concentrations, topo interacts with the acid, thus lowering the topo concentration; the extracted species is [UO$_2$(ClO$_4$)(PhCOO) (topo)].

Topo–PhCOOH–CCl$_4$ offers an excellent method in acidic solution (pH 2.5–3.5) for the separation of uranium from rare earths, which are virtually unextracted by this combination[1592] (separation factor 800–2500 for U/rare earths). This method was used for the determination of uranium in rocks and minerals. Topo–salicylic acid showed synergistic extraction of UO$_2^{2+}$ from aqueous NO$_3^-$, Cl$^-$ or ClO$_4^-$ solutions[1592]. By contrast, PhCOOH showed synergism up to a certain concentration of NO$_3^-$ ions (and for > 0.1 M NaNO$_3$, it showed antisynergism because the benzoate ions cannot compete with NO$_3^-$ in their coordinating ability to uranium(VI). Since the salicylic acid acts as a chelating agent, and forms stable chelates, no antisynergism was observed even at high NO$_3^-$ concentration. There was no extraction of UO$_2^{2+}$ from sulphate solutions.

In the extraction of uranium(VI) with topo in CCl$_4$ from dilute HNO$_3$ (pH 1–5)[1593,1594] in the presence of aromatic monocarboxylic acids, it was demonstrated that the presence of salicylic acid showed the highest extraction. The method was suitable for the separation of uranium(VI) from rare earths, Y, Th, Zr, Ir and Fe, followed by direct spectrophotometric determination. These elements interfere when uranium(VI) is determined with arsenazo III reagent. At pH ≈ 5, the *D* values decreased in the order salicyclic acid (693) > phenylpropionic acid (363.0) > *o*-chlorobenzoic acid (223) > benzoic acid (93.9) > hydroxycinnamic acid (37.4) > *trans*-cinnamic acid (32.9) > *o*-nitrobenzoic acid (8.4). The action of the acids varied from antagonistic below pH 1.8 to synergistic above pH 2.0. The synergistic effect depends linearly on the p*K* values except for salicylic acid. At low pH, acids are protonated and then interact with topo, lowering its activity when the pH is increased. Organic acids dissociate and transfer to the aqueous phase, forming complexes with UO$_2$$^{2+}$.

A series of fatty acids (valeric acid, Me(CH$_2$)$_3$COOH; capric acid, Me(CH$_2$)$_8$COOH; pentadecanoic acid, Me(CH$_2$)$_{11}$COOH; palmitic acid, Me(CH$_2$)$_{10}$COOH; and margaric acid, Me(CH$_2$)$_{15}$COOH) acted as synergists (pH > 1.9) during the extraction of UO$_2^{2+}$ with topo in different organic acids[1595]. Since the dissociation constants of the acids are similar, the corresponding synergistic effect was also similar. An increase in pH increased the synergism, as expected. The chain length did not have any extra effect on the synergism. The *D* values decreased in the sequence $C_6H_6 > C_6H_{12} > CCl_4$. The behaviour of xylene and toluene was similar to that of cyclohexane.

Recovery of uranium from wet-process phosphonic acid/ores. The recovery of uranium from wet-process phosphonic acid solutions and ores has recieved special attention. For effective recovery, uranium must be present in oxidation state VI, and therefore any uranium(IV) present has to be converted into uranium(VI) using an oxidizing agent. Topo–H_2dehp is commonly employed for extraction; however, a few other reagents have also been used.

A number of workers have described the extraction of uranium(VI) from wet-process phosphonic acid solutions of phosphate ores using H_2dehp–topo[1596–1608]. Some important conclusions drawn are (a) typical yields in uranium recovery from H_3PO_4 and phosphate ores are 95 and 80.8%, respectively[1607]; however recoveries of > 98% and concentration of uranium in H_3PO_4 from ~ 60 mg l^{-1} to 7 g l^{-1} was achieved in another study[1608]; (b) the extracted species was identified as $[UO_2A_2(topo)]$[609] (HA = H_2dehp); (c) iron present in the uranium-loaded organic layer was removed by placing it in contact with a stream of 30% P_2O_5–H_3PO_4[1596–1598]; (d) the extraction decreased on changing the solvent in the order kerosene > hexane > C_6H_6 > CCl_4; and (e) the recovery of uranium from the Itataia wet-process H_3PO_4 involved first reduction of uranium(VI) to uranium(IV) followed by its extraction with octylpyrophosphoric acid in kerosene[1602,1603,1605,1606]. The organic layer was then stripped with concentrated H_3PO_4 and the uranium(IV) converted to uranium(VI) with an oxidizing agent followed by re-extraction with H_2dehp–topo. The extract was stripped with $(NH_4)_2CO_3$ and the uranium(VI) recovered as a commercial concentrate.

Other reagents used for uranium(VI) extraction are topo and a mixture of H_2dehp and mono- and di-(nonylphenyl) phosphate in kerosene (I)[1610]; topo–$(R_2CHO)_2P(O)(OH)$ (R = $BuOCH_2$) in kerosene (II)[1611,1612]; dialkylphosphoric acid and mixed phosphine oxides (III)[1613]; and R_3PO (R = alkyl)[1614] and bifunctional chelating agents incorporating a phosphine oxide and phosphoric acid diester, *O*-methyldihexylphosphine oxide–*O*′-2-ethylhexylphosphoric acid (IV)[1615]. System I gives a recovery of uranium(VI) present to the extent of 0.00092% in H_3PO_4 with > 90% efficiency[1616]. System II was superior to H_2dehp–topo ($D = 14.0$ versus 4.2). Iron(III) present showed poor extraction ($D = 0.40$ versus 0.04). Similarly, system III showed a greater extraction efficiency than H_2dehp–topo ($K_{ex} = 31.5$ versus 25.0). System IV appears to be an excellent and superior alternative to H_2dehp–topo for the extraction of uranium(VI)[1615].

Neptunium. Investigations on the extraction of neptunium(IV) from HNO_3 have involved (a) Ph_3PO in CCl_4, C_6H_6 or $CHCl_3$[1617], (b) Hpmbp–topo in C_6H_{12}[1618] and (c) Htta–Bu^n_3PO[1550]. Ph_3PO extracted neptunium as $[Np(NO_3)_4(Ph_3PO)]$ whereas with other reagents the extracted species were $[Np(tta)_2(NO_3)_2(Bu^n_3PO)_2]$. $[Np(tta)_3(NO_3)(Bu^n_3PO)]$ and $[Np(tta)_4]$. Hpmbp-topo could separate neptunium(V) the transplutonium elements, uranium(VI) and the rare earths. In the last two synergistic systems, the synergism was attributed to the ability of neptunium to acquire 8-coordination and not to the replacement of H_2O by topo.

Plutonium(IV, VI). Topo in hexane extracted plutonium(IV) quantitatively (99.5%) from HNO_3 over a range of concentrations (0.3–11.0 M)[1619]; however, the extraction of plutonium(VI) required a lower acidity (0.3–0.7 M HNO_3). Both plutonium(IV) and plutonium(VI) were readily separated from plutonium–americium mixtures. From HCl solutions, the extraction of both of these was quantitative at 5 M HCl but poor at < 5 M HCl. The formation of species of the type $[PuX_4L_2]$ or $[PuX_6L_2]$ (X = Cl, NO_3) was suggested.

Plutonium(IV) was extracted from uranium fission products in the presence of $NaNO_3$ using Bu^n_3PO in CCl_4[1620] and from HNO_3 solutions with a range of phosphine oxides, $R_2R'PO$(R, R′ = Me to C_8H_{17}, Ph), and observations similar to those for zirconium–niobium were noted[1366]. Use of Bu^n_3PO with H_2dehp gave a 50-fold enhanced extraction of plutonium(IV) and plutonium(VI) than with either of these reagents separately[1588]. Bu^n_3PO–Htta in hexane extracted plutonium(IV) synergistically from HNO_3 solutions[1550]. Here the synergism was attributed to the ability of the actinides to achieve a coordination number of eight and not to the replacement of H_2O by Bu^n_3PO or similar molecules. The formation of $[Pu(tta)_2(NO_3)_2(Bu^n_3PO)_2]\cdot[Pu(tta)_3(NO_3)(Bu^n_3PO)]$ and $[Pu(tta)_4]$ was observed.

Topo–H_2dehp in kerosene was used to extract plutonium quantitatively from H_2SO_4 solutions (containing $NaNO_3$ or HNO_3) obtained by acid digestion of plutonium-contaminated waste free from sulphate[1621]. The presence of H_3PO_4 in the feed did not influence the extraction of plutonium, but uranium(VI), if present, is also extracted. Stripping of the organic phase with $(NH_4)_2CO_3$ or 1 M HNO_3 transfers only plutonium to the aqueous layer, leaving uranium(VI) in the organic phase. The extraction of americium(III) as noted above was poor ($K_{ex} < 1\%$).

Transplutonium elements (TPE). The yield of TPE from the irradiation of plutonium is usually a few percent of the target material. The atom ratio of the fission products, TPE/lanthanides, is Ca 1:10. The separation of lanthanide group elements from TPE is difficult owing to the similarity of their chemical properties. The studies described below provide various methods for the separation of TPE from one another or other elements.

Extraction of TPE with R_3PO alone. Topo in xylene showed poor extraction of americium(III) from HCl but the extraction increased by a factor of 10^5 from LiCl solutions[1497]. An increase in the concentration of LiCl lowers the water activity, which in turn leads to higher ligation of americium(III) by topo. The extracted species was $[AmCl_3(topo)_n]$ ($n = 1, 3$, depending on the LiCl concentration). In another study[1622], the separation factors for californium and einsteinium from americium and curium increased with increase in the number of the halide ions in the inner-sphere coordination to the metal with a simultaneous decrease in the degree of complexation in the aqueous phase. Bromide ions showed less inner-sphere coordination than chloride ions.

Topo (in *n*-octane) showed a similar extraction of americium(III) and curium(III) from aqueous nitrate medium ($K_{ex} = 1.5 \times 10^7\,l^3\,mol^{-3}$ for Cm and $2.9 \times 10^7\,l^3\,mol^{-3}$ for Am)[1623]. Bu^n_3PO in benzene or topo in xylene also extracted curium and americium from aqueous nitrate or HNO_3 solutions[1498,1499,1623]. The extracted species appeared to be $[M(NO_3)_3L_3]$. It was observed that at constant NO_3^- concentration, the value of D was higher at lower acid concentration. Addition of tbp to the topo solution enhanced the extraction of americium(III) from concentrated HNO_3[1624]. Tbp was labelled as a modifier. Similar behaviour was noted in the extraction of americium(III) with diaryldialkylcarbamoylmethylphosphine oxide[1625].

The extraction of the TPE (Am, Cm, Cf) from nitrate media with trioctylamine nitrate is enhanced by the addition of topo or Ph_3PO in benzene[1542]. $(R_3NH)[M(NO_3)_4L]$ and $[M(NO_3)_5L_n]^{2-}$ ($n = 1, 2$) were suggested to be the extracted species. The behaviour of triaurylamine–topo for americium, curium, and promethium was similar[1626]. The extraction of americium(III) or curium(III) with *N*-benzoyl-*N*-phenylhydroxylamine in $CHCl_3$ was enhanced after the addition of R_3PO, but the synergistic extraction decreased in the sequence tbp > topo > bipy, which is the reverse of the basicity of these donor ligands[1539].

The extraction of americium(III) from 1 M NH_4SCN solution with topo or Bu^n_3PO in xylene was increased when a liquid anion exchanger, ASCN (ASCN = thiocyanate form of a quaternary ammonium chloride, Aliquat 336)[537,1516,1627], was added. The synergic species were $[Am(NCS)_4.A.(topo)_m]$ ($m = 2,3$) and $[Am(NCS)_4.A.(Bu^n_3PO)_3]$. The separation factors for Am/Eu increased from 2.9 to 6.0 for topo and from 3.3 to 6.2 for Bu^n_3PO on addition of ASCN. The greater participation of 5f orbitals in bonding to

TABLE 26. Extraction of metals with bis(tertiary phosphine oxides)

$R_2P(O)(CH_2)_nP(O)R_2$			
R	*n*	Metal	Ref.
		d-Block elements	
n-Octyl	2	Sc(III)[a]	1633, 1634
n-Octyl	2	Fe(III)[a]	1633–1636
Ph	1	Fe(III)[a]	1633–1636
Ph	2–4, 6	Co(II)[b]	1637
n-Octyl, Ph	1	Y(III)[a]	1638, 1639
n-Hexyl	1	Zr(IV), Hf(IV)[a,c,d]	1640–1642
n-Octyl	1–6, 8, 10	Mo(VI), Ga(III)[e]	1324, 1325, 1382
n-Hexyl	1	Nb(III), Ta(III)[a,d]	1643
n-Octyl	2	Ca(II), Al(III)[c]	1633
n-Hexyl	1	Alkaline earth metals[c]	1644
		f-block elements	
n-Octyl	4	Ce(III)[a,f]	1633, 1644
n-Octyl, Ph	1	Nd(III)[a]	1639
Ph	2–4, 6	Pm(III), Eu(III), Tm(III)[b], Am(III), Cm(III), Cf(III)	1637, 1645–1647
n-Hexyl	1–4	Pr(III), Nd(III), Sm(III)[a,c,e], Tm(III), U(VI)	1648–1654
Ph, *n*-octyl	1	Eu(III), Am(III)[c]	1655, 1656
Ph	1	Ce(III), Eu(III), Am(III), Cm(III)[g]	1657
Ph, etc.	1	Eu(III), Am(III), Cm(III), Bk(III), Cf(III), Es(III), U(VI)[a]	1658, 1659–1667
Ph, *n*-octyl	1	Eu(III), Am(III)[a,c]	1534, 1668
n-Hexyl, 2-ethylbutyl	1	Th(IV)[a]	1669
n-Butyl, *n*-octyl, Ph	1,2	Pu(III), Pu(IV), Pu(VI), Pa(V)[a]	1661, 1662
Ph, *n*-butyl, *n*-octyl	1–3	Am(III)[a]	1636, 1670
Ph	1, 4, 5	Am(III), Cm(III), Cf(III)[h], etc.	1671
Ph, *n*-octyl	2	U(VI)[a]	1672, 1673

Miscellaneous ligands				
Reagent	R	*n*	Metal	Ref.
$Ph_2P(O)CH_2P(O)R_2$ (R = octyl)	—	—	Eu(III), Am(III)[c]	1655, 1656 1674
cis- and *trans*-$R_2P(O)CH{=}CHP(O)R_2$	Ph	—	Mo(VI)[a]	1675
	Ph, *p*-Tol	—	Eu(III), Am(III), Pu(III), Pu(IV), Pu(VI), Pa(V), U(VI)[a,c]	1660–1662, 1668 1673, 1676, 1678
$Ph_2P(O)C{\equiv}CP(O)Ph_2$	—	—	Pu(III), Pu(IV), Pu(VI), Pa(V), U(VI)	1660, 1662 1673
$Ph_2P(O)CH(R')P(O)Ph_2$ (R′ = Cl, allyl etc)	—	—	Eu(III), Am(III), Cm(III)[a,c] Bk(III), Cf(III), Es(III), Eu(III), U(VI)	1658, 1668
$p\text{-}C_6H_4[CH_2P(O)R_2]_2$[i]	*n*-Octyl	—	Mo(VI), Ga(III)	1324, 1325, 1382

(*continued*)

TABLE 26. (*continued*)

Miscellaneous ligands				
Reagent	R	*n*	Metal	Ref.
o-, *m*-, *p*-$C_6H_4[CH_2P(O)Ph_2]_2$	—	—	Eu(III), U(VI), TPE, Pu(IV), U(IV), etc.	1678, 1679
$R_2P(O)(CH_2)_nP(O)R_2$–HA:				
HA = Hbfa, Hpvtfa	Ph	1,2	Zn(II)	1472, 1473
Hbfa	Ph	1,2	Eu(III)[c]	1473, 1515, 1680
Htta	*n*-Hexyl	1,3,4	Eu(III)[e]	1473, 1515, 1680
Htta	Ph	2	Ln(III)[b](except Ce, Pm, Er, Lu)	1681
Hpmtfp	Ph	1	La(III), Pr(III), Eu(III)[c], Ho(III), Yb(III)	1524, 1525
Hpmbp	Ph	1	Am(III)[a]	1677

[a] HNO_3.
[b] $LiNO_3$–KNO_3 (eutectic, 160 °C).
[c] $HClO_4$.
[d] H_2SO_4.
[e] HCl.
[f] HNO_3–H_3DO_4.
[g] H_3PO_4.
[h] $NaNO_3$.
[i] *p*-xylene–αα′-diylbis(di-*n*-octylphosphine oxide).

americium as compared with europium appears to be responsible for this difference. Americium(III) and curium(III) were extracted as $[M(tta)_3(topo)_2]$ from 0.01 M HCl with Htta–topo in different organic solvents[1318,1319]. The highest extraction was found with cyclohexane as the diluent and the lowest with $CHCl_3$. Further, the extraction constant (K_{ex}) decreased in the order topo > Ph_3PO > tbp (3320, 7.0 and 0.11, respectively). Htta–Bu^n_3PO and Hdbm–topo have also been used for the synergistic extraction of americium(III)[1310,1514].

Htta–topo in cyclohexane has been exploited for the separation of traces of americium(III) from other rare earths or actinide congeners in HNO_3 media [1628]. The method involved prior oxidation of americium(III) to americium(V) using aqueous peroxodisulphate solution. Americium(V) remained in the aqueous phase, whereas the other elements (e.g. Ce, Eu, Cm, Pm) were extracted. Interestingly, the Cm/Am separation factor depended on the concentration of the oxidant, being 2187 for 0.05 M $(NH_4)_2S_2O_8$ vs 389 for 0.25 M $(NH_4)_2S_2O_8$. This decrease in the separation factor was attributed to the coordination of curium(III) by the peroxodisulphate ions. The *D* values for the elements extracted decreased in the order Cm > Ce > Pm > Eu (105, 89.5, 76.3 and 63.7, respectively). The separation of americium(III) from Ce, Eu, U, Np, Pu, Cm, Bk and Cf was effected with Hpmbp–topo in C_6H_{12}[1629] in a similar way to that described for Htta–topo[1628]. The extraction of americium(III), curium(III), californium(III) and berkelium with Hpmbp–R_3PO varied with R in the sequence[1630,1631] topo > Ph_3PO > Bu^n_3PO > Ph_3PS. A comparative study[1631,1632] of the extraction of TPE with β-diketones and pyrazolones along with topo showed an extraction sequence Hbfa < Htta < Hpmdbp < Hpmbp. Interestingly, the extraction of americium(III) from $HClO_4$ by 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-thione (HA) in benzene was undetectable; however, the addition of topo led to the synergistic extraction as [AmA$_3$(topo)$_2$] with a selectivity of 68 for americium over europium[1529]. Finally, mono-2-ethylhexylphosphoric acid–topo in toluene extracted americium(III) from HCl, but the synergism was lower than that for thulium, yttrium, and europium[1533].

b. Extraction with di-tertiary phosphine oxides. This section describes the liquid–extraction chemistry of di-tertiary phosphine oxides. A previous review in this area gives an excellent account of their solvent extraction properties[36]. For a balanced treatment, a summary of various extraction systems is given in Table 26, from which some interesting conclusions can be drawn:

a. Generally, the metals were extracted as [Sc(NO$_3$)$_3$L$_2$], [Y(NO$_3$)$_3$L$_2$], [MoO$_2$LCl$_2$], [GaCl$_3$L$_m$] ($m = \frac{1}{2}$ or 1), [ZnA$_2$L], [M(NO$_3$)$_3$L$_n$] M = Ce, Nd, Pm, Eu, etc.; $n = 1$–3), [Th(NO$_3$)$_4$L$_2$], [ML$_m$(ClO$_4$)$_3$] ($m = 2, 3$; M = Eu, Am), [UO$_2$(NO$_3$)$_2$L] and [MA$_3$L], (M = La, Eu, etc.; HA = β-diketone or pyrazolone).
b. Di-tertiary phosphine oxides are better extractants than monotertiary phosphine oxides, probably owing to the chelate effect and the more hydrophobic environments created by the bulky organophosphorus moieties of the bidentate ligands.
c. dpmO$_2$ and *cis*-R$_2$P(O)CH=CHP(O)R$_2$ (R = Ph, *p*-Tol) are for superior extractants to other bidentate ligands. There is no clear relationship between the extraction efficiency and chain length, although ligands with smaller numbers of CH$_2$ groups generally showed higher extraction.
d. *trans*-Ph$_2$P(O)CH=CHP(O)Ph$_2$ and Ph$_2$P(O)C≡CP(O)Ph$_2$ are poor extractants in comparison with the bidentate ligands discussed above[1673].
e. When a phenyl or aryl group on phosphorus is replaced with an alkyl group such as butyl, hexyl, octyl or ClCH$_2$CH$_2$, PhCH$_2$, the extraction decreases. This difference is attributed to aryl stabilization, which is an entropy effect[1638,1682,1683]. Further, the introduction of electron-withdrawing substituents on phosphorus leads to a decrease in extraction and vice versa[1684,1685].
f. The extraction of a metal in the presence of H$_3$PO$_4$ was low, owing to possible complexation of the metal ion together with extensive hydration of the complex. Generally, the extraction decreased in the sequence $HNO_3 \approx HClO_4 > HCl > H_2SO_4 > H_3PO_4$.
g. Using Ph$_2$P(O)CH$_2$P(O)Ph$_2$ and hydroxyethylenediphosphoric acid[1686], a separation factor for Am/Fe of $> 10^4$ (from HNO$_3$) was achieved, making the quantitative separation of the two possible.
h. Stability constant data on TPE with Ph$_2$P(O)(CH$_2$)$_n$P(O)Ph$_2$ ($n = 1,4,5$) revealed that the order of extraction of the metals was Am > Cm ≫ Cf[1671]. Further bidentate phosphine oxides with branched groups were most effective for the extraction of TPE[1687].
i. The replacement of hydrogen in the methylene of dpmO$_2$ by other atoms or groups such as allyl, Cl or *n*-dodecyl lowered the extraction[1658].
j. Ph$_2$P(O)(CH$_2$)$_4$P(O)Ph$_2$ was shown to possess a separation factor for Eu/Am of $> 10^4$ in the molten state[1637]; other ligands also showed a higher extraction of lanthanides over actinides.
k. R$_2$P(O)CH$_2$P(O)R$_2$(R = *n*-hexyl,2-ethylbutyl) showed quantitative extraction of thorium(IV) from nitrate media[1669].
l. Uranium(VI) and Protactinium(IV) were separated from cerium(III) in acidic solution using Ph$_2$P(O)CH$_2$CH(R)P(O)Ph$_2$[1688]. For R = Me, a maximum separation factor for plutonium(IV)/uranium(VI) was achieved from 1 M HNO$_3$. Curium(III), cenium(III) and europium(III) were poorly extracted. Addtition of H$_2$dehp had no effect.

m. The replacement of PO with SO (sulphoxide) was shown to lower the extraction. For example, for the extraction of europium(III) and americium(III) [1659] the extraction capacity decreased in the order PO–PO > PO–SO > SO–SO.

n. *o*- and *m*-$C_6H_4(CH_2P(O)Ph_2)_2$ were shown to possess high degrees of specificity, which in turn depended on the size of the metal ion[1658]. The *O*-substituted isomer was highly selective for uranium(VI) (U/Am separation factor $= 10^5$), whereas the *m*-substituted isomer was selective for americium(III) and was 3×10^3 times better than the *o*-substituted isomer.

c. Extraction with poly-tertiary phosphine oxides. Only a few investigations of the use of poly-tertiaryphosphine oxides have been made. The ligands used and the metals extracted are $\{Ph_2P(O)CH_2\}_2P(O)R$ (R = Ph, OH, OEt) for zirconium(IV) and hafnium(IV)[1689,1690] and 1,3,5-$C_6H_3\{CH_2P(O)Ph_2\}_3$, 1,2,4,5-$C_6H_2\{CH_2P(O)Ph_2\}_4$ and 2,3,5,6-$C_6H_2\{CH_2P(O)Ph_2\}_4$ for TPE, uranium(VI) and europium(III)[1658,1678]. It was observed that these ligands did not provide any enhanced extraction over bidentates, probably owing to steric factors.

d. Extraction with mono- and di-tertiary phosphine sulphides/selenides. Extraction studies on tertiary phosphine sulphides or selenides are few[21] compared with the extensive work reported on tertiary phosphine oxides. Bu^n_3PS quantitatively extracted silver(I) from H_2O and HNO_3 media[1691,1692,1693], gold(III) from HNO_3[1692] and mercury(II) from 0.1 M HCl and HNO_3 media[1691,1692]. Extraction of other metals such as copper(II), zinc(II), lead(II) and bismuth(III) was poor ($D < 0.56$)[1691,1692]. Using Bu^i_3PS and Oct_3PS, more than 95% recovery of mercury(II) from waste waters and waste solids was achieved[1695]. In a study with Cl^- or SCN^- media, the formation of $[HgX_2L_n]$ ($n = 1,2$; L = Bu^i_3PS, Oct_3PS, X = Cl, SCN)[1694] was established.

n-Oct_3PS showed high levels of extraction of silver(I), mercury(II) and palladium(II) from HNO_3 media[1695]. From HCl media extraction of mercury(II) was less ($D = 10\,600$ vs 586) and gold(III) showed high extraction ($D = 6280$)[1695]. Increasing the HCl concentration enhanced the extraction of gold(III) and lowered that of mercury(II). Extractions of palladium(II), platinum(IV), molybdenum(VI) and selenium(IV) from HCl were poor or nil (platinum)[1695].

Bu^i_3PS and di-2-ethylhexylphosphoric acid in Varsol DX-364 quantitatively extracted silver(I) or palladium(II) from dilute H_2SO_4[1697]. The extraction using Bu^i_3PS in toluene from HNO_3 media was also quantitative[1697]. Similarly, Pr^i_3PS is highly selective for silver(I), from acidic sulphate solutions containing copper(I) and zinc(II)[1698]. Ph_3PS in $CHCl_3$ was also used for the extraction of silver(I) deposited on electrodes[1699]. Bu^i_3PS in toluene or a mixture of Bu^i_3PS, 2-ethylhexanol (or *p*-nonylphenol)[1700,1701] and di-*n*-hexyl sulphide extracted palladium(II) from HCl solutions [1702–1704] containing Pd, Pt, Rh and Ni. In the absence of the alcohol or phenol, precipitates are formed. The formation of $[PdCl_2L_n]$ ($n = 1,2$) was identified[1700–1701].

n-Oct_3PSe is a very suitable extractant for palladium(II), the *D* value being $> 10^3$ versus $(C_{10}H_{21})_2(C_8H_{17})PS$ or $(C_9H_{19})_2(C_{10}H_{21})PS$ ($D \approx 500$)[1705]. *D* values for platinum(II), rhodium(I) and iridium(I) were low. However, in another study, Bu^n_3PS and Ph_3PS were used for the recovery of the fission product rhodium from aqueous HNO_3[1706].

Rhenium(VII) showed higher extraction with *n*-Oct_3PE in the sequence *n*-Oct_3PO > *n*-Oct_3PS > *n*-Oct_3PSe[1707].

Studies on di-tertiary phosphine sulphides are limited[1699,1708,1709]. However, these reagents were found to be more efficient extractants for silver(I) and mercury(II) than Ph_3PS ligands[1699,1708,1709].

2. Reversed-phase chromatography

Reversed-phase chromatography (RPC) is another useful technique for the separation of metals. Here a paper or a resin acts as a solid phase which is soaked with a suitable organophosphorus reagent. Investigations in this area are few compared with liquid–liquid separations.

a. d-Block elements. Zirconium(IV) was recovered from HNO_3 solution by sorption on macroporous styrene–divinylbenzene resin saturated with Bu^n_3PO. The extraction was increased by the use of a solid extractant, eliminating loss of the reagent[1710].

Tantalum(V) (in traces) was selectively removed from a niobium extract (Nb 76.3 g l^{-1}, Ta 0.08 g l^{-1})[1711] containing tantalum and other metal ions in addition to HF, NH_3, K^+ or H_2SO_4, by sorption with topo fixed on porous polypropylene beads. The spent sorbent was regenerated by eluting the tantalum into an aqueous solution containing NH_4^+, K^+ or HF.

Noble metals (Rh, Pd, Pt, Au, Ir) were separated and determined by paper and column reversed-phase chromatography using tris(2-ethylhexyl)phosphine oxide as the extracting agent[1712]. Topo has been used to remove cobalt(II) from cations sorbed on anion-exchange resins[1713]. Ruthenium(III) was equilibrated between a 2 M HCl phase and a solid phase consisting of R_3PO ($R =$ n-butyl or octyl) on Kieselguhr[1414]. Addition of *n*-octanol or cyclohexanol lowered the extraction of ruthenium(III) due to hydrogen-bonded interaction with R_3PO.

b. Main Group elements. Gallium(III) was separated from 2–6 M HCl solutions of a number of binary and multi-component mixtures with topo as a stationary phase on a silica gel column[1714]. The method was suitable for the separation of trace amounts of gallium from bauxite samples. Similarly, selenium(IV) and tellurium(IV) were extracted from 4–6 M HCl solution and separated from several elements with topo fixed on a resin as the stationary phase[1715].

Various alkali metals were separated from each other, e.g. Li from Na, Be from Mg, using methylenebis(di-*n*-hexylphosphine oxide) as the stationary phase in RPC (paper and column)[1716].

c. Lanthanides and actinides. The distribution of rare earth elements (Ce, Nd, Eu and Gd), Am and Cm between dilute HNO_3 and isopentyldialkylphosphine oxide–solid resin sorbent was studied under static and dynamic conditions[1717]. The separation factors $Cm/Ce = 500$, $Cm/Nd = 260$, $Cm/La = 250$, $Cm/Eu = 14$ and $Cm/Gd = 14$ indicate the possibility of group separation of TPE and rare earth elements. Separation of TPE and rare earths from palladium was also studied.

A series of rare earths were separating using methylenebis{di(2-ethylhexyl)phosphine oxide} as the stationary phase in RPC[1718]. The separation factors were higher in HNO_3 than in $HClO_4$ or HCl solutions. Lanthanum, cerium, thorium and uranium were recovered from HNO_3 solution by sorption on macroporous divinylbenzene saturated with phosphine oxides such as Bu^n_3PO[1710]. Various rare earth impurities present in traces in Sc_2O_3 were separated with topo as a stationary phase in RPC prior to their determination by inductively coupled plasma atomic emission spectrometry (ICP-AES)[1719]. Similarly, methylenebis(di-*n*-hexylphosphine oxide) and topo were used as the stationary phases in RPC to separate the rare earths from each other[1716]. The D values generally increase as the charge to radius ratio of the unhydrated cation increases.

Uranium and thorium were separated from H_3PO_4 solutions by trialkylphosphine oxide (R_3PO, R groups containing C_7 or C_8 atoms) fixed on Levextrel resin[1720]. The separation of uranium(VI) from solutions using topo and polyurethane foam is efficient and specific[1721]. A desorption method was investigated which recovered 77.3% of the uranium and 94% of the topo from an ore. The absorption and desorption steps are fairly specific for uranium, although other actinides could interfere.

A column of glass beads coated with tri-*m*-tolylphosphine oxide adsorbed uranium from partially digested urine[1722]; the recovery was 73%. Uranium(VI) was transported from acidic media with topo as a liquid membrane supported on a microporous polymer in the form of a flat sheet or tube[1723]; the uranium(VI) was extracted as $[UO_2(NO_3)_2L_2]$.

The recovery of plutonium even at trace levels from nitric acid waste was best carried out with topo sorbed on Amberlite XAD-4 resin as compared with the use of tbp, dihexyl-*N*,*N*-diethylcarbamoylmethylphosphine oxide or octylphenyl-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide[1724,1725]. Topo on Dowex 1-X4 (50–100 mesh) was found to be superior to Amberlite XAD-4 for the recovery of plutonium[1726].

Topo supported on a microporous polyethylene (Microthene) was used to separate uranium from radium-226 present in phosphorites and their industrial derivatives[1727]. Trialkylphosphine oxide–GDX-301 resin separated uranium from acidic solutions of pH 5.8–6.2[1728]. Htta–topo extracted uranium, neptunium and plutonium from the waste water of a nuclear plant; the extract was passed over active carbon, which led to their separation by adsorption[1729]. A liquid membrane system consisting of H_2dehp–topo on Escaid 100 extracted uranium from H_3PO_4[1730]. The emulsifier Paranox was used at 3% in a solution containing 5 M H_3PO_4 and 5 g l^{-1} of iron(II) at 45 °C. In a continuous process treating 5 l min^{-1} of H_3PO_4, the recovery of uranium was $>90\%$. Divinylbenzene copolymer resin impregnated with H_2dehp–topo selectively adsorbed uranium from wet-process H_3PO_4 solutions[1731]. Uranium was recovered from wet-process H_3PO_4 by extraction with a liquid membrane with H_2dehp–topo showing a synergistic effect[1732].

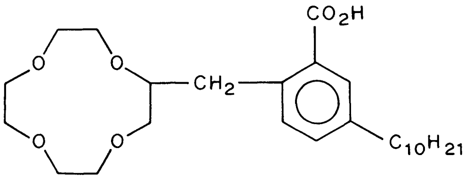
Recently, sorption of europium and actinides was carried out by means of octylphenyl-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide loaded on silica[1733].

3. Ion-selective electrodes

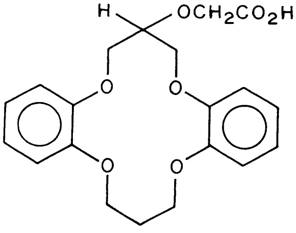
a. Alkali and alkaline earth elements. Topo acted as a neutral lithium carrier in a lithium ion-selective electrode membrane[1734]. Thus, when topo was used with 1% potassium tetrakis (*p*-chlorophenyl)borate in *o*-nitrophenyl octyl ether–PVC membrane, the electrodes exhibited a nearly Nernstian response with an Li/Na selectivity of 1:60, better than that achieved with previous electrode sensors. Further, topo dramatically improved the Li/Na selectivity of a 14-crown-4 electrode and was used for analysing diluted serum samples. The addition of topo and lipophilic $Bu^n_4BF_4$ to a PVC membrane lithium ion-selective electrode (based on synthesized non-cyclic neutral carriers) showed an increased selectivity for lithium over the other alkali metal ions[1735]. The selectivity coefficient ($\log k_{Li,M}$) increased from 1.5 to 2.2 for Li^+ over Na^+ and from 2.0 to 3.0 for Li^+ over K^+. The results obtained are of practical use in developing lithium ion-selective electrodes, as the proposed additives exert positive effects on several kinds of non-cyclic lithium-selective carriers in PVC matrix ion-selective electrodes.

PVC membranes made from ether carboxylic acid ionophores (crowns) (**165** or **166**) and potassium tetrakis(*p*-chlorophenyl)borate, with or without topo as additive, when coated on the tips of silver wires and combined with flow-injection analysis showed increased selectivity[1736]. Membranes made from **165** and topo showed increased selectivity for K over Na, Rb, Cs and Sr at low contents of phenylborate and decreased selectivity for K over Li, Ca and Mg at high contents of phenylborate; however, topo enhanced the selectivity of potassium over the cations examined, excluding lithium. For membranes of **166**, the addition of topo decreased the selectivity for Cs over Rb, K, Na, Li and Mg, whereas the selectivity was increased over Ca and Sr.

The selectivity characteristics of ion-selective electrodes, especially Ca^{2+} ion-selective electrodes based on $R_2PXP(O)R_2\{X = CH_2,\ o\text{-}C_6H_4(CH_2)_2,\ R = \text{alkyl, Ph or Tolyl}\}$



(165)



(166)

have been studied using several plasticizing agents with different dielectric constants such as dioctyl phthalate and dibutylphthalate[1737]. The selectivity depends on the concentration of lipophilic anion in the membrane. An electrode based on tetratolyl-*o*-xylylenediphosphine dioxide[1738] was best for Ca^{2+}. Using the *meta*- in place of the *ortho* isomer made it possible to develop a calcium ion-selective electrode with a high magnesium selectivity, ($K_{Ca/Mg} = 1.8 \times 10^{-5}$)[1739].

b. Main Group elements. Trace antimony(III) in water was preconcentrated by electrolytic deposition on a topo-modified wire electrode before its determination by atomic absorption spectrometry (AAS)[1740]. Various metal ions and organic compounds did not interfere. In another study, antimony(III) in water was determined by potentiometric stripping analysis with a topo-modified glassy carbon electrode[1741]. Improvements in the characteristics of the electrode depend on the complex absorbing property of the thin film on the surface of the modified electrode. Such modified electrodes show good reproducibility and sensitivity.

In cyclic voltammetric experiments, a gold film electrode modified with a film of topo in a PVC matrix showed that the electrode is useful for highly selective determinations of a number of metals, namely antimony, bismuth and lead[1742].

c. Transition elements. Technetium-(IV) and -(VII) were concentrated from 3 M HCl by complexing them with topo applied as a thin layer to a glassy carbon electrode[1743–1744]. After an enrichment time of 10 min, about 1.8×10^{-8} M technetium(VII) could be determined using differential-pulse cathodic stripping voltammetry. Technetium(IV) produces a peak near that of technetium(VII) and can therefore be used for a rough estimation of the technetium(VII)/technetium(IV) ratio.

A gold film electrode modified with a film of topo in a PVC matrix showed that the electrode is useful for the highly selective determination of chromium, iron, mercury and uranium[1742]. Down to 0.02–50 ppm of mercury in environmental samples (e.g. river sediments) can be determined with good precision and accuracy. A topo-modified mercury electrode was used for the preconcentration of cadmium(II) by immersing the electrode in cadmium(II) solution prior to its determination by cyclic voltammetry[1745]. A topo-coated glassy carbon electrode was used for the voltammetric determination of uranyl ions after preconcentration on a topo layer[1746]. The method was fairly selective for UO_2^{2+} because the topo layer electrochemically masked some metal ions which gave reduction waves at a glassy carbon electrode without a topo coating. A mercury film electrode modified with a film of topo in a PVC matric was used for the galvanostatic stripping determination of bismuth in copper alloys[1747]. The method is simple, selective and rapid, but tin(IV) interferes (the detection limit was 0.002–0.5% of bismuth).

In a recent study, organotransition metal complexes were used as selective surfaces for the reversible detection of SO_2 with a piezoelectric crystal sensor[1748]. For instance, $[Mn(OPPh_3)_4(SO_2)_2I_2]$ was identified as a candidate coating for the reversible detection of SO_2 on piezoelectric crystal sensors. A specified copper complex acts as a reversible coating for the detection of SO_2 in the range 10–1000 $mg\,l^{-1}$.

4. Miscellaneous applications

a. Extractive and direct determination of metals. This section covers some applications not discussed earlier. The only application in which organophosphorus reagents have been used for direct determination without extraction is in the determination of palladium and rhodium using $Ph_2PCH_2CH_2P(O)Ph_2$ and $\{Ph_2P(O)CH_2CH_2\}_2P(O)Ph$. Metals such as platinum, iridium, copper, nickel and cobalt did not interfere[1749]. Mono-phosphine oxide formed 1:2 and 1:4 complexes and tris-phosphine oxide formed 1:2 complex with palladium. Rhodium formed 1:6 and 1:3 complexes respectively. Topo–mibk extracted trace metals (Ag, Bi, Cd, Pb, Se, Te, Sn and Zn) present in steels and superalloys as their iodo complexes prior to their determination by AAS[1750]. Similarly, this extractant separated Cu, Zn, Mo, Ag, Cd, In, Sn, Sb, Te, Tl, Pb and Bi from the matrix of geological samples which were subsequently determined by AAS[1751].

A series of elements, Cd, Mn, Pb, Co, Ni and Cu, were quantitatively separated and concentrated from sea water using a low concentration of topo-1,1,1-trifluoro-4-mercapto-4(2-thienyl) but-3-en-2-one in cyclohexane[1752] before their determination by AAS. Topo–dithizone in ethyl benzoate extracted Cd, Ni, Fe, V, Cu, Pb, Zn, Ti, Al, Zr and Co simultaneously[1753]. The method can be used for the preconcentration of trace metals from natural waters prior to determination. Topo-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl octane-4,6-dione in dodecane extracted several metals from aqueous chloride solutions[1754a].

Using topo–Hhfa and Triton X-100, simultaneous determination of terbium, samarium and europium was carried out[1754b]. Topo was used for the separation of rare earth elements and yttrium from geological samples followed by their determination using ICP-AES[1754c].

b. Fluorimetric determinations and related applications. Organophosphorus reagents have played a significant role in fluorescence; accordingly, this section briefly discusses analytical and related applications based on fluorescence.

Htta–topo has been used for the determination of europium and samarium by laser-excited fluorimetry[1756,1757] (emission line 619 nm for Eu and 650 nm for Sm). The detection limits were 0.2–10 ppb Eu and 0.1–1 ppm Sm. A flow-injection spectrofluorimetric[1757] method was developed for the determination of terbium(III) based on solubilizing its ternary complex with topo and pivaloyltrifluoroacetone in a micellar solution of nona (oxyethylene) dodecyl ether at pH 3.5. Excitation and fluorescence wavelengths of 310 and 611 nm were used. The accuracy and reproducibility are good up to 16 $\mu g\,l^{-1}$ of terbium(III). No interference from a 20-fold excess of rare earths tested was observed.

Fluorescent paint compositions containing fluorine-containing β-diketone and alkylphosphine complexes of europium or terbium are useful for commercial displays[1758]. Thus $[Eu(HFA)_3(topo)]$ complex was mixed with ABS-100 paint and a thinner to give a composition which was screen-printed onto an acrylic plate and dried. The print showed bright-red fluorescence on UV irradiation.

B. Catalytic Applications

Most of the catalytic applications pertain to complexes of tertiary phosphine oxides and are discussed here. The applications of complexes of tertiary phosphine chalcogenides, which are few, were described in a recent review[21].

TABLE 27. Metal complexes as catalysts

	Catalyst	Applications	Ref.
		d-Block elements	
A	(i) $[TiCl_4(OPPh_3)]$	In pinacol rearrangement of benzpinacol	59
	(ii) $TiCl_3–Ph_3PO–AlCl_3$	For preparation of polybut-1-ene foam from but-1-ene at 80 °C	1759a
B	(i) $[CrO(O_2)_2(OPPh_3)]$	It oxidized tetralin and cyclohexene at 20 °C in the presence of Me_3COOH to give tetralone and cyclohex-2-enone, respectively. Admantane and cyclohexane also oxidized to alcohols, etc. Safe to handle compared with $[CrO(O_2)_2L]$ (L = pyridine-*N*-oxide)	1759b
	(ii) $[CrCl_2(NO)_2(OPPh_3)_2]$, $[CrCl_3(OPPh_3)_3]$	Used for the dimerization of alkenes such as C_2H_4	1760, 1761
	(iii) $[CrCl_2L_2]$, $[CrCl_2L_2(NO)_2]$, $[CrCl_3L_3]$ and $[(CrCl_3L_2)_2]$ (L = Bu_3PO, Ph_3PO) and $RAlX_2$	Used for the dimerization, polymerization and copolymerization of ethylene and propylene	1762a
	(iv) $[Mo(NO)_2(OEt)_2(OPPh_3)_2]$ or $[Mo(N)Cl_3(OPPh_3)_2]$ and $EtAlCl_2$	Used in the metathesis of olefins such as pent-2-ene	185, 1762b
	(v) $[Mo(NO)Cl_3(OPPh_3)_2]$ and $EtAlCl_2$	Used in disproportionation of pent-2-ene to hex-3-ene and but-2-ene. Activity comparable to other known catalysts; corresponding $[W(NO)Cl_3(OPPh_3)_2]$ showed lower activity	180, 181, 1763–1767
	(vi) $[MoCl_n(NO)_{4-n}L_2]$ (L = Ph_3PO, $n = 1–3$)	Used in epoxidation of alkenes. Activity was comparable to that of $[Mo(O_2)(acac)_2]$	1768, 1769
	(vii) $[MoO_2Cl_2(OPPh_3)_2]$ and $[MoO_2Cl_2(dpeO_2)]$	Used in epoxidation of cyclohexene, $dpeO_2$ showed higher activity over Ph_3PO or even other neutral ligands such as 1,10-phenanthroline	1770
	(viii) $[MO(O_2)_2(OPR_3)_2]$ (M = Mo, W)	Used in epoxidation of alkenes	175
C	(i) $[Fe(OPPh_3)_4(I_3)_2]$	Used for oxidation of Ph_3P to Ph_3PO	1771
	(ii) $[FeX_3(OPPh_3)_2]$ (X = Cl, Br, I, NCS)	(a) Used for oxidation of Ph_3P to Ph_3PO by O_2. Bromo or thiocyanato complex showed the highest effect. The oxidation in MeCN is quantitative and selective at 30–70 °C under atmospheric pressure of O_2. For X = NCS, reduction of iron(III) to iron(II) takes place with oxidation of Ph_3P to Ph_3PO. The reduction rate depends on iron(III) to Ph_3P ratio. Order of activity: NCS > I > Br > Cl	278, 302, 303, 1772–1775
		(b) Selective catalyst for organic compounds	1776
	(iii) $[M(NO)_2(R_3PO)X]$ (M = Fe, Co; R = alkyl or aryl; X = Cl, Br, I)	Used in the dimerization of dialkenes	1785

D	(i) $[CoI_2(OPPh_3)_2]$	Used in reductive carbonylation of MeOH to MeCHO	1777
	(ii) $[Co(NO_3)_2(OPPh_3)_2]$ and Et_3Al	Used for the hydrogenation of butadiene or isoprene	1780
	(iii) $[Rh(hdmg)_2(O_2)L]$ ($L = Ph_3PO$; H_2dmg = dimethylglyoxine) and $NaBH_4$–NaOH	Used for preparing cyclododecane and in hydrogenation reactions	1778, 1789
	(iv) $[Rh(CO)_2(acac)(topo)]$	Used for hydroformylation and oxidation of aldehydes. E.g. C_2H_4 was converted to EtCHO which then gave $EtCO_2H$, $(EtCO)_2O$ and some Et_2CO	1781
	(v) $[Rh(cod)(L)](ClO_4)$ ($L = dpmO_2$, $dpeO_2$)	Used for reduction of cyclohexene and acetophenone	961
E	(i) $[NiCl_2L_2]$ ($L = Ph_2EtPO$, etc.)	Used for hydrosilylation of alkenes by alkyldichlorosilanes	392, 1782
	(ii) $[NiCl_2(OPR_3)_2]$ (R = Bu, Ph) and $EtAlCl_2$	Used for dimerization of alkenes	1783
	(iii) $[NiX_2(OPR_3)_2]$ (X = Cl, Br, NO_3; R = alkyl or aryl)	Used for hydrosilylation of alkenes ($RCH{=}CH_2$, R = hexyl, pentyl). Alkyl catalysts were more effective than aryl catalysts	1784
	(iv) $[Ni(NO)LX]$ (X = Cl, Br, I; $L = R_3PO$)	Used for dimerization of conjugated dialkenes	1785
	(v) $[NiX_2L_2]$ (X = Cl, Br; $L = Bu_3PO$, Bu_2PhPO, etc.)	Used for preparing organosilanes from reaction hydrosilanes and alkenes at 100–120 °C	1786
F	Copper(II)–R_3PO complex	Used in the preparation of carbonic esters	1787
		Main Group elements	
G	$AlCl_3$–Ph_3PO complex	(a) Used for the preparation of poly(oxazolidones) from phenyl isocyanate and phenyl glycidyl ether	1788
		(b) Used in synthesis of model 2-oxazolidone and poly(oxazolidones) involving terpolymerization of (3-vinylphenylazo)methylmalodinitrile, (3-vinylphenylazo)phenyl sulphide or 1-(3-vinylphenylazo)-1,1-diphenylmethyl acetate with methylmethacrylate and butane-1,4-diol dimethylacrylate	1789
H	(i) $[Bu_2SnX_2]$–Ph_3PO (X = Cl, NCS)	Used as latent cross-linking catalysts for the manufacture of flexible polyurethane foam with good heat resistance (up to 140 °C in air)	1790
	(ii) $[Bu_3SnI(Bu_3PO)]$	Used in the addition of CO_2 to oxetone giving trimethylene carbonate. $Bu_2SnI_2(Bu_3PO)$ showed no activity. Hence the coordination mode of ligands and the stability of the complexes are important	1791

(*continued*)

TABLE 27. (*continued*)

	Catalyst	Applications	Ref.
I	(i) $[SbF_3L_n]$ ($n = 2$ for Ph_3PO and 1 for $dpmO_2$)	Used for polycondensation of the monomer forming non-discoloured poly(ethylene terephthalate), which is useful as thermoplasts for fibres, yarns and films	1792a
	(ii) $[SbX_3L]$ $\{X = Cl, F;$ $L = R_2P(O)(CH_2)_nP(O)R_2;$ $R = Me, Pr^i, Ph;$ $n = 1{,}2\}$	Used for polymerizations, oligomerizations and oxidations	1792b
	(iii) $[SbCl_5(OPPh_3)]$	Used for pinacol rearrangement of benzpinacol	59
		s-Block elements	
J	(i) $[LiBr(OPPh_3)]$	Used for rearrangement of epoxides to carbonyl compounds. Thus 1-methylcyclohexene epoxide was converted into 1-methylcyclopentane-1-carboxaldehyde	1793
	(ii) $[LiClO_4(OPPh_3)]$	Showed similar catalytic properties, but the products were different. Thus 1-methylcyclohexene gave 2-methylcyclohexanone and a small amount of 1-methylcyclopentane-1-carboxaldehyde	1793

Table 27 describes various metal complexes of phosphine oxides which have been used as catalysts for various organic reactions. It can be seen that complexes of the d-block elements have generally been used, whereas complexes of the main group elements have been used comparatively little and only a few s-block element complexes have been used. There is no complex of an f-block element whose catalytic properties have been explored. From Table 27 it can be seen that a variety of organic reactions have been catalysed and that in some cases phosphine oxide complexes were superior to other known catalysts. Examples given in Table 27 and those in the previous review[21] provide further scope for organic reactions which can be studied using metal complexes of phosphine oxides or chalcogenides.

VI. CONCLUSIONS

From this survey of the literature, it is apparent that the coordination chemistry of tertiary phosphine oxides, sulphides and selenides has been extensively studied; the work on phosphine telluride chemistry is limited, however. Further, the work on mono-tertiary phosphine oxides, sulphides and selenides is much greater than that on di- and poly-tertiary phosphine oxides and chalcogenides. However, it should be pointed out that the coordination chemistry of di- and poly-tertiary phosphine oxides and chalcogenides will continue to attract attention, particularly in opening up new areas where anionic ligands of the type $\{R_2P(E)\}_2CH^-$ and $\{R_2P(E)\}_3C^-$ and unsymmetrical phosphorus ligands such as $R_2P(CH_2)_nP(E)R_2$ and $R_2P(S)(CH_2)_nP(Se)R_2$ ($E = O, S, Se$; $R =$ aryl or alkyl) can be used. Their coordination chemistry is rich in NMR spectroscopy and interesting from the point of view of both metal–ligand bonding and the formation of homo- and hetero-polymetallic complexes. A new ligand, the neutral methanide $Ph_2P(S)CHPPh_2Me$, discussed in connection with the gold chemistry of phosphine chalcogenides[1221], is likely to attract attention on a significant scale in view of its interesting bonding properties.

It may be noted that most of the coordination chemistry of these ligands reported so far has been with transition metals, while Main Group and s-group elements have been poorly studied, with a few exceptions such as tin–bis(phosphine oxide) chemistry. Further studies may be expected for various complexes mentioned in the text.

Apart from coordination chemistry of tertiary phosphine oxides, these ligands have been used (a) for the extraction of metals (liquid–liquid separation), (b) in reversed-phase chromatography for the separation of metals (c) in ion-selective electrodes, (d) for extractive and direct determination of metals and (e) for the fluorimetric determination of metals. Complexes of these ligands have also been used in the catalysis of several organic compounds. Similarly, tertiary phosphine chalcogenides find use in these areas but to only a very small extent. However, great scope exists for the development of the metal extraction chemistry (and related areas) of tertiary phosphine chalcogenides.

VII. ACKNOWLEDGEMENTS

The author thanks Randhir Singh, Pushvinder Kaur, Dr Kuldip Singh and Dr Maninderjeet Kaur for their help in collecting literature in part related to Section II.A. He is also grateful to his wife for bearing patience and to his children for preliminary help. Library facilities provided by the Guru Nanak Dev University and Delhi University are also gratefully acknowledged.

VIII. REFERENCES

1. C. A. McAuliffe (Ed.), *Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands*, Macmillan, London, 1973.

2. C. A. McAuliffe and W. Levason, *Phosphine, Arsine and Stibine Complexes of the Transition Elements*, Elsevier, Amsterdam, 1979.
3. G. Booth, *Adv. Inorg. Chem. Radiochem.*, **6**, 1 (1964).
4. G. Booth, in *Organic Phosphorus Compounds* (Eds G. Kosolapoff and L. Maier), Vol. , Wiley, New York, 1972, p. 433.
5. O. Stelzer, Top. Phosphorus Chem., **9**, 1 (1977).
6. W. Levason and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, **14**, 173 (1972).
7. W. R. Cullen, *Adv. Inorg. Chem. Radiochem.*, **15**, 323 (1972).
8. L. Sacconi and F. Mani, *Transition Met. Chem.*, **8**, 179 (1982).
9. D. I. Hall, J. H. Ling and R. S. Nyholm, *Struct. Bonding (Berlin)*, **15**, 3 (1973).
10. J. R. Verkade and K. J. Koskran, in *Organic Phosphorus Compounds* (Eds G. Kosolapoff and L. Maier), Vol. 2, Wiley, New York, 1972, p.1.
11. F. Matthey, J. Fischer and J. H. Nelson, *Struct. Bonding (Berlin)*, **55**, 153 (1983).
12. R. J. Puddephatt, *Chem. Soc. Rev.*, **12**, 99 (1983).
13. C. A. McAuliffe, in *Comprehensive Coordination Chemistry* (Eds G. Wilkinson, R. D. Gillard and J. A. McCleverty), Vol. 2, Pergamon Press Oxford, 1987, p. 989.
14. L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, **3**, 453 (1964).
15. W. Levason, in *The Chemistry of Organophosphorus Compounds* (Ed. F. R. Hartley), Chapter, 15, Vol. 1, p. 567 Wiley, New York, 1990.
16. R. H. Pickard and J. Kenyon, *J. Chem Soc.*, 262 (1906).
17. L. Malatesta, *Gazz. Chim. Ital.*, **77**, 518 (1947).
18. E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1959 (1960).
19. N. Kuhn, H. Schumann and G. Wolmershaeuser, *J. Chem. Soc., Chem Common.*, 1595 (1985).
20. S. O. Grim, P. H. Smith, S. Nittolo, H. L. Ammon, L. C. Satek, S. A. Sangokoya, R. K. Khanna, I. J. Colquhoun, W. McFarlane and J. R. Holden, *Inorg. Chem.*, **24**, 2889 (1985).
21. T. S. Lobana, *Prog. Inorg. Chem.*, **37**, 495 (1989).
22. C. Draguescu and N. Valceanu, *Stud. Cercet. Chim.*, **16**, 141 (1968); *Chem. Abstr.*, **69**, 32536v (1968).
23. A. C. Massabni, *Ecletica Quim.*, **1**, 81 (1976).
24. M. L. R. Gibran and W. Saffioli, *Ecletica Quim.* **1**, 105 (1976).
25. U. Casellato, P. A. Vigato and M. Vidali, *Coord. Chem. Rev.*, **36**, 183 (1981).
26. V. O. Gel'mbol'dt and A. A. Ennan, *Koord. Khim.*, **9** 579 (1983).
27. C. D. Garner and K. R. Seddon, *Coord. Chem. Rev.*, **57**, 359 (1984).
28. V. V. Skopenko, Yu. L. Zub and A. A. Kapschuk, *Zh. Neorg. Khim.*, **29**, 582 (1984).
29. Z. A. Sheka and E. I. Sinyavskaya, *Usp. Khim., Koord. Soedin.*, 113 (1975); *Chem. Abstr.*, **85**, 115909a (1976).
30. T. S. Lobana and S. S. Sandhu, *J. Chem. Sci.* (*Guru Nanak Dev Univ., Amritsar*), **5**, 102 (1979).
31. N. M. Karayannis, C. M. Mikulski and L. D. Pytlewski, *Inorg. Chim. Acta. Rev.*, **5**, 69 (1971).
32. L. Maier, in *Organic Phosphorus Compounds* (Ed. G. M. Kosolapoff), Vol. 4, Interscience, New York, 1972, p.1.
33. E. W. Ainscough and A. M. Brodie, *Coord. Chem. Rev.*, **27**, 59 (1976).
34. S. R. Postle, *Phosphorus Sulphur*, **3** 269 (1977).
35. T. S. Lobna and S. S. Sandhu, *J. Chem. Sci.* (*Guru Nanak Dev Univ., Amritsar*), **4**, 37 (1978); *Chem. abstr.*, **91**, 67636j (1979).
36. T. S. Lobna and S. S. Sandhu, *Coord. Chem. Rev.*, **47** 283 (1982).
37. A. M. Rozen, Z. I. Nikolotova and N. A. Kartasheva, *Radiokhimiya*, **28**, 407 (1986).
38. T. B. Yaquero and P. G. Nadal, *Ing. Quim.* (*Madrid*), **19**, 323 (1987); *Chem. Abstr.*, **108**, 983336k (1988).
39. W. A. Ricklton and R. J. Boyle, *Sep. Sci. Technol.*, **23** 1227 (1988).
40. B. Walther, *Coord. Chem. Rev.*, **60**, 67 (1984).
41. N. Burford, B. W. Royan, R. E. V. H. Spence, T. S. Cameron, A. Linden and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 152 (1990).
42. (a) S. Ikuta and P. Kebarle, *Can. J. Chem.*, **61**, 97 (1983); (b) G. M. Bancroft, T. Chan and R. J. Puddephatt, *Inorg. Chem.*, **22** 2133 (1983). (c) G. M. Bancroft, L. Dignard-Bailey and R. J. Puddephatt, *Inorg. Chem.*, **25**, 3675 (1986). (d) B. E. Bursten, D. J. Darensbourg, G. E. Kellogg and D. L. Lichtenberger, *Inorg. Chem.*, **23**, 4361 (1984).
43. (a) J. Behan, R. A. W. Johnstone and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 444 (1978); (b) R. J. Puddephatt, G. M. Bancroft and T. Chan, *Inorg. Chim. Acta*, **73**, 83 (1983).

44. (a) M. J. Kabachnik and T. A. Mastryukova, *Russ. Chem. Rev.*, **38**, 795 (1969); (b) R. G. Goel and T. Allman, *Can. J. Chem.*, **716** (1982); (c) C. A. Streuli and W. A. Henderson, *J. Am. Chem. Soc.*, **82**, 5791 (1960); (d) B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1044 (1979).
45. (a) S. X. Xiao, W. C. Trogler, D. E. Ellis and Z. Berkowitch- Yellin, *J. Am. Chem. Soc.*, **105**, 7033 (1983);
    (b) D. S. Marynick, *J. Am. Chem. Soc.*, **106**, 4064 (1984).
46. F. A. Cotton, R, Barnes and E. Bannister, *J. Chem. Soc.*,2199 (1960).
47. G. A. Kirakosyan, V. P. Tarasov and Yu. A. Buslaev, *Magn. Reson. Chem.*, **27** 103 (1989).
48. N. P. Crawford and G. A. Melson, *J. Chem. Soc. A*, 1049 (1969).
49. J. R. Ferraro and T. V. Healy, *J. Inorg. Nucl. Chem.*, **24** 1463 (1962).
50. J. R. Ferraro, *J. Inorg. Nucl. Chem.*, **26** 225 (1964).
51. T. V. Healy, D. F. Peppard and G. W. Mason, *J. Inorg. Nucl. Chem.*, **24**, 1449 (1962).
52. E. M. Gavrishchuk, N. G. Dzyubenko, L. L. Martynenko, and P. E. Gaivor onskii, *Zh. Neorg. Khim.*, **28**, 871 (1983).
53. E. M. Gavrishchuk and N. G. Dzyubenko, *Deposited Doc. 1982*, VINIT 3676-83, 249-53; *Chem. Abstr.*, **101**, 180535p (1984).
54. P. B. Hitchcock, M. F. Lappert and A. Singh, *J. Chem. Soc., Chem. Commun.*, 1499 (1983).
55. N. P. Grawford and G. A. Melson, *J. Chem. Soc. A*, 141 (1970).
56. F. Kutek and B. Durek, *Collect. Czech. Chem. Commun.*, **35**, 3768 (1970).
57. H. Gehrke, Jr, and R. De Jong, *Proc. S. D. Acad. Sci.*, **47**, 210 (1968); *Chem. Abstr.*, **71**, 108605f (1969).
58. B. E. Bridgland and W. R. McGregor, *J. Inorg. Nucl. Chem.*, **32**, 1729 (1970).
59. J. Yamamoto and N. Maeta, *Chem. Express*, **2**, 29 (1987); *Chem. Abstr.*, **106**, 206708c (1987).
60. E. Lindner, R. Lehner and H. Scheer, *Chem. Ber.*, **100**, 1331 (1967).
61. M. B. Goehring and A. Slawisch, *Z. Anorg. Allg. Chem.*, **346**, 295 (1966).
62. A. I. Kuzmin and S. I. Kuznetsov, *Koord. Khim.*, **8** 159 (1982).
63. J. C. Sheldon and S. Y. Tyree, *J. Am. Chem. Soc.*, **80**, 4775 (1985).
64. S. Y. Tyree, Jr, *US Dep. Commer., Off. Tech. Serv., AD*, 418, 217, 3pp. (1963); *Chem. Abstr.*, **61**, 11598d (1964).
65. M. E. Ignatov, E. G. Ill'in, V. G. Yagodin and Yu. A. Buslaev, *Dokl. Akad. Nauk SSSR*, **243**, 1179 (1978).
66. F. J. Welch and H. J. Paxton, Jr, *US Pat.*, 3 422 079; *Chem. Abstr.*, **70**, P58396v (1969).
67. K. C. Malhotra, K. C. Mahajan and S. C. Chaudhry, *J. Indian Chem. Soc.*, **61**, 658 (1984).
68. R. C. Paul, P. K. Gupta and S. L. Chadha, *J. Inorg. Nucl. Chem.*, **39**, 1854 (1977).
69. R. C. Paul, P. Sharma, P. K. Gupta and S. L. Chadha, *Inorg. Chim. Acta*, **20**, 7 (1976).
70. J. Sala Pala and J. E. Guerchais, *Bull. Soc. Chim. Fr.*, **12**, 2683 (1974).
71. A. K. Majumdar and R. G. Bhattacharya, *J. Inorg. Nucl. Chem.*, **29**, 2359 (1967).
72. B. Kautzner and P. C. Wailes, *Aust. J. Chem.*, **22**, 2295 (1969).
73. S. H. Hunter, V. M. Langford, G. A. Rodley and C. J. Wilkins, *J. Chem. Soc. A*, 305 (1968).
74. G. P. Nikitina and M. F. Pushlenkov, *Radiokhimiya*, **5**, 436 (1963).
75. G. P. Nikitina and M. F. Pushlenkov, *Radiokhimiya*, **5**, 456 (1963).
76. R. K. Agarwal, A. K. Srivastava and T. N. Srivastava, *Indian J. Chem., Sect. A*, **18**, 459 (1979).
77. J. R. Chopra, A. N. Pandey, S. P. Sharma and R. K. Agarwal, *Croat. Chem. Acta*, **53**, 283 (1982); *Chem. Abstr.*, **98**, 62387p (1983).
78. R. K. Agarwal, A. K. Srivastava and T. N. Srivastava, *Curr. Sci.*, **48**, 1077 (1979); *Chem. Abstr.*, **92**, 120951g (1980).
79. M. T. H. Tarafder and A. A. M. Anwarul Islam, *Polyhedron*, **8**, 109 (1989).
80. M. T. H. Tarafder and M. A. L. Miah, *Inorg. Chem.*, **25**, 2265 (1986).
81. S. Singh, M. Bedi and R. D. Verma, *J. Fluorine Chem.*, **20**, 107 (1982).
82. L. N. Markovskii, V. D. Romanenko, V. F. Shul'gin, A. V. Ruban, A. N. Chernega, M. Yu. Antipin and Yu. T. Struchkov, *Zh. Obshch. Khim.*, **55**, 1752 (1985).
83. T. Cuenca and P. Royo, *J. Organoment. Chem.*, **293**, 61 (1985).
84. W. Hieber, J. Peterhans and E. Winter, *Chem. Ber.*, **94** 2572 (1961).
85. K. Issleib and G. Bohn, *Z. Anorg. Allg. Chem.*, **301**, 188 (1959).
86. C. C. Su and H. Y. Kang, *Proc. Natl. Sci. Counc. Republ. China, Part B*, **6**, 157 (1982); *Chem. Abstr.*, **97**, 48607h (1982).
87. B. Gahan and F. E. Mabbs, *J. Chem. Soc., Dalton Trans.*, 1713 (1983).
88. D. Collison, B. Gahan, C. D. Garner and F. E. Mabbs, *J. Chem. Soc., Dalton Trans.*, 667 (1980).

89. M. R. Caira and B. J. Gellatly, *Acta Crystallogr., Sect. B*, **36**, 1198 (1980).
90. S. M. Horner, S. Y. Tyree and D. L. Venezky, *Inorg. Chem.*, **1**, 844 (1962).
91. J. Zah-Letho, E. Samuel and J. Livage, *Inorg. Chem.*, **27**, 2233 (1988).
92. J. Cave, P. R. Dixon and K. R. Seddon, *Inorg. Chim. Acta*, **30**, L349 (1978).
93. W. Beck, H. G. Fick, K. Lottes and K. H. Schmidtner, *Z. Anorg. Allg. Chem.*, **416**, 97 (1975).
94. P. J. Durand, *Inorg. Chem.*, **19**, 3211 (1980).
95. T. Sato and T. Nakamura, *Denki Kagaku Oyoki Koygo Butsuri Kagaku*, **50**, 812 (1982).
96. R. K. Aggarwal, V. Kapur, S. Sharma, P. C. Jain and A. K. Srivastava, *Proc. Natl. Acad. Sci. India, Sect. A*, **51**, 260 (1981).
97. N. A. Geraseva, A. A. Shklyaev, A. S. Zanina and V. F. Anufrienko, *Zh. Strukt. Khim.*, **19**, 660 (1978).
98. F. Naeumann and D. Rehder, *Z. Naturforsch., Teil B*, **39**, 1654, (1984).
99. S. L. Chadha, T. Singh, K. Uppal and C. M. Jaswal, *Indian J. Chem., Sect. A*, **24**, 781 (1985).
100. S. Singh, Amita, M. S. Gill and R. D. Verma, *J. Fluorine Chem.*, **27**, 133 (1985).
101. R. C. Paul, R. C. Kumar and R. D. Verma, *J. Fluorine Chem.*, **11**, 203 (1978).
102. D. Brwon, J. F. Easey and J. G. H. du Preez, *J. Chem. Soc. A*, 258 (1966).
103. A. R. Roy and A. Thompson, *J. Less Common Met.*, **61**, 1 (1978).
104. D. Brown, J. Hill and C. E. F. Rickard, *J. Less-Common Met.*, **20**, 57 (1970).
105. J. Sala-Pala, J. Y. Claves and J. E. Guerchais, *J. Inorg. Nucl. Chem.*, **37**, 1294 (1975).
106. K. Behzadi, A. O. Baghlaf and A. Thompson *J. Less-Common Met.*, **57**, 103 (1978).
107. K. Behzadi, A. I. T. Ahwaz Iran and A. Thompson, *J. Less-Common Met.*, **124**, 135 (1986).
108. D. B. Copley, F. Fairbrother and A. Thompson, *J. Less-Common Met.*, **8**, 256 (1965).
109. Yu. A. Buslaev, M. Gilushkova and N. A. Ovchinnikova, *Koord. Khim.*, **1**, 319 (1975).
110. D. Brown and C. E. F. Rickard, *J. Chem. Soc. A*, 81 (1971).
111. K. Behzadi and A. Thompson, *J. Less-Common Met.*, **56**, 9 (1977).
112. L. G. Hubert Pfalzgraf, J. Guion and J. G. Reiss, *Bull. Soc. Chim. Fr.*, **11**, 3855 (1971).
113. R. A. Field and D. L. Kepert, *J. Less-Common Met.*, **13**, 378 (1967).
114. N. Brenicevic, *J. Inorg. Nucl. Chem.*, **37**, 719 (1975).
115. N. Brenicevic, and B. Kojic-Prodic, *Proc. Int. Conf. Coord. Chem., 16th, Univ. Coll. Dublin, Ireland, 1974, Sect.4.34; Chem. Abstr.*, **85**, 71484b (1976).
116. G. W. A. Fowles, D. A. Rice and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 2313 (1972).
117. G. W. A. Fowles, D. A. Rice and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 961 (1973).
118. G. W. A. Fowles, D. A. Rice and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 1080 (1974).
119. C. Santini-Scampucci and J. G. Reiss, *J. Chem. Soc., Dalton Trans.*, 1433 (1974).
120. F. A. Urbanos, M. Mena, P. Royo and A. Antinolo, *J. Organomet. Chem.*, **276**, 185 (1984).
121. M. E. Ignatov and E. G. Il'in, *Koord, Khim.*, **8**, 31 (1982).
122. Yu. A. Buslaev, E. G. Il'in, M. E. Ignatov, L. S. Butorina and T. A. Mastryukova, *J. Fluorine Chem.*, **12**, 381 (1978).
123. E. G. Il'in, M. E. Ignatov, L. S. Butorina, T. A. Mastryukova and Yu. A. Buslaev, *Dokl. Akad. Nauk SSSR*, **236**, 609 (1977).
124. E. G. Il'in, M. E. Ignatov and Yu. A. Buslaev, *Koord. Khim.*, **5**, 949 (1979).
125. E. G. Il'in, M. E. Ignatov and Yu. A. Buslaev, *Koord. Khim.*, **3**, 46 (1977).
126. M. E. Ignatov, E. G. Il'in and Yu. A. Buslaev, *Dokl. Akad. Nauk SSSR*, **245**, 604 (1979).
127. M. E. Ignatov, E. G. Il'in and Yu. A. Buslaev, *Koord. Khim.*, **9**, 1067 (1983).
128. M. E. Ignatov, E. G. Il'in, A. A. Shvets and Yu. A. Buslaev, *Koord. Khim.*, **4**, 1818 (1978).
129. M. E. Ignatov, E. G. Il'in, A. A. Shvets and O. A. Osipov, *Zh. Obshch. Khim.*, **53**, 1532 (1983).
130. M. E. Ignatov, E. G. Il'in, A. A. Shvets and Yu. A. Buslaev, *Dokl. Akad. Nauk SSSR*, **240**, 865 (1978).
131. D. E. Scaife, *Aust. J. Chem.*, **20**, 845 (1967).
132. K. Issleib, A. Tzschach and H. O. Frohlich, *Z. Anorg. Allg. Chem.*, **298**, 164 (1958).
133. N. V. Martin and A. C. Massabni, *Ecletica Quim.*, **11–12**, 59 (1987).
134. S. J. Patel, *Bol. Soc. Chil. Quim.*, **17**, 61 (1971); *Chem. Abstr.*, **77**, 83056m (1972).
135. W. Beck and K. Lottes, *Chem. Ber.*, **96**, 1046 (1963); *Chem. Abstr.*, **59**, 2854a (1963).
136. (a) C. J. Bilgrien, R. S. Drago, C. J. O.' connor and N. Wong, *Inorg. Chem.*, **27**, 1410 (1988). (b) D. A. Edwards and S. C. Jennison, *Transition Met. Chem.*, **6**, 235 (1981).
137. N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski and M. M. Labes, *Inorg. Chem.*, **9**, 582 (1970).
138. K. Issleib and W. Seidel, *Z. Anorg, Allg. Chem.*, *288*, **201** (1956).

139. S. Mishra and K. M. Purohii, *J. Indian Chem. Soc.*, **65**, 588 (1988).
140. G. Garcia, G. Lopez and J. Ruiz, *An. Univ. Mureia, Cienc.*, **42**, 43 (1988); *Chem. Abstr.*, **101**, 111100f (1984).
141. K. Srinivasan and J. K. Kochi, *Inorg. Chem.*, **24**, 4671 (1985).
142. A. M. Galleev, N. A. Chadaeva, A. Sh. Mukhtarov and A. Il'yasov, *Zh. Strukt. Khim.*, **15**, 927 (1974).
143. S. O. Grim, L. C. Satek, C. A. Tolman and J. P. Jesson, *Inorg. Chem.*, **14**, 656 (1975).
144. F. J. Kohl, J. Lewis and R. Whyman, *J. Chem. Soc. A*, 630 (1966).
145. T. Kukuchi, Y. Sugiura and H. Tanaka, *Inorg. Chim. Acta*, **66**, L5 (1982).
146. J. Lewis and R. Whyman, *J. Chem. Soc.*, 6027 (1965).
147. G. V. Romanenko, N. V. Podberezskaya, V. P. Fedin, O.A. Gerasko. V. E. Fedorov and V. V. Bakakin, *Zh. Strukt. Khim.*, **29**, 93 (1988).
148. C. D. Garner, N. C, Howlader, F. E. Mabbs, A. T. McPhail and K. D. Onan, *J. Chem. Soc., Dalton Trans.*, 1848 (1978).
149. C. D. Garner, M. R. Hyde, F. E. Mabbs and V. I. Routledge, *Proc. Int. Conf. Coord. Chem., 16th Univ. Coll. Dublin, Ireland* 1974, Sect., 1.2; *Chem. Abstr.*, **85**, 42884b (1976).
150. W. A. Carmichael and D. A. Edwards, *J. Inorg. Nucl. Chem.*, **30**, 2641 (1968).
151. D. L. Kepert and R. Mandyczewsky, *J. Chem. Soc., A*, 530 (1968).
152. A. Bartecki and D. Dembicka, *Rocz. Chem.*, **39**, 1783 (1965); *Chem. Abstr.*, **64**, 18932d (1966).
153. S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, **2**, 568 (1963).
154. M. Abu Baker, A. Hills, D. L. Hughes and G. J. Leigh, *J. Chem. Soc. Dalton Trans.*, 1417 (1989).
155. B. J. Brisdon, *Inorg. Chem.*, **6**, 1791 (1961).
156. L. H. Bill, N. C. Howlader, F. E. Mabbs, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1475 (1980).
157. S. M. Horner and S. Y. Tyree, Jr. *Inorg. Chem.*, **1**, 122 (1962).
158. R. J. Butcher, B. R. Penfold and E. K. K. Sinn, *J. Chem. Soc., Dalton Trans.*, 668 (1979).
159. G. W. A. Fowles, D. A. Rice and K. J. Shanton, *J. Chem. Soc., Dalton Trans.*, 2128 (1977).
160. A. K. Majumdar. R. G. Bhattacharyya and D. C. Bera, Proceedings of Chemistry Symposium **2**, 121 (1972); *Chem. Abstr.*, **82**, 9610z (1975).
161. K. E. Voss, J. D. Hudman and J. Kleinberg, *Inorg. Chim. Acta*, **20**, 79 (1976).
162. R. Kergoat and J. E. Guerchais, *Bull. Soc. Chim. Fr.*, 2932 (1970).
163. M. Postle, J. G. Reiss, J. Y. Calves and J. Guerchais, *Inorg. Chim. Acta*, **32**, 175 (1979).
164. (a) M. E. Ignatov, E.G. Il'in, B. V. Golovanov, V. D. Butskii and Yu. A. Buslaev, *Dokl. Akad. Nauk SSSR*, **277**, (1984); (b) P. M. Boorman, C. D. Garner and F. E. Mabbs, *J. Chem. Soc., Dalton Trans.*, 1299 (1975).
165. N. Agh-Atabay, F. M. Ashmawy, C. A. McAuliffe and W. E. Hill, *Inorg. Chim. Acta*, **104**, 73 (1985).
166. M. E. Ignatov, B. V. Golovanov, V. D. Butskii and E. G. Il'in, *Zh. Neorg. Khim.*, **28**, 1734 (1983).
167. M. Kersting, C. Friebel, K. Dehnicke, M. Krestel and R. Allmann, *Z. Anorg. Allg. Chem.*, **563**, 70 (1988).
168. F. A. Cotton and R. Poli, *Inorg. Chem.*, **25**, 3587 (1986).
169. C. Miniscloux, G. Martino and L. Sajus, *Bull. Soc. Chim. Fr.*, 2179 (1973).
170. E. A. Allen, K. Feenan and G. W. A. Fowles, *J. Chem. Soc.*, 1636 (1965).
171. D. Britnell, G. W. A. Fowles and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, 213 (1975).
172. J. C. Sheldon, *J. Chem. Soc.*, 750 (1961).
173. H. Mimoun, I. S. DeRoch and L. Sajus, *Bull. Soc. Chim. Fr.*, 1481 (1969).
174. J. Lewis and R. Whyman, *J. Chem. Soc. A*, 211 (1966).
175. A. D. Westland, F. Haque and J. M. Bouchard, *Inorg. Chem.*, **19**, 2255 (1980).
176. M. T. H. Tarafder and A. Ahmed, *Indian J. Chem., Sect. A*, **25**, 729 (1986).
177. N. A. Ovchinnikova and M. A. Glushkov, *Koord, Khim.*, **1**, 280 (1975).
178. F. King and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 429 (1977).
179. L. Bencze, J. Kohan, B. Mohai and L. Marko, *J. Organomet. Chem.*, **70**, 421 (1974).
180. K. Seyferth, K. Rosenthal, G. Kuehn and R. Taube, *Z. Anorg. Allg. Chem.*, **513**, 57 (1984).
181. R. Taube and K. Seyferth, *Z. Anorg, Allg. Chem.*, **437**, 213 (1977).
182. F. Canziani, U. Sartorelli and F. Cariati, *Ann. Chem. (Rome)*, 1354 (1964). *Chem. Abstr.*, **62**, 14159g (1965).
183. L. Bencze and B. Mohai, *Inorg. Chim. Acta*, **12**, 5 (1975).

184. J. Kohan, S. Vastag and L. Bencze, *Inorg. Chim. Acta*, **14**, L1 (1975).
185. A. Keller, *Inorg. Chim. Acta*, **149**, 165 (1988).
186. K. H. Al-Obaidi and Y. J. Hassani, *Transition Met. Chem.*, **3**, 15 (1978).
187. G. R. Beilharz, D. Scott and A. G. Wedd, *Aust. J. Chem.*, **29**, 2167 (1976).
188. D. Scott and A. G. Wedd, *J. Chem. Soc., Chem. Commun.*, 527 (1974).
189. J. Chatt, R. Choukrown, J. R. Dilworth, J. Hyde, P. Vella and J. Zubieta, *Transition Met. Chem.*, **4**, 59 (1979).
190. A. J. Nielson and J. M. Waters, *Aust. J. Chem.*, **36**, 243 (1983).
191. J. Chatt and J. R. Dilworth, *Proc. Int. Conf. Coord. Chem., 16th, Chem. Abstr.*, 1974, Sect. 4.9; 3pp. *Univ. Coll. Dublin, Ireland*, **85**, 40276f (1976).
192. J. Chatt and J. R. Dilworth, *J. Indian Chem. Soc.*, **54**, 13 (1977).
193. N. Meyama, H. Fukase, H. Zaima, S. Kishider and A. Nakamura, *J. Mol. Catal.*, **43**, 141 (1987).
194. H. Bock and H. T. Dieck, *Z. Naturforsch. Teil B*, **21**, 739 (1966).
195. F. Canziani, F. Zingales and U. Sartorelli, *Gazz. Chim. Ital.*, **94**, 841 (1964).
196. R. L. Keiter, K. M. Fasig and L. W. Cary, *Inorg. Chem.*, **14**, 201 (1975).
197. D. J. Darensbourg, M. Pala, D. Simmons and A. L. Rheingold, *Inorg. Chem.*, **25**, 3537 (1986).
198. S. Z. Goldberg and K. N. Raymon, *Inorg, Chem.*, **12**, 2923 (1973).
199. S. P. Nolan, V. Lopez de la and C. D. Hoff, *Organometallics*, **5**, 2529 (1986).
200. W. Hieber, K. Englert and K. Rierga, *Z. Anorg. Allg. Chem.*, **300**, 295 (1959).
201. L. Chandrasegaran and G. A. Rodley, *Inorg. Chem.*, **4**, 1360 (1965).
202. B. Mohai and L. Bencze, *Thermochim. Acta*, **11**, 323 (1975).
203. B. Mohai and L. Bencze, *Magy. Kem. Foly.*, **81**, 128 (1975).
204. P. K. Baker and D. A. Kendrick, *J. Coord. Chem.*, **17**, 355 (1988).
205. F. Canziani, F. Zingales, U. Sartorelli and A. Chiesa, *Rend. Ist. Lomb. Acad. Sci. Lett. A*, **98**, 709 (1964).
206. C. G. Young and J. H. Enemark, *Aust. J. Chem.*, **39**, 997 (1986).
207. B. Alegre, E. De Jesus, A. Vazquez, P. Royo, A. M. M. Lanfredi and A. T iripicchio, *J. Chem. Soc., Dalton Trans.*, 819 (1988).
208. G. W. A. Fowles, W. M. W. Mohammed and D. A. Rice, *J. Organomet. Chem.*, **170**, 203 (1979).
209. J. H. Wengrovius, J. Sancho and R. R. Schrock, *J. Am. Chem. Soc.*, **103**, 3932 (1981).
210. C. Santini-Scampucci and J. G. Reiss, *J. Organomet. Chem.*, **73**, C13 (1974).
211. C. Santini-Scampucci and J. G. Reiss, *J. Chem. Soc., Dalton Trans.*, 195 (1976).
212. G. S. Girolami, V. V. Mainz and R. A. Andersen, *Inorg. Chem.*, **19**, 805 (1980).
213. D. M. Baird, P. E. Fanwick and T. Barwick, *Inorg. Chem.*, **24**, 3735 (1985).
214. O. A. Rajan and A. Chakravorty, *Inorg. Chem.*, **20**, 660 (1981).
215. I. Ball, M. Toanne, P. M. Boorman and J. F. Richardson, *Inorg. Chem.*, **25** 3325 (1986).
216. F. J. Lalor and P. L. Pauson, *J. Organomet. Chem.*, **25**, C51 (1970).
217. K. Tomita, *Acta Crystallogr., Sect. C*, **41**, 1832 (1985).
218. D. Periotto, S. A. Antonio and K. Tomita, *Ecletica Quim.*, **8**, 11 (1983).
219. G. E. Hardy and J. I. Zink, *Inorg. Chem.*, **15**, 3061 (1976).
220. R. D. Dowsing, J. F. Gibson, D. M. L. Goodgame, M. Goodgame and P. J. Hayward, *J. Chem. Soc. A*, 1242 (1969).
221. D. Negoiu, *An. Univ. Bucuresti, Ser. Stiint. Nat. Chim.*, **16**, 25 (1967).
222. S. Casey, W. Levason and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 886 (1974).
223. B. Beagley., C. A. McAuliffe, R. G. Pritchard and E. W. White, *Acta Chem. Scand., Ser. A*, **42**, 544 (1988).
224. D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 3735 (1961).
225. D. Negoiu and D. Ciomartan, *Rev. Roum. Chim.*, **11**, 349 (1966); *Chem. Abstr.*, **65**, 4754b (1966).
226. C. Furlani, E. Cervone and P. Cancellieri, *Atti Accad, Naz. Lincei Cl. Sci. Fis. Mat. Nat, Rend.*, **37**, 446 (1964).
227. O. A. Raevskii, T. I. Ignat'eva, V. P. Novikov, A. F. Solotnov, T. E. Kron and E. N. Tsvetkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1095 (1983).
228. D. M. L. Goodgame, M. Goodgame and P. J. Hayward, *J. Chem. Soc., A*, 1352 (1970).
229. E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1878 (1960).
230. F. A. Cotton. R. D. Barnes and E. Bannister, J, Chem. Soc., 2199 (1960).
231. S. H. Hunter R. S. Nyholm and G. A. Rodley, *Inorg, Chim. Acta*, **3**, 631 (1969).
232. N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewskii and M. M. Labes, *J. Inorg. Nucl. Chem.*, **33**, 2691 (1971).

233. M. W. G. DeBolster, I. E. Kortram and W. L. Groeneveld, *J. Inorg. Nucl. Chem.*, **34**, 575 (1972).
234. M. W. G. De Bolster, C. Boutkan, T. A. Van der Knaap, L. Van Zweeden, I. E. Kortram and W. L. Groeneveld, *Z. Anorg. Allg. Chem.*, **443**, 269 (1978).
235. K. Al-Farhan, B. Beagley, Q. El-Sayrafi, G. A. Gott, C. A. McAuliffe, P. P. M. Rory and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1243 (1990).
236. A. Hosseiny, A. G. Mackie, C. A. McAuliffe and K. Minten, *Inorg. Chim. Acta*, **49**, 99 (1981).
237. C. A. McAuliffe, H. F. Al-Khateeb, D. S. Barratt, J. C. Briggs, A. Challita, A. Hosseiny. M. G. Little, A. G. Mackie and K. Minten, *J. Chem. Soc., Dalton Trans.*, 2147, (1983).
238. L. I. Zheleznova, S. V. Volkov, E. A. Mazuranko and N. V. Gerasimenko, *Ukr. Khim. Zh.*, **55**, 122 (1989); *Chem. Abstr.*, **111**, 208166b (1989).
239. C. G. Benson, M. G. Little and C. A. McAuliffe, *Inorg, Chim. Acta.*, **87**, 169 (1984).
240. V. F. Newberry, H. D. Burkett, S. D. Worley and W. E. Hill, *Inorg. Chem.*, **23**, 3911 (1984).
241. D. Negoiu, *An. Univ. Bucuresti, Ser. Stiint. Nat.*, **14**, 145 (1965).
242. H. D. Burkett, V. F. Newberry, W. E. Hill and S. D. Worley, *J. Am. Chem. Soc.*, **105**, 4097 (1983).
243. B. Beagley, C. G. Benson, G. A. Gott, C. A. McAuliffe, R. G. Pritchard, and S. P. Tanner, *J. Chem. Soc., Dalton Trans.*, 2261 (1988).
244. G. A. Gott, J. Fawcett, C. A. McAuliffe and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1283 (1984).
245. B. Namirovskaya, A. G. Ginzberg, V. N. Setkina and D. N. Kursanov, *Zh. Obshch. Khim.*, **45**, 893 (1975).
246. N. J. Coville and I. S. Butler, *J. Organomet, Chem.*, **57**, 335 (1973).
247. I. S. Butlerand N. J. Coville, *J. Organomet. Chem.*, **80**, 235 (1974).
248. G. Ciani, M. Manassero and M. Sansoni, *J. Inorg. Nucl. Chem.*, **34**, 1760 (1972).
249. V. Sartorelli, F. Canziani and L. Garlaschelli, *Gazz. Chim. Ital.*, **104**, 567 (1974).
250. (a) E. Lindner, H. J. Eberle and S. Hoehne, *Chem. Ber.*, **114**, 413 (1981); (b) C. W. J. Ansell, J. Lewis, J. N. Ramsden and M. Schroeder, *Polyhedron*, **2**, 489 (1983).
251. E. Contreras, V. Riera and R. Uson, *Rev. Acad. Cienc. Exactas, Fis-Quim. Nat. Zaragoza*, **28**, 43 (1973).
252. R. Uson, V. Riera, M. A. Ciriano and M. Valderrama, Transition Met. Chem., **1**, 122 (1976).
253. D. W. Johnsons and D. Sutton, *Can. J. Chem.*, **50**, 3326 (1972).
254. S. K. Larsen, C. G. Pierpont, G. De Munno and G. Dolcetti, *Inorg. Chem.*, **25**, 4828 (1986).
255. N. P. Johnson, C. J. L. Lock and G. Wilkinson *J. Chem. Soc.*, 1054 (1964).
256. C. J. L. Lock and G. Wilkinson, *Chem. Ind. (London)*, 40 (1962).
257. F. A. Cotton, S. J. Lippard and J. T. Mague, *Inorg. Chem.*, **4**, 508 (1965).
258. N. Kh. Ashurova, S. M. Basitova and N. K. Kobilov, *Dokl. Akad. Nauk Tadzh. SSR*, **25**, 667 (1982).
259. (a) K. V. Kotegov, G. N. Sedova, N. K. Kobilov, and Yu. N. Kukushkin, *Koord, Khim.*, **6**, 897 (1980); (b) V. S. Sergienko, M. A. Porai-Koshits, V. E. Mistryukov and K. V. Kotegov, *Koord. Khim.*, **8**, 230 (1982); (c) Yu.N. Kukushin, K. V. Kotegov, G. N. Sedova and N. K. Kobilov, *Koord. Khim.*, **4**, 1384 (1978).
260. G. Rouchias and G. Wilkinson, *J. Chem. Soc. A*, 993 (1967).
261. G. LaMonica and S. Cenini, *J. Chem. Soc., Dalton Trans.*, 1145 (1980).
262. (a) K. V. Kotegov, G. N. Sedova, Z. A. Lovchikova and Yu. N. Kukushkin, *Zh. Neorg. Khim.*, **24**, 3301 (1979) (b) K. V. Kotegov, Z. A. Lovchikova and Yu.N. Kukushkin, Zh. Neorg, Khim., **28**, 2277 (1983).
263. K. V. Kotegov, Z. A. Lovchikova and G. B. Avetikyan, *Zh. Neorg. Khim.*, **26**, 2167 (1981).
264. G. La Monica and S. Ceini, *Inorg, Chim. Acta*, **29**, 183 (1978).
265. N. Mronga, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, **502**, 35 (1983).
266. J. M. Fernandez and J. A. Gladysz, *Organometallics*, **8**, 207 (1989).
267. G. M. Larin, R. A. Bukharizoda and P. M. Solozhenkin, *Dokl. Akad. Nauk SSSR*, **251**, 1417 (1980).
268. U. Sartorelli, F. Canziani and F. Zingales, *Inorg. Chem.*, **5**, 2233 (1966).
269. F. Zingales, A. Trovati, F. Cariati and P. Uguagliati, *Inorg. Chem.*, **10**, 507 (1971).
270. A. A. Kotel'nikova, T. V. Misailova, P. A. Koz'min , T. B. Larina and M. D. Surazhskaya, *Koord. Khim.*, **3**, 127 (1977).
271. A. I. Kuzmin, A. V. Shtemenko and A. S. Kotel'nikova, *Zh. Neorg. Khim.*, **25**, 3024 (1980).

272. T. V. Misailova, A. S. Kotel'nikova, I. F. Golovaneva, O. N. Evstafeva and V. G. Lebedev, *Zh. Neorg. Khim.*, **26**, 634 (1981).
273. (a) J. G. Kuchler, E. Herdtweck, R. A. Paciello and W. A. Herrmann, *Angew Chem.*, **100**, 975 (1988); (b) Yu. A. Buslaev, M. A. Glushkova and N. A. Ovchinnikova, *Zh. Neorg Khim.*, **19**, 743 (1974).
274. R. C. Paul, R. C. Kumar and R. D. Verma, *J. Indian Chem. Soc.*, **56**, 251 (1979).
275. C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc., A*, 1074 (1968).
276. N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta*, **10**, 97 (1974).
277. I. Ondrejkovicova and G. Ondrejovic, *Czech. Pat.*, 245 880, 1988; *Chem. Abstr.*, **108**, 134385m (1988).
278. I. Ondrejkovicova and G. Ondrejovic, *Proc. Conf. Coord, Chem., 10th*, 303 (1985); *Chem. Abstr.*, **104**, 236144s (1986).
279. I. Ondrejkovicova, V. Vancova and G. Ondrejovic, *Proc. Conf. Coord. Chem., 12th*, 263 (1989); *Chem. Abstr.*, **112**, 150751r (1990).
280. W. Hieber and A. Lipp, *Chem. Ber.*, **92**, 2085 (1959).
281. F. Calderazzo, S. Frediani, B. R. James, G. Pampalani, K. J. Reimer, J. R. Sams. A. M. Serra and D. Vitali, *Inorg. Chem.*, **21**, 2302 (1982).
282. T. Mashiko, M. E. Kastner, K. Spartalian, W. R. Scheidt, and C. A. Reed, *J. Am. Chem. Soc.*, **100**, 6354 (1978).
283. E. F. Epstein, I. Bernal and A. L. Balch, J. Chem. Soc. D, 136 (1970).
284. A. L. Balch, *Inorg. Chem.*, **10**, 276 (1971).
285. J. K. Yandell and N. Sutin, *Inorg. Chem.*, **11**, 448 (1972).
286. V. I. Ponomarev, K. I. Turti, G. V. Shilov, S. A. Babkova, L. O. Atovmyan and R. A. Stukan, *Koord. Khim.*, **12**, 398 (1986).
287. D. T. Sawyer, M. S. McDowell, L. Spencer and P. K. S. Tsang, *Inorg. Chem.*, **28**, 1166 (1989).
288. B. F. G. Johnson, J. Lewis and S. R. Postel, J. Organomet. Chem., **121**, C7 (1976).
289. V. Vancova and I. Ondrejkovicova, *Czech. Pat.*, 214 985, 1984; /Chem. Abstr., **103**, 53806u (1985).
290. Ya. A. Letuchii, I. P. Lavrent'ev and M. L. Khidekel, *Koord. Khim.*, **8**, 1477 (1982).
291. (a) S. A. Cotton and J. F. Gibson, *J. Chem. Soc. A*, 859 (1971); (b) T. S. Lobana, R. K. Bhatia and P. K. Bhatia, *Indian J. Chem. Sect. A*, **29**, 1062 (1990).
292. S. I. Klein, A. C. Massabni, J. C. Moreira and A. Tancredo, *Ecletica Quim.*, **13**, 7 (1988).
293. L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta*, **8**, 91 (1974).
294. G. Stephan and H. Specker, *Naturwissenschaften*, **55**, 443 (1968).
295. P. Giannoccaro, E. Pennacciulli, F. Moziazzoni and A. Gervasini, *Gazz. Chim. Ital.*, **116**, 147 (1986).
296. S. L. Chadha, V. Sharma, C. Mohini and S. P. Taneja, *Z. Anorg, Allg. Chem.*, **536**, 164 (1986).
297. H. Schmidbauer and W. Richter, *Chem. Ber.*, **107**, 2427 (1974).
298. R. C. Paul, C. Mohini and S. L. Chadha, *Transition Met. Chem.*, **6**, 300 (1981).
299. F. Schindler and H. Schmidbauer, *Chem. Ber.*, **101**, 1656 (1968).
300. T. S. Lobana and A. Sharma, *Transition Met. Chem.*, **14**, 13 (1989).
301 F. Tomi, H. L. K. Wah and M. Postle, *New J. Chem.*, **12**, 289 (1988).
302. I. Ondrejkovicova and G. Ondrejovic, *Czech. Pat.*, 283 920, 1987; *Chem. Abstr.*, **109**, 47365g (1988).
303. I. Ondrejkovicova and G. Ondrejovic, *Czech. Pat.*, 238 918, 1987; *Chem. Abstr.*, **109**, 47367j (1988).
304. E. Durcanska, T. Glowiak, J. Kozisek, I. Ondrejkovicova and G. Ondrejovic, *Acta Crystallogr., Sect. C*, **45**, 410 (1989).
305. A. Araneo and A. Trovati, *Inorg. Chim. Acta*, **3**, 471 (1969).
306. P. G. Antonov, Yu.N. Kukushkin, V. F. Shkredov and V. I. Anufriev, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, **24**, 941 (1981).
307. S. R. Hall, B. W. Skelton and A. H. White, *Aust. J. Chem.*, **36**, 267 (1983).
308. P. B. Critchlow and S. D. Robinson, *Inorg. Chem.*, **17**, 1896 (1978).
309. B. A. Moyer, B. K. Sipe and T. J. Meyer, *Inorg. Chem.*, **20**, 1475 (1981).
310. V. N. Pichkov, O. E. Zvyagintsev and N. M. Sinitsyn, *Zh. Neorg. Khim.*, **11**, 2560 (1960).
311. (a) F. A. Urbanos, M. C. Barral and R. Jimenez-Asparicio, *Polyhedron*, **7**, 2597 (1988); (b) M. C.

Barrall, J. R. Jimnez-Aparicio, E. C. Royer, C. Ruiz-Valero, F. A. Urbanos, E. Gutierrez-Puebla and A. Mage, *Polyhedron,* **8**, 2571 (1989).
312. C. M. Che, T. F. Lai, W. C. Chung, W. R. Schaefer and H. B. Gray, *Inorg. Chem.*, **26**, 3907 (1987).
313. J. C. Dobson and T. J. Meyer, *Inorg. Chem.*, **28**, 2013 (1989).
314. T. J. Collins and J. T. Keech, *J. Am. Chem. Soc.*, **110**, 1162 (1988).
315. J. A. Christie, T. J. Collins, T. E. Krafft, B. D. Santarsiero and G. H. Spies, *J. Chem. Soc., Chem. Commun.*, 198 (1984).
316. W. Hieber and K. Heinicke, *Z. Anorg. Allg. Chem.*, **316**, 305 (1962).
317. D. D. Schmidt and J. T. Yoke, *Inorg. Chem.*, **9**, 1176 (1970).
318. A. Bencini, C. Benelli, D. Gatteschi and C. Zanchini, *Inorg. Chem.*, **18**, 2137 (1979).
319. F. Edelmann and U. Behrens, *Acta Crystallogr., Sect. C*, **42**, 1715 (1986).
320. Y. P. Mascarenhas and K. Tomita, *An. Acad. Bras. Cienc.*, **47**, 227 (1975); *Chem. Abstr.*, **85**, 200856 (1976).
321. K. Issleib and B. Mitscherling, *Z. Anorg. Allg. Chem.*, **304**, 73 (1960).
322. E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 2276 (1960).
323. K. Issleib and A. Brack, *Z. Anorg. Allg. Chem.*, **277**, 258 (1954).
324. C. A. Strydom and H. J. Strydom, *Inorg. Chim. Acta*, **159**, 191 (1989).
325. O. L. Alves and Y. Hase, *Spectrosc. Lett.*, **15**, 423 (1982); *Chem. Abstr.*, **97**, 15326x (1982).
326. J. Rimbault, J. C. Pierrard and R. P. Hugel, *Nouv. J. Chim.*, **7**, 653 (1983).
327. H. Kato and K. Akimoto, *J. Am. Chem. Soc.*, **96**, 1351 (1974).
328. J. Rimbault, J. C. Pierrard and R. Hugel, *Bull. Soc. Chim. Fr.*, 1705 (1976).
329. R. H. Nuttall and D. W. Taylor, *Chem. Commun.*, 1417 (1968).
330. P. Spacu and M. Negoiu, *An. Univ. Bucuresti, Ser. Stiint. Nat. Chim.*, **18**, 21 (1969).
331. O. A. Serra, and A. C. Massabni, *Inorg, Nucl. Chem. Lett.*, **7**, 275 (1971).
332. F. A. Cotton, D. M. L. Goodgame, M. Goodgame and T. E. Haes, *Inorg. Chem.*, **1**, 565 (1962).
333. F. A. Cotton, D. M. L. Goodgame, M. Goodgame and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).
334. A. C. Massabni and O. A. Serra, *J. Coord. Chem.*, **7**, 67 (1977).
335. J. C. Pierrard, J. Rimbault and R. P. Hugel, *J. Chem. Res. (S)*, 323 (1982).
336. K. Moedritzer and R. E. Miller, *J. Thermal Anal.*, **1**, 151 (1969).
337. E. Uhlig and M. Schaefer, *J. Inorg, Nucl. Chem.*, **30**, 3109 (1968).
338. J. Rimbault, J. C. Pierrard and R. P. Hugel, *J. Chem. Res. (S)*, 330 (1982).
339. J. Rimbault and R. P. Hugel, *Rev. Chim. Miner.*, **10**, 773 (1973); *Chem. Abstr.*, **81**, 71982e (1974).
340. J. Rimbault and R. P. Hugel, *Inorg. Nucl. Chem. Lett.*, **9**, 1 (1973).
341. R. D. Lampeka, V. V. Skopenko, N. V. Zaporozhets, *Ukr. Khim. Zh.*, **51**, 679 (1985); *Chem. Abstr.*, **104**, 27802r (1986).
342. S. V. Volkov, L. I. Zheleznova and E. A. Mazurenko, *Tezisy Dokl. Ukr. Resp. Konf. Fiz. Khim., 12th*, 80 (1977); *Chem. Abstr.*, **92**, 188579x (1980).
343. N. C. Li, S. M. Wang and W. R. Walker, *J. Inorg. Nucl. Chem.*, **27**, 2263 (1965).
344. O. I. Kuntyi, D. I. Semenishin and I. P. Dzikh, *Koord. Khim.*, **6**, 914 (1980).
345. M. W. G. De Bolster and J. F. Scholte, *Z. Anorg. Allg. Chem.*, **503**, 201 (1983).
346. S. L. Chadha and K. Uppal, *Bull. Soc. Chim. Fr.*, 340 (1989).
347. (a) J. Sznajder, A. Jablonski and C. W. Wojcie, *J. Inorg. Nucl. Chem.*, **41**, 305 (1979). (b) J. T. Yoke and D. D. Schmidt, *J. Am. Chem. Soc.*, **93**, 637 (1971).
348. W. E. Daniels, *Inorg. Chem.*, **3**, 1800 (1964).
349. Yu. N. Kukushkin, E. D. Ageeva, U. E. Aleshin, G. B. Avetikyen and G. N. Sedova, *Zh. Neorg. Khim.*, **25**, 1014 (1980).
350. Yu. N. Kukushkin, E. D. Ageeva, G. N. Sedova, M. L. Perez and G. B. Avetikyan, *Koord, Khim.*, **4**, 1710 (1978).
351. H. A. Tayim, A. Bouldoukian and F. Awad, *J. Inorg. Nucl. Chem.*, **32**, 3799 (1970).
352. S. K. Thabet, H. A. Tayimand M. V. Karkanwi, *Inorg. Nucl. Chem. Lett.*, **8**, 211 (1972).
353. F. A. Cotton R. H. Roderberg, *J. Am. Chem. Soc.*, **85**, 2402 (1963).
354. (a) A. M. G. Dias Rodrigues, R. H. P. Francisco and J. R. Lechat, *Cryst. Struct. Commun.*, **11**, 847 (1982). (b) Z. Zhang, X Wang, Z.Xi, R. Wang and H. Wang, *Jiegou Huaxue*, **8**, 107 (1989).
355. D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **4**, 721 (1965).
356. C. R. Leite, N. Barelli and A. C. Massabni, *J. Appl. Crystallogr.*, **9**, 52 (1976).

357. F. A. Cotton, D. M. L. Goodgame and R. H. Soderberg, *Inorg. Chem.*, **2**, 1162 (1963).
358. J. G. H. Du Preez, B. J. A. M. Van Brecht and I. Warden, *Inorg. Chim. Acta*, **131**, 259 (1987).
359. Z. A. Sheka, M. A. Ablova and K. B. Yatsimirskii, *Zh. Neorg. Khim.*, **14**, 2783 (1969).
360. Z. A. Sheka, M. A. Ablova, E. I. Sinyavskaya and K. B. Yatsimirskii, *Zh. Neorg. Khim.*, **14**, 3081 (1969).
361. Z. A. Sheka, M. A. Ablova and K. B. Yatsimirskii, *Izv. Akad. Nauk Mold. SSR*, 73 (1970); *Chem. Abstr.*, **74**, 117907v (1971).
362. M. Molina, C. Melios, A. C. Massabni and H. Yamanaka, *Ecletica Quim.*, **3**, 17 (1978).
363. K. B. Yatsimirskii, Z. A. Sheka and E. I. Sinyavskaya, *Teor. Eksp. Khim.*, **3**, 595 (1967).
364. Melios, M. Molina, J. O. Tognolli and A. C. F. Espeleta, *Ecletica Quim.*, **4**, 39 (1979).
365. K. B. Yatsimirskii, E. I. Sinyavskaya, L. V. Tsymbal, T. A. Mastryukova, I. M. Aladzheva, I. V. Leont'eva and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2094 (1988).
366. F. A. Cotton, E. Bannister, R. Barnes and R. H. Holm, *Proc. Chem. Soc.*, 158 (1959).
367. M. Dartiguenave, Y. Dartiguenave, M. J. Oliver and A. L. Beauchamp, *J. Coord. Chem.*, **21**, 275 (1990).
368. S. Gorter, W. Hinricks, J. Reedijk, J. Rimbault, J. C. Pierrard, R. P. Hugel, *Inorg. Chim. Acta.*, **105**, 181 (1985).
369. J. C. Pierrard, J. Rimbault and R. P. Hugel, *J. Chem. Res. (S)*, 316 (1984).
370. D. J. Darensbourg, M. Y. Darensbourg and N. Walker, *Inorg. Chem.*, **20**, 1918 (1981).
371. D. Fenske, J. Meyer and K. Merzweiler, *Z. Naturforsch., Teil B*, **42**, 1207 (1987).
372. Yu. N. Kukushkin, A. V. Iretskii and L. I. Danilina, *Koord. Khim.*, **9**, 1405 (1983).
373. P. Uguayliati, G. Deganello and U. Belluco, *Inorg. Chim. Acta*, **9**, 203 (1974).
374. G. Bandoli, D. A. Clemente, G. Deganello, G. Carturan, P. Uguayliati and U. Belluco, *J. Organomet. Chem.*, **71**, 125 (1974).
375. M. V. Klyuev, B. G. Rogachev, Yu. M. Shul'ga and M. L. Khidekel, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1869 (1979).
376. R. Uson, L. A. Oro, M. A. Ciriano, F. J. Lahoj and M. C. Bello, *J. Organomet. Chem.*, **234**, 205 (1982).
377. Yu. N. Kukushkin, L. I. Danilina, A. I. Osokin and V. P. Kotel'nikov, *Zh. Neorg. Khim.*, **24**, 2253 (1979).
378. K. A. Khokhryakov, I. G. Maslennikov, and E. I. Grigrov, *Koord. Khim.*, **13**, 226 (1987).
379. Yu. N. Kukushkin, A. V. Iretskii, L. I. Danilina and R. O. Abdurakhmanov, *Zh. Neorg. Khim.*, **31**, 413 (1986).
380. R. W. Wegman, A. J. Abatjoglou and A. M. Harrison, *J. Chem. Soc., Chem. Commun.*, 1891 (1987).
381. I. I. Bhayat and W. R. McWhinnie, *J. Organomet. Chem.*, **46**, 159 (1972).
382. P. B. Critchlow and S. D. Robinson, *J. Organomet. Chem.*, **114**, C46 (1976).
383. S. A. Dias, A. W. Downs and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, 162 (1975).
384. F. A. Cotton and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **82**, 5771 (1960).
385. Badische Anilin und Soda-Fabrik, *Ger. Pat.*, 805 641, 1951; *Chem. Abstr.*, **47**, 9602i (1953).
386. J. Csaszar and M. Ban, *Magy. Kem. Foly.*, **75**, 491 (1969); *Chem. Abstr.*, **72**, 27911w (1970).
387. K. Issleib and W. Seidel, *Chem. Ber.*, **92**, 2681 (1959).
388. D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, **4**, 139 (1965).
389. M. Gorio, C. Castellani Bisi, M. Cola and A. Peratti, *J. Inorg. Nucl. Chem.*, **36**, 1168 (1974).
390. A. A. Shvets, E. G. Amarskii and O. A. Moisseva, *Koord. Khim.*, **5**, 1510 (1979).
391. M. Negoiu and E. N. Mizil, *Rev. Chim.* (*Bucharest*), **28**, 228 (1977); *Chem. Abstr.*, **87** 46102j (1977).
392. N. F. Moldavskaya, G. G. Peshkova, G. N. Sedova, N. R. Skvortsov and V. O. Reikhsfel'd, *Zh. Obshch. Khim.*, **51**, 2654 (1981).
393. G. B. Avetikyan, Yu. V. Chebrakov and V. I. Vshivtsev, *Koord. Khim.*, **11**, 951 (1985).
394. N. Hilje and O. Serra, *Ing. Cienc. Quim.*, **3**, 33 (1979); *Chem. Abstr.*, **91**, 221604f (1979).
395. L. Maier, *Helv. Chem. Acta*, **51**, 1608 (1968).
396. S. A. Bhaduri, I. Bratt, B. F. G. Johnson, A. Khair, J. A. Segal, R. Walters and C. Zuccaro, *J. Chem. Soc., Dalton Trans*, 234 (1981).
397. K. P. Sarma and R. K. Poddar, *Transition Met. Chem.*, **8**, 31 (1983).
398. K. P. Sarma and R. K. Poddar, *Transition Met. Chem.* **8** 225 (1983).
399. F. A. Cotton and E. Bannister, *J. Chem. Soc.*, 1873 (1960).

400. N. Hilje and O. A. Serra, *Ing. Cienc. Quim.*, **4**, 144 (1980); *Chem. Abstr.*, **95**, 53969r (1981).
401. Q. N. Hilje and O. A. Serra, *Col. Quim. Ing. Quim. Costa Rica*, **6**, 24 (1976); *Chem Abstr.*, **89**, 122064g (1978).
402. N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski and M. M. Labes, *Inorg. Nucl. Chem. Lett.*, **5**, 897 (1969).
403. A. M. Brodie, S. H. Hunter, G. A. Rodley and C. J. Wilkins, *Inorg. Chim. Acta*, **2**, 195 (1968).
404. N. Kumar, P. L. Kachroo and R. Kant, *Indian J. Chem., Sect. A*, **18**, 265 (1979).
405. N. Kumar, P. L. Kachroo and R. Kant, *Bull. Chem. Soc. Jpn.*, **53**, 1787 (1980).
406. N. Kumar, P. L. Kachroo, A. K. Gandotra and R. Kant, *Indian J. Chem., Sect. A*, **24**, 524 (1985).
407. A. Areas and P. Royo, *Inorg. Chim. Acta*, **30**, 205 (1978).
408. G. Booth and J. Chatt, *J. Chem. Soc.*, 2099 (1962).
409. Yu. N. Kukushkin, G. N. Sedova, G. B. Avetikyan, E. D. Ageeva and M. L. Perez, *Zh. Neorg. Khim.*, **24**, 973 (1979).
410. Yu. N. Kukushkin, E. D. Ageeva, G. N. Sedova, G. B. Avetikyan and T. M. Lukicheva, *Koord. Khim.*, **3**, 1872 (1977).
411. Yu. N. Kukushkin, G. N. Sedova, V. E. Aleshin, E. D. Ageeva and G. B. Avetikyan, *Zh. Neorg. Khim.*, **25** 772 (1980).
412. Yu. N. Kukushkin, G. N. Sedova, E. D. Ageeva and M. A. Kirillova, *Zh. Neorg. Khim.*, **23**, 3046 (1978).
413. V. K. Polovnyak, V. Sh. Slobodina, T. E. Busygina and A. E. Ivantsov, *Journal of Molecular Liquids* **28**, 123 (1984).
414. Yu. N. Kukushkin, G. N. Sedova and R. A. Vlasova, *Zh. Neorg. Khim.*, **24**, 431 (1979).
415. N. A. Shorokhov and V. S. Shmidt, *Zh. Neorg. Khim.*, **28**, 1240 (1983).
416. W. Winter, *Chem. Ber.*, **109**, 2405 (1976).
417. C. J. Jones, J. A. McCleverty, A. S. Rothin, H. Adams and N. A. Bailey, *J. Chem. Soc., Dalton Trans.*, 2055 (1986).
418. G.Garcia and G. Lopez, *Inorg. Chim. Acta*, **52**, 87 (1981).
419. R. Uson, J. Fornies and S. Gonzalo, *J. Organomet. Chem.*, **104**, 253 (1976).
420. S. J. Higgins, R. J. Taylor and B. L. Shaw, *J. Organoment. Chem.*, **325**, 285 (1987).
421. R. Uson, P. Royo and J. Gimeno, *J. Organoment. Chem.*, **72**, 299 (1974).
422. I. N. Saez, G. Lobez and G. Garcia, *An. Univ. Murcia, Cienc.*, **35**, 157 (1976).
423. R. Uson, J. Fornier, P. Espinet and M. P. Garcia, *Rev. Acad. Cienc. Exactas, Fis.-Quim. Nat., Zaragoza*, **32**, 85 (1977).
424. R. Uson, J. Fornies, P. Espinet and M. P. Garcia, *Rev. Acad. Cienc. Exactas, Fis. Quim. Nat., Zaragoza*, **32**, 193 (1977).
425. D. E. Berry, J. Browning, K. R. Dixon and R. W. Hilts, *Can. J. Chem.*, **66**, 1272 (1988).
426. A. Pidcock, K. R. Dixon, G. W. Bushnell and J. Browning, *Inorg. Chem.*, **22**, 2226 (1983).
427. N. Hadj-Bagheri and R. J. Pudhephatt, *Inorg. Chem.*, **28**, 2384 (1989).
428. J. A. Bertrand, S. L. Graham, H. M. Deutsch, and D. G. Van der Veer, *Inorg. Chim. Acta*, **19**, 189 (1976).
429. J. Gazo, G. Onderjovic and D. Makanova, *Proc. Int. Conf. Coord. Chem., 6th*, R36 (1974); *Chem. Abstr.*, **85**, 40270z (1976).
430. F. G. Moers. P. J. W. M. Muskens and J. Francot, *J. Inorg. Nucl. Chem.*, **41**, 759 (1979).
431. I. Bertini, D. Catteschi and G. Martini, *J. Chem. Soc., Dalton Trans.*, 1644 (1973).
432. M. P. P. Mattioli and A. C. Massabni, Ecletica Quim., **6**, 29 (1981).
433. D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 2298 (1961).
434. M. B. Ferrari, G. F. Gasparri, C. Pelizzi and P. Tarasconi, *Acta Crystallogr., Sect. C.*, **42**, 1148 (1986).
435. T. I. Ignatieva, V. P. Novikov, T. E. Kron and O. A. Raevskii, *Zh. Neorg. Khim.*, **30**, 378 (1985).
436. M. A. Hitchman, R. G. McDonald and M. J. Riley, *Inorg. Chem.*, **23**, 2359 (1984).
437. G. Ondrejovic, J. Kozisek, M. Dunaj-Jurco, D. Makanova and J. Gazo, *Proc. Conf. Coord. Chem.*, 7th, 197 (1978); *Chem Abstr.*, **92**, 103502u (1980).
438. D. Makanova, G. Ondrejovic, M. Melnik and J. Gazo, *Chem. Zvesti*, **30**, 73 (1976).
439. E. Grazynska and W. Wojciechowski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **26**, 393 (1978).
440. V. K. Voronkova, L. V. Mosina, Yu. V. Yablokov and M. A. Yampol'skaya, *Dokl. Akad. Nauk SSSR*, **246**, 910 (1979).
441. D. H. Tom, *Inorg. Chim. Acta*, **7** 397 (1973).

442. A. A. Dvorkin, Yu. A. Simonov, M. A. Yampol'skaya and T. I. Malinovskii, *Kristallografiya*, **28**, 811 (1983).
443. T. D. Black, R. S. Rubbins, D. K. De, R. C. Dickinson and W. A. Baker, Jr, *J. Chem. Phys.*, **80** 4620 (1984).
444. M. E. Lines, A. P. Ginsberg, R. L. Martin and R. C. Sherwood, *J. Chem. Phys.*, **57**, 1 (1972).
445. M. E. Lines, A. P. Ginsberg and R. L. Martin, *Phy. Rev. Lett.*, **28**, 684 (1972).
446. (a) J. A. Bertrand and J. A. Kelley, *J. Am. Chem. Soc.*, **88**, 4747 (1966); (b) J. A. Bertrand, *Inorg. Chem.*, **6**, 495 (1967).
447. C. H. Ke and N. C. Li, *J. Inorg. Nucl. Chem.*, **28**, 2255 (1966).
448. A. A. Shklyaev, V. F. Anufrienko and V. D. Ogorodnikov, *Zh. Strukt. Khim.*, **14**, 994 (1974).
449. W. R. Walker and N. C. Li, *J. Inorg. Nucl. Chem.*, **27**, 411 (1965).
450. R. Lahiri and G. N. Rao. *Thermochim. Acta*, **90** 53 (1985).
451. I. N. Marov, O. M. Petrukhin, V. V. Zhukov and N. B. Kalinichenko, *Koord. Khim.*, **1**, 1394 (1975).
452. B. Carr and J. F. Harrod, *Can. J. Chem.*, **50**, 2792 (1972).
453. J. R. Wasson, C. Trapp, C. I. Shyr and D. Smith, *J. Chem. Phys.*, **49**, 5197 (1968).
454. G. Nifrontova, I. P. Lavrent'ev, Ya. A. Letuchii and M. L. Khidekel, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, (4), 129 (1982).
455. D. Makanova, G. Ondrejovic and J. Gazo, *Proc. Conf. Coord. Chem., 3rd*, 215 (1971); *Chem Abstr.*, **76**, 125242v (1972).
456. D. Makanova, G. Ondrejovic and J. Gazo, *Chem. Zvesti*, **27**, 4 (1973).
457. A. C. Massabni and A. G. Neto, *Ecletica Quim.*, **4**, 17 (1979).
458. H. D. Coughman and R. G. Taylor, *Inorg. Nucl. Chem. Lett.*, **6**, 623 (1970).
459. M. G. Newton, H. D. Caughman and R. C. Taylor, *J. Chem. Soc. D*, 1227 (1970).
460. D. Makanova, G. Ondrejovic and J. Gazo, *Chem. Zvesti*, **30**, 81 (1976).
461. M. Bressan and A. Morvillo, *Inorg. Chim. Acta*, **120**, 33 (1986).
462. R. G. Herman, *Inorg. Chim. Acta*, **34**, 119 (1979).
463. N. Kumar, P. L. Kachroo and R. Kant, *J. Indian Chem. Soc.*, **57**, 98 (1980).
464. M. Melnik and J. Mrozinski, *J. Mol. Struct.*, **78**, 85 (1982).
465. R. C. Paul, P. R. Sharma and S. L. Chadha, *Indian J. Chem., Sect. A*, **15** 27 (1977).
466. M. Melnik, and J. Mrozinski, *Z. Anorg. Allg. Chem.*, **500** 210 (1983).
467. M. Melnik, B. Zurowska, M. Janik and J. Mrozinski, *Pr. Nauk. Akad. Ekon. Oskara Langego Wroclaw.*, **426**, 200 (1988); *Chem Abstr.*, **110**, 184752r (1989).
468. M. Melnik and J. Mrozinski, *Finn. Chem. Lett.*, (3–4), 81 (1983); *Chem. Abstr.*, **99**, 114891r (1983).
469. P. Sharrock, M. Melnik, F. Belanger-Garvepy and A. L. Beauchamp, *Can. J. Chem.*, **63**, 2564 (1985).
470. B. Koren, P. Sivy, F. Valach, M. Melnik and J. Jecny, *Acta Crystallogr., Sect. C*, **44**, 646 (1988).
471. Y. Muto, A. Sasaki, T. Tokii, and M. Nakashima, *Bull. Chem. Soc. Jpn.*, **58**, 2572 (1985).
472. S. L. Chadha and P. R. Sharma, *J. Inorg. Nucl. Chem.*, **41**, 252 (1979).
473. S. S. Sandhu and J. S. Jaswal, *Indian J. Chem., Sect. A*, **29**, 245 (1990).
474. F. Brezina and E. Banatska, *Acta Univ. Palacki. Olomuc., Fac. Rerum Nat.*, **69**, (*Chem.* 20), 5 (1981); *Chem. Abstr.*, **97**, 229138b (1982).
475. M. Negoiu and P. Spacu, *An. Univ. Bucuresti, Chem.*, **19**, 73 (1970).
476. T. Kauffman and R. Joussen, *Chem. Ber.*, **110**, 3930 (1977).
477. Q. Mingoia, *Gazz. Chim. Ital.*, **62**, 333 (1932).
478. A. R. Hands, and A. J. H. Mercer, *J. Chem. Soc. A*, 449 (1968).
479. R. Uson, A. Laguna, M. Laguna, B. R. Manzano, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 285 (1984).
480. R. Uson, P. Royo, A. Laguna and J. Garcia, *Rev. Acad. Cienc. Exactas, Fis.-Quim. Nat., Zaragoza*, **28**, 67 (1973).
481. R. Uson, A. Laguna, and J. L. Sanjoaquin, *J. Organoment. Chem.*, **80**, 147 (1974).
482. R. A. Potts, *Inorg. Chem.*, **9** 1284 (1970).
483. D. R. Williamson and M. C. Baired, *J. Inorg. Nucl. Chem.*, **34**, 3393 (1972).
484. I. Collamati, *Ric. Sci., Parte 2, Sez. A*, **6** 363 (1964).
485. P. G. Jones and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, **34**, 1353 (1978).
486. J. P. Rose, R. A. Lalancette, J. A. Potenza and H. J. Schugar, *Acta Crystallogr., Sect. B*, **36** 2409 (1980).

487. W. Ried and H. Appel, *Justus Liebigs Ann. Chem.*, 646, 82 (1961); *Chem. Abstr.*, **56**, 10057h (1962).
488. Y. Hase and O. L. Alves, *J. Mol. Struct.*, **50**, 293 (1978).
489. G. B. Deacon and J. H. S. Green, *Chem. Ind.* (*London*), 1031 (1965).
490. M. J. Frazer, W. Gerrard and R. Twaits, *J. Inorg. Nucl. Chem.*, **25**, 637 (1963).
491. I. Lindqvist and G. Olofsson, *Acta Chem. Scand.*, **13**, 1753 (1959).
492. M. Zackrisson and K. Inge, *Acta Chem. Scand.*, **14**, 994 (1960).
493. G. N. Rao and N. C. Li, *Can. J. Chem.*, **44**, 2775 (1966).
494. G. N. Rao and N. C. Li, *Inorg. Nucl. Chem.*, **28**, 2931 (1966).
495. M. Negoiu and P. Spacu, *An. Univ. Bucuresti, Chem.*, **20**, 71 (1971); *Chem. Abstr.*, **78**, 66393x (1973).
496. P. A. W. Dean and G. K. Carson, *Can. J. Chem.*, **61**, 1800 (1983).
497. P. A. W. Dean, *Can. J. Chem.*, **59**, 3221 (1981).
498. (a) K. H. Tan, and M. J. Taylor, *Inorg. Nucl. Chem. Lett.*, **16**, 337 (1980); (b) S. Singh, A. Vij, M. Lal and R. D. Verma, *Indian J. Chem., Sect. A*, **28**, 890 (1989).
499. J. C. Queioz, C. Airoldi and A. Chagas, *J. Chem. Thermodyn.*, **18**, 709 (1986); *Chem Abstr.*, **105**, 198059d (1986).
500. R. A. Jorge, C. Airoldi and A. P. Chagas, *J. Chem. Soc., Dalton Trans.*, 1102 (1978).
501. V. D. Romanenko, V. F. Shul'gın, V. V. Skopenko and L. N. Markovskii, *Zh. Obshch. Khim.*, **54**, 2791 (1984).
502. A. J. Canty and G. B. Deacon, *Aust. J. Chem.*, **24** 489 (1971).
503. V. A. Tartakovskii and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **10**, 2279 (1971).
504. G. B. Deacon, A. Florenti, M. Hughes and F. P. Larkins, *Croat. Chem. Acta*, **57**, 757 (1984); *Chem Abstr.*, **102**, 220969n (1985).
505. D. L. Kepert, D. Tailor and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1658 (1973).
506. R. A. Potts and A. L. Allred, *Inorg. Chem.*, **5**, 1066 (1966).
507. J. Barry, J. G. H. DuPreez and T. I. Gerber, A. Litthauer, E. H. Rohwer and B. J. Van Brecht, *J. Chem. Soc., Dalton Trans.*, 1265 (1983).
508. F. Brezina and D. Krausova, *Acta Univ. Palacki. Olomuc., Fac. Rerum Nat.*, **41**, (*Chem.* 13), 13 (1973); *Chem. Abstr.*; **81**, 69693t (1974).
509. F. Brezina, *Collect. Czech. Chem. Commun.*, **36**, 3850 (1971); *Chem. Abstr.* **76**, 53863j (1972).
510. F. Brezina, *Collect. Czech. Chem. Commun.*, **36**, 2889 (1971).
511. E. P. Buchikhin, V. A. Ivanova and L. I. Sokal'skaya, *Zh. Neorg. Khim.*, **30**, 1712 (1985).
512. D. R. Cousins and F. A. Hart, *Chem. Ind.* (*London*), 1259 (1965).
513. D. R. Cousins and F. A. Hart, *J. Inorg. Nucl. Chem.*, **30**, 3009 (1968).
514. E. I. Sinyavskaya and Z. A. Sheka, *Zh. Neorg. Khim.*, **17**, 645 (1972).
515. A. Sen, V. Chekolu and E. M. Holt, *Inorg. Chim. Acta*, **118**, 87 (1986).
516. E. Stucchi, D. M. Berwerth and A. M. G. Massbni, *Publ. ACIESP 1982, 36 (An. Simp. Anu. ACIESP, 6th*, 172 (1982); *Chem. Abstr.*, **98**, 226865w (1983).
517. J. B. Marquesnovo, E, Berwerth Stucchi, J. Maquez Luiz and A. M. G. Massabni, *Ecletica Quim.*, **13**, 111 (1988).
518. J. V. Kingston, E. M. Krankovits and R. J. Magee, *Inorg. Nucl. Chem., Lett.*, **5**, 485 (1969).
519. V. K. Manchanda, K. Chander, N. P. Singh and G. M. Nair, *J. Inorg. Nucl. Chem.*, **39**, 1039 (1977).
520. H. Wang, M. Zhang, X. Jing, J. Wang, R. Wang and H. Wang, *Inorg. Chim. Acta*, **163**, 19 (1989).
521. X. Wang, M. Zhang, J. Wang. R. Wang and X. Yao, *Jiegou Huaxue*, **7**, 142 (1988).
522. X. Wang, M. Zhang, Z. Wang, X. Jing and J. Wang, *Gaodeng Xuexue Xuebao*, **10**, 886 (1989).
523. C. Huang, R. Xu, Y. Zhou, G. Xu, F. Guo and N. Zhu, *Wuli Xuaxue Xuebao*, **3**, 491 (1987).
524. F. Brezina, *Inorg. Synth.*, **23**, 178 (1985).
525. W. Zhu, D. Wang, B. Chen and L. Jin, *Gaodeng Xuexiao Huaxue Xuebao*, **5** 460 (1984).
526. F. Brezina, *Collect. Czech. Chem. Commun.*, **37**, 31 74 (1972).
527. C. N. Caughlan, H. F. A. Mazhar-ul-Haque and R. Van Nice, *Inorg. Chem.*, **10**, 115 (1971).
528. A. M. G. Massabni, M. L. R. Gibran and O. A. Serra, *Inorg. Nucl. Chem. Lett.*, **14**, 419 (1978).
529. Y. P. Mascarenhas, S. R. H. DeAlmeide, G. R. Leite and O. A. Serra, J. Inorg. Nucl. Chem.., **35**, 2595 (1973).
530. C. Huang, G. Li. Y. Thou, T. Jin and G. Xu, *Beijing Daxue Xuebao, Ziran Kexueban*, (6), 12 (1985).
531. G. Valle, G. Cassotto, P. L. Zauonato and B. Zarli, *Polyhedron*, **5**, 2093 (1985).

532. F. Grandjean, G. J. Long, M. L. Buhl, U. Russo, B. Zarli and G. Valle, *Inorg. Chim. Acta*, **139**, 113 (1987).
533. (a) T. Shigematsu, M. Tabushi, M. Matsui and T. Honjyo, *Bull. Chem. Soc. Jpn.*, **40**, 2807 (1967); (b) T. Shigematsu and T. Honjyo, *Bull. Inst. Chem. Res. Kyoto Univ.*, **25**, 282 (1967).
534. M. Kh. Karapet'yants, N. N. Guseva, A. I. Mikhailichenko and E. V. Sklenskaya, *Tezisy Dokl.- Vses. Chugaevskoe Soveshch. Khim. Kompleksn. Soedin., 12th*, **3**, 352 (1975); *Chem Abstr.*, **85**, 186077p (1976).
535. D. R. Cousins and F. A. Hart, *J. Inorg. Nucl. Chem.*, **29** 1745 (1967).
536. J. Vandegans and G. Duykaerts, *Anal. Chim. Acta*, **66**, 179 (1973).
537. P. K. Khopkar and P. Narayanankutty, *J. Inorg. Nucl. Chem.*, **34**, 2617 (1972).
538. (a) C. Huang, R. Xu, X. Xu and G. Xu, *Wuji Hauxan*, **1**, 103 (1985); (b) A. M. G. Massabni, E. B. Stuechi and A. C. P. Caires, *Ecletica Quim.*, **4**, 181 (1979).
539. K. Nakamura, *Bull. Chem. Soc. Jpn.*, **41**, 1254 (1968).
540. O. A. Serra, M. L. R. Gibran, A. M. B. Galindo, *Inorg. Nucl. Chem. Lett.*, **8**, 673 (1972).
541. H. Fan, Y. Liu, P. Zhou, L. Shi, C. Huang, R.Xu, X. Xu and G. Xu, *Wuji Huaxue*, **4**, 10 (1988).
542. C. Huang, R. Xu, B. Li, G. Xu, Y. Fan, Y. Liang, *Zhongguo Xitu Xuebao*, **5**, 1 (1987).
543. O. A. Serra and M. Moraes, *Rare Earths Mod. Sci. Technol.*, **3**, 91 (1982).
544. C. M. Mikulski, N. M. Karayannis, and L. L. Pytlewski, *J. Less-Common Met.*, **51**, 201 (1977).
545. A. M. da Silva, S. M. Melo, E. F. de Sousa and M. A. de Almedia, *Publ. ACIESP 1984, 44 (An. Simp. Anu. ACIESP, 8th 1983)*, **17**, 115 (1984); *Chem. Abstr.*, **103**, 204808z (1985).
546. S. Plostinaru and P. Spacu, *Rev. Roum. Chim.*, **18**, 2051 (1973).
547. G. Vicetini, L. R. F. Carvalho, and P. O. Dunstan, *Lanthanide Actinide Res.* **1**, 49 (1985).
548. S. I. Anufrieva, N. I. Snezhko, L. I. Martynenku and N. I. Pechurova., *Zh. Neorg. Khim.*, **26**, 3248 (1981).
549. N. I. Pechurova, L. I. Martynenko, N. I. Snezhko and S. I. Anufrieva, in *Teor. Prikl. Khim. β-Diketonatov Met.* Edi. by V. I. Spitsyn and L. I. Martynenko, Nauka, Moscow, 1985, p.142; *Chem. Abstr.*, **105**, 153179b (1986).
550. S. I. Anufrieva, *Deposited DOC*, VINITI 1575-82, 283 (1981); *Chem. Abstr.*, **98**, 154258a (1983).
551. S. I. Anufrieva, *Deposited DOC*, VINITI 3167-81, 78 (1981); *Chem. Abstr.*, **97**, 119480z (1982).
552. S. I. Anufrieva, G. V. Polyakova, N. I. Snezhko, N. I. Pechurova, L. I. Martynenko and V. I. Spitsyn, *IZv. Akad. Nauk SSSR, Ser. Khim.*, 1452 (1981).
553. W. Zhu, S. Yin and Z. Zhao, *Gaodeng Xuexiao Huaxue Xuebao*, **8**, 779 (1987).
554. L. A. Aslanov, V. M. Ionov, V. B. Rybakov, E. F. Korytnyi and L. I. Martynenko, *Koord. Khim.*, **4**, 1427 (19178).
555. E. F. Korytneji, in *Probl. Khim. Primen β- Diketonatov Met., Mater Vses. Semin. 1978* (Edi. V. I. Spitsyn), Nauka, Moscow, 1982, p.43, *Chem. Abstr.*, **98**, 44619n (1983).
556. V. S. Khomenko, M. O. Lozinskii, Yu. A. Fialkov, L. I. Krasovskaya and T. A. Rasshinina, *Koord. Khim.* **12**, 740 (1986).
557. J. G. Leipoldt, L. D. C. Bok, A. E. Laubscher and S. S. Bosson, *J. Inorg. Nucl. Chem.*, **37**, 3477 (1975).
558. V. I. Vovna, V. V. Gorchakov, A. Yu. Mamaev, V. E. Karasev, M. P. Kandinskii and A. G. Mirochnik, *Koord. Khim.*, **10**, 1362 (1984).
559. V. I. Vovna, V. A. Gorchakov, V. K. Karasev and A. I. Cherednichenko, *Zh. Strukt. Khim.*, **30**, 147 (1989).
560. V. E. Karasev, A. G. Mirochink and T. Y. Lysun, *Zh. Neorg. Khim.*, **33**, 343 (1988).
561. Y. Li. Y. Yang and T. C. W. Mak, *Jiegou Huaxue*, **7**, 165 (1988).
562. V. S. Khomenko, M. O. Lozinskii, Yu. A. Fialkov, T. A. Rasshinina and L. I. Krasovskaya, *Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk*, (2), 46 (1984).
563. N. Denlier, I. A. Murav'eva, L. I. Martynenko, V. I. Spitsyn, A. V. Davy dov and B. F. Myasoedov, *Izv. Akad. Nauk. SSR, Ser. Khim.*, 1455 (1976).
564. I. A. Murav'eva, L. I. Martynenko and V. I. Spitsyn, *Zh. Neorg. Khim.*, **22**, 3009 (1977); *Chem. Abstr.*; **88**, 31390y (1978).
565. N. P. Kuzmina, T. N. Chieu and L. I. Martynenko., *Metalloorg. Khim.*, **1**, 575 (1988); *Chem. Abstr.*, **109**, 182505t (1988).
566. G. A. Catton, F. A. Hart, G. P. Moss, *J. Chem. Soc., Dalton Trans.*, 208 (1976).
567. S. I. Anufrieva, N. I. Snezhko, L. I. Martynenko and N. I. Pechurova, *Zh. Neorg. Khim.*, **27**, 2784 (1982).

568. J. P. Quaegebeur, S. Belaid, C. Chachaty and H. LeBail, *J. Phys. Chem.*, **85**, 417 (1981).
569. B. T. Khan, S. Ali and M. Fazal, *Indian J. Chem., Sect. A*, **19**, 701 (1980).
570. N. I. Steblevskaya, V. E. Karasev and R. N. Shchelokov, *Zh. Neorg. Khim.*, **29** 2230 (1984).
571. E. S. Panin, V. E. Karaser, N. I. Steblenskaya and B. V. Bukvetskii, *Koord. Khim.*, **11**, 1127 (1987).
572. U. Casellato, P. A. Vigato, S. Tamburini, R. Graziani and M. Vidali, *Inorg. Chim. Acta*, **81**, 47 (1984).
573. B. Chen and Z. Ming, *Gaodeng Xuexiao Huaxue Xuebao*, **8**, 869 (1987).
574. B. Chen, M. Wang and L. Jin, *Wuji Huaxue*, **3**, 30 (1987).
575. E. Daire, H. Mimoun and L. Saussine, *Nouv. J. Chim.*, **8**271 (1984).
576. H. C. Aspinall, D. C. Bradley and K. D. Sales, *J. Chem. Soc., Dalton Trans.*, 2211 (1988).
577. D. C. Bradley, J. S. Ghotra, F. A. Hart, M. B. Hursthouse and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1166 (1977).
578. H. A. Stecher, A. Sen and A. L. Rheingold, *Inorg. Chem.*, **27**, 1130 (1988).
579. S. Singh, Maninder and R. D. Verma, *Indian J. Chem., Sect. A*, **23**, 1038 (1984).
580. S. A. A. Zaidi, S. R. A. Zaidi, T. A. Khan, S. A. Shaheur and S. A. Siddiqi, *Indian J. Chem., Sect. A*, **25**, 779 (1986).
581. S. Aftab, A. Zaidi, S. Rehan and T. A. Khan, *Synth. React. Inorg. Met.-Org. Chem.*, **17**, 901 (1987).
582. V. E. Karasev, N. I. Steblevskaya and N. V. Petrochenkova, *Koord. Khim.*, **14**, 1377 (1988).
583. G. A. Catton, F. A. Hart and G. P. Moss, *J. Chem. Soc., Dalton Trans.*, 221 (1975).
584. M. O. Lozinskii, Yu. A. Fialkov, V. S. Khomenko and T. A. Pavich, *Teor. Eskp. Khin.*, **26** 245 (1990).
585. A. A. Pinkerton, Y. Meseri and C. Rieder, *J. Chem. Soc., Dalton Trans.*, 85 (1978).
586. A. A. Pinkerton and D. Schwarzenbach, *J. Chem. Soc., Dalton Trans.*, 2466 (1976).
587. W. J. Evans, J. W. Grate, I. Bloom, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc.*, **107**, 405 (1985).
588. W. J. Evans, J. W. Grate and R. J. Duedans, *J. Am. Chem. Soc.*, **107**, 1671 (1985).
589. M. A. Wassef, *Indian J. Chem.*, **13**, 1203 (1975).
590. G. Bombieri, F. Benetollo, K. W. Bagnall, M. J. Plews and D. Brown, *J. Chem. Soc., Dalton Trans.*, 343 (1983).
591. A. G. M. Al-Daher and K. W. Bagnall, *J. Less-Common Met.*, **119**, 247 (1986).
592. A. G. M. Al-Daher and K. W. Bagnall, *J. Less-Common Met.*, **116**, 359 (1986).
593. B. C. Smith and M. A. Wassef, *J. Chem. Soc. A*, 1817 (1968).
594. G. Van der Bossche, J. Rebizant, M. R. Spiolet and J. Goffart, *Acta Crystallogr., Sect. C*, **44**, 994 (1988).
595. D. Brown, J. Hill and C. E. F. Rickard, *J. Chem. Soc. A*, 497 (1970).
596. I. Ahmed and K. W. Bagnall, *J. Less-Common Met.*, **98**, 309 (1984).
597. Z. M. S. Al-Kazzaz and R. A. Louis, *Z. Anorg. Allg. Chem.*, **440**, 286 (1978).
598. Z. M. S. Al-Kazzaz, K. W. Bagnall and D. Brown, *J. Inorg. Nucl. Chem.*, **35** 1493 (1973).
599. D. Brown, D. G. Holah and C. E. F. Rickard, *Chem. Commun.*, 651 (1968).
600. J. P. Day and L. M. Venanzi, *J. Chem. Soc. A* 197 (1966).
601. P. Gans, B. J. Hathaway and B. C. Smith, *Spectrochim. Acta*, **21**, 1589 (1965).
602. P. Gans and B. C. Smith, *J. Chem. Soc.*, 4172 (1964).
603. G. Bombieri, D. Brown and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1873 (1975).
604. A. D. Westland and M. T. H. Tarafder, *Inorg. Chem.*, **20**, 3992 (1981).
605. A. T. Falkengof, G. T. Bolotova, V. V. Zelentsov and R. N. Shchelokov, *Koord. Khim.*, **1**, 664 (1975).
606. B. C. Lane and L. M. Venanzi, *Inorg. Chim. Acta*, **3**, 239 (1969).
607. K. W. Bagnall, G. F. Payne and D. Brown, *J. Less-Common Met.* **109**, 31 (1985).
608. (a) G. Bombieri, D. Brown and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1873 (1975); (b) J. G. H. DuPreez, B. J. Gettatly and M. L. Gibson, *J. Chem. Soc., Dalton Trans.*, 1062 (1977).
609. G. Bombieri, E. Forsellini, D. Brown and B. Whittaker, *J. Chem Soc., Dalton Trans.*, 735 (1976).
610. J. D. Du Preez and B. Zeelie, *J. Chem. Soc., Chem Commun.*, 743 (1986).
611. D. Brown, J. Hill and C. E. F. Rickard, *J. Chem. Soc. A*, 476 (1970).
612. G. Bombieri, D. Brown and C. Mealli, *J. Chem. Soc., Dalton Trans.*, 2025 (1976).
613. J. A. Berry, J. H. Holloway and D. Brown, *Inorg. Nucl. Chem. Lett.*, **17**, 5 (1981).

614. D. Brown and C. Hurtgen, *J. Chem. Soc., Dalton Trans.*, 1709 (1979).
615. (a) J. H. Holloway and G. M. Staunton, *J. Less-Common Met.*, **120**, 71 (1986); (b) J. H. Holloway, D. Laycock and R. Bougon, *J. Fluorine Chem.*, **26**, 281 (1984).
616. G. Bombieri, E. Forrellini, J. P. Day and W. I. Azeez, *J. Chem. Soc., Dalton Trans.*, 677 (1978).
617. P. A. Vigato, M. Vidali and U. Casellato, *Gazz. Chim. Ital.*, **104**, 1283 (1974).
618. F. A. Hart and J. E. Newbery, *J. Inorg. Nucl. Chem.*, **28**, 1334 (1966).
619. J. P. Day and L. M. Venanzi, *J. Chem. Soc. A*, 1363 (1966).
620. F. A. Hart and J. E. Newbery, *J. Inorg. Nucl. Chem.*, **30**, 318 (1968).
621. P. Gans and B. C. Smith, *Chem. Ind. (London)*, 911 (1963).
622. E. V. Komarov and M. F. Pushlenkov, *Radiokhimiya*, **3**, 575 (1961).
623. S. M. Sinitsyna and N. M. Sinitsyn, *Dokl. Akad. Nauk SSSR*, **164**, 351 (1965).
624. B. W. Fitzsimmons, P. Gans, B. Hayton and B. C. Smith, *J. Inorg. Nucl. Chem.*, **28**, 915 (1966).
625. (a) S. A. Nikitins and A. A. Lipovskii, *Zh. Neorg. Khim.*, **18**, 1617 (1973); (b) V. Serban and I. Serban, *Bul. Inst. Politeh. Bucuresti, Ser. Chim.*, **50**, 67 (1988).
626. V. M. Vdovenko, T. V. Kovoleva, N. A. Kanevskaya and D. N. Suglobov, *Radiokhimiya*, **16**, 66 (1974).
627. V. A. Vodovatov, L. G. Mashirov and D. N. Suglobov, *Radiokhimiya*, **21**, 830 (1979).
628. V. A. Vodovatov, L. G. Mashirov and D. N. Suglobov, *Radiokhimiya*, **15**, 446 (1973).
629. V. M. Vdovenko, A. I. Skoblow and D. N. Suglobov, *Radiokhimiya*, **8**, 651 (1966).
630. Yu. I. Belyaev, U. M. Vdovcnko and A. I. Skoblo and D. N. Suglobov, *Radiokhimiya*, **9**, 720 (1967).
631. K. W. Bagnall and M. W. Wakerley, *J. Less-Common Met.*, **35**, 267 (1974).
632. P. A. Vigato, U. Casellato and M. Vidali, *Gazz. Chim. Ital.*, **107**, 61 (1977).
633. S. M. Sinitsyna and N. M. Sinitsyn, *Dokl. Akad Nauk SSSR*, **168**, 110 (1966).
634. K. W. Bagnall and M. W. Wakerley, *J. Inorg. Nucl. Chem.*, **37**, 329 (1975).
635. V. A. Vodovatov, L. G. Mashirov, D. N. Suglobov, *Radiokhimiya*, **17**, 900 (1975).
636. A. I. Skoblo and D. N. Suglobov, *Radiokhimiya*, **16**, 518 (1974).
637. R. C. Paul, S. Singh and R. D. Verma, *J. Indian Chem. Soc.*, **58**, 24 (1981).
638. D. Baudry and M. Ephiritikhine, *J. Organomet. Chem.*, **349**, 123 (1988).
639. P. Charpin, M. Lance, E. Soulie, D. Vigner and H. Marquet-Ellis, *Acta Crystallogr., Sect. C*, **41**, 1723 (1985).
640. N. W. Alcock, J. S. Esperas, K. W. Bagnall and W. Hsian-Yun, *J. Chem. Soc. Dalton Trans.*, 638 (1978).
641. N. Kumar and D. G. Tuck, *Can. J. Chem.*, **62**, 1701 (1984).
642. K. M. A. Malik and J. W. Joeffery, *Acta Crystallogr., Sect. B*, **29**, 2687 (1973).
643. V. M. Vdovenko, T. V. Kovaleva, N. A. Kanevskaya, V. P. stantevich and D. N. Suglobov, *Radiokhimiya*, **14**, 134 (1972).
644. K. W. Bagnall and M. W. Wakerley, *J. Chem. Soc., Dalton Trans.*, 889 (1974).
645. U. Casellato, D. Fregona, S. Tampurini, P. A. Vigato and R. Graziani, *Inorg. Chim. Acta*, **110**, 41 (1985).
646. J. G. H. Du Preez and C. P. J. Van Vuuren, *J. Chem. Soc., Dalton Trans.*, 1548 (1975).
647. J. R. Parker and C. V. Banks, *J. Inorg. Nucl. Chem.*, **27**, 631 (1965).
648. C. A. Strydom, C. P. J. Van Vuuren and H. J. Strydom, *Inorg. Chim. Acta*, **146**, 119 (1988).
649. J. G. H. Du Preez, and C. P. J. Van Vuuren, *J. Inorg. Nucl. Chem.*, **36**, 81 (1974).
650. J. L. M. Dillen, P. H. Van Rooyen, C. A. Strydom and C. P. J. Van Vuuren, *Acta Crystallogr., Sect. C*, **44**, 1921 (1988).
651. C. A. Strydom and C. P. J. Van Vuuren , *Inorg. Chim. Acta*, **117**, 83 (1986).
652. V. V. Yakshin, A. V. Romanov, M. I. Tymonyuk B. N. Laskorin, *Dokl. Acad. Nauk SSSR*, **252**, 162 (1980).
653. K. T. Basuki, *Majalah BATAN*, **18**, 54 (1985).
654. G. Bandoli, G. Bortolozzo, D. A. Clemente, U. Croatto and C. Panattoni, *Inorg. Nucl. Chem. Lett.*, **7**, 401 (1971).
655. J. E. Mrochek, J. W. O'Laughlin and C. U. Banks, *J. Inorg. Nucl. Chem.*, **27**, 603 (1965).
656. A. M. Rozen, Z. I. Nikolotova, N. A. Kartasheva, B. V. Martynov, and D. A. Denisov, *Tezisy Dokl. Vses. Knof. Khim. Uruna 1st*, 65, 1974; *Chem. Abstr.*, **87**, 173543d (1977).
657. R. Graziani, B. Zarli and G. Bandoli, *Ric. Sci.*, **37**, 984 (1967); *Chem. Abstr.*, **69**, 71298p (1968).
658. J. H. Burns, *Inorg. Chem.*, **20**, 3868 (1981).

659. I. A. Volodin, T. V. Kolyvanova, L. V. Kotova, M. A. Kovalenko and E. A. Filippov, *Radiokhimiya*, **22**, 504 (1980).
660. L. V. Kobets, I. M. Kopashova, T. A. Dik, I. A. Volodin, M. A. Kovalenko and V. Ya. Semenii, *Radiokhimiya*, **24**, 313 (1982).
661. J. H. Burns, *Inorg. Chem.*, **22**, 1174 (1983).
662. K. W. Bagnall and M. W. Wakerley, *J. Less-Common Met.*, **37**, 149 (1974).
663. Z. M. S. Al-Kazzaz, K. W. Bagnall and D. Brown, *J. Inorg. Nucl. Chem.*, **35**, 1501 (1973).
664. C. E. F. Rickard and D. C. Woollard, *Aust. J. Chem.*, **32**, 2181 (1979).
665. G. Bombieri, G. De Paoli, E. Forsellini and D. Brown, *J. Inorg. Nucl. Chem.*, **41**, 1315 (1979).
666. V. V. Skopenko, Yu. L. Zub, V. N. Yankorich, R. N. Shchelokov, A. V. Rotov and G. T. Bolotova, *Ukr. Khim. Zh.*, **50**, 1011 (1984).
667. G. Bombieri, E. Forsellini, G. De Paoli, D. Brown and T. C. Tso, *J. Chem. Soc., Dalton Trans.*, 2042 (1979).
668. V. M. Vdovenko, A. I. Skoblo and D. N. Suglobov, *Radiokhimiya*, **9**, 119 (1967).
669. K. W. Bagnall, G. F. Payne and D. Brown, *J. Less-Common Met.*, **116**, 333 (1986).
670. O. Velasquez, K. W. Bagnall, H. H. Alvarez, I. Berrio and L. Montalvo, *Rev. Colomb. Quim*, **13**, 37 (1984).
671. I. Ahmed and K. W. Bagnall, *J. Chem. Soc., Dalton Trans.*, 1527 (1984).
672. K. W. Bagnall, O. V. Lopez and L. Xing-Fu, *J. Chem. Soc., Dalton Trans.*, 1153 (1983).
673. M. T. H. Tarafder, M. B. H. Howlader, B. Nath, R. Khan and A. A. M. Anwarul Islam, *Polyhedron*, **8**, 977 (1989).
674. M. T. H. Tarafder, *Indian J. Chem., Sect. A*, **26**, 876 (1987).
675. R. N. Shchelokov, I. M. Orlova, A. V. Sergeev and A. G. Beirakhov, *Koord. Khim.*, **7**, 1062 (1981).
676. H. A. Tayim, S. K. Thabet, and M. U. Karkanawi, *Inorg. Nucl. Chem. Lett.*, **8**, 235 (1972).
677. C. Panattoni, R. Graziani, G. Bandoli, B. Zarli and G. Bombieri, *Inorg. Chem.*, **8**, 320 (1969).
678. C. Panattoni, G. Bandoli, R. Graziani and U .Croatto, *Chem. Commun.*, 278 (1968).
679. T. H. Siddall, III, W. E. Stewart and R. L. McDonald, *Inorg. Nucl. Chem. Lett*, **5**, 101 (1969).
680. I. A. Yuranov, K. M. Dunaeva and L. E. Gvozdeva, *Zh. Neorg. Khim.*, **33**, 983 (1988).
681. L. M. Alikhanova, V. F. Zolin, P. S. Fisher and G. V. Ellert, *Zh. Neorg. Khim.*, **17**, 762 (1972).
682. L. V. Kobets, T. A. Dik, D. S. Umreiko, I. A. Volodin, L. V. Vinogradov and E. A. Fillippov, *Radiokhimiya*, **26**, 630 (1984).
683. (a) J. Goffart, J. Piret-Meunier and G. Duyckaerts, *Inorg. Nucl. Chem. Lett.*, **16**, 233 (1980); (b) G. S. Rao, S. C. Jain and M. S. Gill, *Indian J. Chem., Sect. A.*, **21**, 526 (1982).
684. (a) N. W. Alcock, D. J. Flanders, K. W. Bagnall and I. Ahmed, *Acta Crystallogr. Sect. C*, **42**, 634 (1986); (b) V. K. Manchanda, G. A. R. Rao and W. D. Lloyd, *J. Radioanal. Nucl. Chem.*, **139**, 223 (1990).
685. A. G. M. Al-Daher and K. W. Bagnall, *J. Chem. Soc., Dalton Trans.*, 355 (1986).
686. W. Zhu, J. Zhao, Y. Ren, X. Zhao, B. Luo and L. Chen, *Wuji Huaxue*, **4**, 55 (1988).
687. B. Luo, L. Chen, W. Zhu and S. Yin, *Jiegou Huaxue*, **6**, 173 (1987).
688. L. Doretti, P. Zanella, S. Fateschini and G. Faraglia, *J. Inorg. Nucl. Chem.*, **35**, 3171 (1973).
689. C. Baudin, P. Charpin, M. Ephritikhine, M. Lance, M. Nierlich and J. Vigner, *J. Organomet. Chem.*, **345**, 263 (1988).
690. C. H. Wong, C. N. Chen., T. H. Lu, K. J. Chao and T. J. Lee, *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.*, **134**, 312 (1971).
691. T. H. Lu, T. J. Lee, T. Y. Lee, and C. Wong, *Inorg. Nucl. Chem. Lett.*, **13**, 363 (1977).
692. V. K. Manchanda and M. S. Subramanian, *Acta. Chim. Acad. Sci. Hung.*, **111**, 69 (1982).
693. V. M. Adamov, B. N. Belyaev, S. O. Berezinskii, G. V. Sidorenko and D. N. Suglobov, *Radiokhimiya*, **27**, 13 (1985).
694. A. B. McLaren, *Inorg. Nucl. Chem. Lett.*, **15**, 167 (1979).
695. V. M. Adamov, B. N. Belyaer, S. O. Berezinskii, G. A. Firsanov, G. V. Sidorenko and D. N. Suglobov, *Radiokhimiya*, **28**, 172 (1986).
696. J. C. Taylor and A. B. McLaren, *J. Chem. Soc., Dalton Trans.*, 460 (1979).
697. N. R. Grebenshchikov, G. V. Sidorenko, D. N. Suglobov and L. A. Shcherbakova, *Radiokhimiya*, **29**, 710 (1987).
698. N. R. Grebenshchikov, G. V. Sidorenko, D. N. Suglobov, L. L. Shcherbakova and V. M. Adamov, *Inorg. Chim. Acta*, **145**, 315 (1988).

699. M. S. Sajun, V. V. Ramakrishna and S. K. Patil, *Proc. Indian Acad. Sci., Chem. Sci.*, **90**, 323 (1981).
700. N. R. Grebenshchikov, G. V. Sidorenko, L. L. Shcherbakova and D. N. Suglobov, *Radiokhimiya*, **28**, 453 (1986).
701. N. R. Grebenshchikov, G. V. Sidorenko, D. N. Suglobov, V. A. Shcherbakov and L. L. Shcherbakov, *Radiokhimiya*, **27**, 526 (1985).
702. V. V. Ramakrishna, P. M. Mapara and S. K. Patil, *J. Radioanal. Chem.*, **78**, 65 (1983).
703. A. V. Davydov, B. F. Myasoedov, S. S. Travnikov and E. V. Fedoseev, *Radiokhimiya*, **20**, 257 (1978).
704. K. W. Bagnall, A. Beheshti, and F. Heatley, *J. Less-Common Met.*, **61**, 63 (1978).
705. K. W. Bagnall, G. F. Payne, N. W. Alcock, D. J. Flanders and D. Brown, *J. Chem. Soc., Dalton Trans.*, 783 (1986).
706. K. W. Bagnall, G. F. Payne and D. Brown, *J. Less-Common Met.*, **113**, 325 (1985).
707. J. G. Brennan, R. A. Andrisen and A. Zalkin, *Inorg. Chem.*, **25**, 1761 (1986).
708. K. W. Bagnall, F. Benetollo, G. Bombieri and G. De Paoli, *J. Chem. Soc., Dalton Trans.*, 67 (1984).
709. K. W. Bagnall, J. Edwards and A. C. Tempest, *J. Chem. Soc., Dalton Trans.*, **295** (1978).
710. I. Ahmed and K. W. Bagnall, *J. Less-Common Met.*, **99**, 285 (1984).
711. D. Baudry, P. Dorion and M. Ephritikhine, *J. Organomet. Chem.*, **356**, 165 (1988).
712. K. W. Bagnall, A. Beheshti, F. Heatley and A. C. Tempest, *J. Less-Common Met.*, **64**, 267 (1979).
713. K. W. Bagnall, J. Edwards, C. E. F. Rickard and A. C. Tempest, *J. Inorg. Nucl. Chem.*, **41**, 1321 (1979).
714. K. W. Bagnall, A. Beheshti, J. Edwards, F. Heatley and A. C. Tempest, *J. Chem. Soc., Dalton Trans.*, 1241 (1979).
715. N. V. Magazeeva, L. I. Martynenko, I. A. Muraveva and V. I. Spitsyn, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1326 (1988).
716. J. L. Stewart, *Report*, 1988, LBL-25240, Order No. DE 88010356; p200 (Eng.). Avail NTIS, from Energy Res. Abstr., **13**, 37087 (1988); *Chem. Abstr.*, **110**, 241564g (1989).
717. W. Wang, Q. Liu, M. S. Caceci and G. R. Choppin, *He Huaxue Yu Fangshe Huaxue*, **6**, 137 (1984).
718. M. S. Nagar, P. B. Ruikar and M. S. Subramanian, *Polyhedron*, **6**, 1913 (1963).
719. L. Cattalini, S. Degetto, M. Vidali and P. A. Vigato, *Inorg. Chim. Acta*, **6**, 173 (1972).
720. A. Pasini, M. Gullotti and E. Cesarotti, *J. Inorg. Nucl. Chem.*, **34**, 3821 (1972).
721. L. Cattalini, P. A. Vigato, M. Vidali, S. Degetto and U. Casellato, *J. Inorg. Nucl. Chem.*, **37**, 1721 (1975).
722. A. T. T. Hsieh, R. M. Sheahan, B. West, *Aust. J. Chem.*, **28**, 885 (1975).
723. U. S. Casellato, S. Sitran, S. Tamburini, P. A. Vigato and R. Graziani, *Inorg., Chim. Acta*, **95**, 37 (1984).
724. U. Casellato, S. Sitran, S. Tamburini, P. A. Vigato and R. Graziani, *Congr. Naz. Chim., Inorg., [Atti], 16th*, 189 (1983); *Chem. Abstr.*, **100**, 44391r (1984).
725. B. C. Bhattacharyya and S. Roy, *Indian J. Chem.*, **13**, 708 (1975).
726. S. Degetto, L. Baracco, G. Marangoni and E. Celon, *J. Chem. Soc., Dalton Trans.*, 1645 (1976).
727. S. Degetto, G. Marangoni, G. Bombieri, R. Graziani, *Atti Acad. Peloritana Pericolanti, Cl. 50, Fis., Mat. Nat.*, **54**, 69 (1974); *Chem. Abstr.*, **85**, 13163k (1976).
728. S. Degetto, G. Marangani, G. Bombieri, E. Forsellini, L. Barracco and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1933 (1974).
729. I. Ahmed, K. W. Bagnall, X.-F. Li and P.-J. Pao *J. Chem. Soc., Dalton Trans.*, 19 (1984).
730. L. Graziani, A. Cassol, G. Bombieri and E. Forsellini, *Bull. Sci. Fac. Chim. Ind. Bologna*, **27**, 87 (1969).
731. R. Graziani, B. Zarli, A. Cassol, G. Bombieri, E. Forsellini and E. Tondello, *Inorg. Chem.*, **9**, 2116 (1970).
732. T. H. Siddal, III, and C. F. Voisin, *J. Inorg. Nucl. Chem.*, **34**, 2078 (1972).
733. C. C. Hadjikostas, G. A. Katsonlos and M. P. Signals, *Inorg. Chim. Acta*, **134**, 175 (1987).
734. I. Haiduc, M. Curtui, *Synth. React. Inorg. Met. Org. Chem.*, **6**, 125 (1976).
735. G. Bombieri, U. Croatto, E. Forsellini, B. Zarli and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 560 (1972).
736. E. I. Ivanova, V. V. Skopenko and K. Keller, *Ukr. Khim. Zh.*, **47**, 1024 (1981).
737. U. Casellato, P. A. Vigato and M. Vidali, *J. Inorg. Nucl. Chem.*, **37**, 1181 (1975).

738. P. A. Vigato, U. Casellato, D. A. Clemente and G. M. Bondoli, *J. Inorg. Nucl. Chem.*, **35**, 4131 (1973).
739. (a) U. Casellato, M. Vidali, P. A. Vigato, G. Bandoli and D. A. Clement, *Inorg. Nucl. Chem. Lett.*, **9**, 299 (1973); (b) J. I. Bullock, *J. Inorg. Nucl. Chem.*, **29**, 2257 (1967); (c) D. L. Plymale, *J. Inorg. Nucl. Chem.*, **31**, 236 (1969); (d) R. Graziani, U. Casellato, P. A. Vigato, M. Vidali, S. Tamburini, *Congr. Naz. Chim. Inorg. [Atti], 15th*, 123 (1982); *Chem Abstr.*, **100**, 1500029p (1984); (e) R. Graziani, U. Casellato, P. A. Vigato, S. Tamburini and M. Vidali, *J. Chem. Soc., Dalton Trans.*, 697 (1983).
740. M. J. Bula, J. S. Hartman and C. V. Raman, *Can. J. Chem.*, **53**, 326 (1975).
741. A. B. Burg and W. E. McKee, *J. Am. Chem. Soc.*, **73**, 4590 (1951).
742. R. Bravo and M. Durand, *C.R. Acad. Sci., Ser. C*, **273**, 37 (1971).
743. R. Bravo, M. Durand and J. P. Laurent, *Org. Magn. Reson.*, **5**, 357 (1973).
744. R. Bravo and J. P. Laurent, *J. Chem. Res. (S)*, 61 (1983).
745. M. E. Beach and T. C. Waddington, *J. Chem. Soc.*, 3450 (1962).
746. M. L. Denniston and D. R. Martin, *J. Inorg. Nucl. Chem.*, **36**, 1461 (1974).
747. R. A. Geanangel, *J. Inorg. Nucl. Chem.*, **36**, 1397 (1974).
748. W. H. Knoth, Jr, *US Pat.* 3 009 961; *Chem. Abstr.* **57**, p12538f (1962).
749. N. E. Miller, *Inorg. Chem.*, **8**, 1693 (1969).
750. F. Seel and H. J. Bassler, *Z. Anorg. Allg. Chem.*, **423**, 67 (1976).
751. N. Burford, R. E. v. H. Spence, A. Linden and T. S. Cameron, *Acta Crystallogr., Sect C*; *Cryst. Struct. Commun.*, **46**, 92 (1990).
752. S. D. Radosavljevic and D. D. Poleti, *Glas. Hem. Drus. Beograd*, **44**, 639 (1979); *Chem. Abstr.*, **93**, 18265v (1980).
753. S. D. Radosavljevic, D. D. Poleti, *Glas. Hem. Drus. Beograd*, **44**, 311 (1979); *Chem. Abstr.* **92**, 87198s (1980).
754. F. Schindler, O. H. Schmidbauer and G. Jonas, *Chem. Ber.*, **98**, 3345 (1965).
755. K. M. Nykerk and D. P. Eyman, *Inorg. Nucl. chem. Lett.*, **4**, 253 (1968).
756. S. D. Radosavljevic and S. M. Radosavljevic, *Glas. Hem. Drus. Beograd*, **41**, 231 (1976); *Chem. Abstr.*, 135646g (1977).
757. H. Demarne and P. Cadiot, *Bull. Soc. Chim. Fr.*, 211 (1968).
758. F. Schindler, H. Schmidbauer and G. Jonas, *Angew. Chem.*, **77**, 170 (1965).
759. F. Schindler and H. Schmidbauer, *Chem. Ber.*, **100**, 3655 (1967).
760. J. Angenault, J. C. Couturier and C. Perchard, *J. Inorg. Nucl. Chem.*, **39**, 369 (1977).
761. C. Perchard, J. Angenault and J. C. Couturier, *Spectrochim. Acta, Part A*, **33**, 793 (1977).
762. J. Angenault and J. C. Couturier, *C.R. Acad. Sci., Ser. C*, **282**, 899 (1976).
763. S. J. Patel and D. G. Tuck, *Can. J. Chem.*, **47**, 229 (1969).
764. V. F. Mikitchenko, V. V. Skopenko and G. V. Tsintsadze, *Ukr. Khim. Zh.*, **37**, 1292 (1971).
765. A. J. Carty and D. G. Tuck, *J. Chem. Soc., Suppl.*, 6012 (1964).
766. A. J. Carty and D. G. Tuck, *J .Chem. Soc. A*, 1081 (1966).
767. S. J. Patel and D. G. Tuck, *J. Chem. Soc. A*, 1870 (1968).
768. R. C. Paul, R. D. Sharma, S. Singh and R. D. Verma, *J. Inorg. Nucl. Chem.*, **43**, 1919 (1981).
769. W. T. Robinson, C. J. Wilkins, and Z. Zeying, *J. Chem. Soc., Dalton Trans.*, 219 (1990).
770. T. B. Brill and D. C. Miller, *Inorg. Chem.*, **15**, 2553 (1976).
771. V. V. Skopenko and V. F. Mikitchenko, *Ukr. Khim. Zh.*, **37**, 878 (1971).
772. S. J. Patel, D. B. Sowerby and D. G. Tuck, *J. Chem. Soc. A*, 1187 (1967).
773. G. B. Deacon, and J. C. Parroltt, *Aust. J. Chem.*, **25**, 1169 (1972).
774. F. A. Cotton, B. F. G. Johnson and R. M. Wing. *Inorg. Chem.*, **4**, 502 (1965).
775. M. R. Bermejo, F. Botana, M. Gayoso, A. Castineiras, W. Hiller, T. Strachle, *Acta Cient. Compostelana*, **22**, 161 (1985); *Chem. Abstr.*, **104**,101231x (1986).
776. S. E. Jeffs, R. W. H. Small and I. J. Worrall, *Acta Crystallogr., Sect. C*, **40**, 381 (1984).
777. M. R. Bermejo and M. Gayoso, *Synth. React. Inorg. Met. Org. Chem.*, **15**, 951 (1985).
778. A. Castineiras, W. Hiller, M. R. Bermejo and M. Gayoso, *Acta Crystallogr. Sect. C*, **42**, 1289 (1986).
779. M. R. Bermejo, A. Rodriguez, A. G. Deibe and J. Tajes, *An. Quim., Ser. B*, **84**, 293 (1988); *Chem. Abstr.*, **110**, 241572h (1989).
780. M. R. Bermejo, A. Fernandez, M. Gayoso, A. Castineiras, W. Hiller and J. Straehle, *Polyhedron*, **7**, 2561 (1988).

781. S. P. Khremenko, L. K. Chuchalin, A. I. Rezvukhin, and Z. N. Mironova, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 53 (1973); *Chem. Abstr.*, **78**, 131544p (1973).
782. T. N. Srivastava and M. N. Pande, *J. Indian Chem. Soc.*, **62**, 649, (1985).
783. A. G. Lee, *J. Organomet. Chem.*, **22**, 537 (1970).
784. G. B. Deacon and V. N. Garg, *Aust. J. Chem.*, **24**, 2519 (1971).
785. G. B. Deacon and R. S. Nyholm, *J. Chem. Soc.*, 6107 (1965).
786. G. B. Deacon and R. J. Phillips, *J. Organomet. Chem.*, **199**, 15 (1980).
787. K. Henrick, M. McPartlin, G. B. Deacon and R. J. Phillips, *J. Organomet. Chem.* **204**, 287 (1980).
788. K. Henrick, M. McPartlin, R. W. Matthews, G. B. Deacon and R. J. Phillips, *J. Organomet. Chem.*, **193**, 13 (1980).
789. G. B. Deacon and V. N. Garg, *Aust. J. Chem.*, **26**, 2355 (1973).
790. R. Uson, A. Laguna, J. A. Abad and E. De Jesus, *J. Chem. Soc., Dalton Trans.*, 1127 (1983).
791. J. R. Beattie and M. Webster, *J. Chem. Soc.*, 3672 (1965).
792. K. Issleib and H. Reinhold, *Z. Anorg. Allg. Chem.*, **314**, 113 (1962).
793. V. O. Gel'mbol'dt and S. P. Petrosyants, *Koord. Khim.*, **15**, 501 (1989).
794. M. Zeldin, P. Mehta and W. D. Vernon, *Inorg. Chem.*, **18**, 463 (1979).
795. F. J. Feher, T. A. Budzichowski and K. J. Weller, *J. Am. Chem. Soc.*, **111**, 7288 (1989).
796. T. B. Absi, R. C. Makhija and M. Onyszchuk, *Can. J. Chem.*, **56**, 2039 (1978).
797. J. D. Donaldson and D. G. Nicholson, *J. Chem. Soc. A*, 145 (1970).
798. P. A. W. Dean, D. D. Phillips and L. Polensek, *Can J. Chem.*, **59**, 50 (1981).
799. N. Dodov, N. Spasovska and S. Varbanov, *Dokl. Bolg. Akad. Nauk*, **42**, 53 (1989).
800. A. I. Kuzmin and G. N. Zviadadze, *Koord. Khim.*, **6**, 1538 (1980).
801. Sh. Bashkirov, I. Ya. Kuramashin, A. S. Khramov and A. N. Pudovik, *Koord. Khim.*, **5**, 1008 (1979).
802. D. Tudela, J. D. Tornero, C. Muro and V. Fernandez, *J. Mol. Struct.*, **143**, 235 (1986).
803. B. C. Smith and M. A. Wassef, *Egypt. J. Chem.*, **18**, 381 (1975).
804. F. P. Mullins and C. Curran, *J. Inorg. Nucl. Chem.*, **39**, 377 (1977).
805. K. G. Huggins, F. W. Parrett and H. A. Patel, *J. Inorg. Nucl. Chem.*, **31**, 1209 (1969).
806. A. I. Tursina, A. V. Yatsenko, S. V. Madvedev, V. V. Cheryshev and L. A. Astanov, *Zh. Struckt. Khim.*, **27**, 157 (1986).
807. A. I. Tursina, L. A. Aslanov, V. V. Chernyshev, S. V. Medvedev and A. V. Yatsenko, *Koord. Khim.*, **12**, 1420 (1986).
808. L. V. Kucheruk, I. P. Gol'dshtein, I. Ya. Kuramshin, E. N. Gur'yanova and A. N. Pudovik, *Zh. Obshch. Khim.*, **47**, 2386 (1977).
809. A. N. Pudovik, A. A. Muratova, M. D. Medvedeva and E. G. Yarkova, *Zh. Obshch. Khim.*, **41**, 766 (1971).
810. A. V. Aganov, A. A. Musina, I. Ya. Kuramshin, E. G. Yarkova, Yu. Yu. Samitov and A. A. Muratov, *Zh. Strukt. Khim.*, **15**, 779 (1974).
811. A. N. Pudovik, A. A. Muratova, E. G. Yarkova and M. D. Medvedeva, *Zh. Obshch. Khim.*, **41**, 1481 (1971).
812. P. G. Harrison, B. C. Lane and J. J. Zuckerman, *Inorg. Chem.*, **11**, 1537 (1972).
813. J. P. Clark, V. M. Langford and C. J. Wilkins, *J. Chem. Soc. A*, 792 (1967).
814. C. J. Wilkins and H. M. Haendler, *J. Chem. Soc.*, 3174 (1965).
815. J. Philip, M. A. Mullins and C. Curran, *Inorg. Chem.*, **7**, 1895 (1968).
816. G. M. Bancroft, V. G. Kumar Das and K. D. Butler, *J. Chem. Soc., Dalton Trans.*, 2355 (1974).
817. A. N. Pudovik, I. Ya. Kuramtsin, A. A. Muratova and R. A. Manapov, *Fiz. Mat. Metody Koord. Khim., Tezisy Dokl., Vses, Soveshch., 5th*, 1974, 132 (1974).
818. A. A. Muratova and A. N. Pudovik, *Zh. Obshch. Khim.*, **45**, 1975 (1975).
819. A. V. Aganov, A. A. Musina, I. Ya. Kuramshin, Yu. Yu. Sanitov and A. A. Muratov, *Tezisy Dokl.-Vses. Chugaevskoe Soveshch. Khim. Kompleksn. Soedin., 12th*, **2**, 159; (1975); *Chem. Abstr.*, **85**, 171014s (1976).
820. E. G. Yarkova, Sh. M. Nazipov, O. B. Sobanova, A. A. Muratova and A. N. Pudovik, *Zh. Obshch. Khim.*, **48**, 749 (1978).
821. A. A. Musina, A. V. Aganov, I. Ya. Kuramshin, Yu. Sanitov and A. A. Muratova, *Zh. Strukt. Khim.*, **17**, 315 (1976).
822. M. Masaki, S. Matsunami, K. Okimoto and H. Ueda, *Chem. Lett.*, 119 (1978).

823. R. C. Paul, P. Sharma, L. Subbiah, H. Singh and S. L. Chadha, *J. Inorg. Nucl. Chem.*, **38**, 169 (1976).
824. A. I. Tursina, L. A. Aslanov, S. V. Medvedev and A. V. Yatsenko, *Koord. Khim.*, **11**, 417 (1985).
825. R. Colton and D. Dakternieks, *Inorg. Chim. Acta*, **71**, 101 (1983).
826. A. C. Sau, R. R. Holmes, K. C. Molloy and J. J. Zuckerman, *Inorg. Chem.*, **21**, 1421 (1982).
827. E. P. Mullins, *Can. J. Chem.*, **49**, 2719 (1971).
828. S. V. Medveda, A. V. Yatsenko and L. A. Aslanov, *Zh. Neorg. Khim.*, **32**, 1518 (1987).
829. A. I. Tursina, S. V. Madvedev, A. V. Yatsenko, V. V. Chernyshev and L. A. Aslanov, *Zh. Strukt. Khim.*, **27**, 145 (1986).
830. I. P. Goldshtein, A. A. Muratova, E. N. Gur'yanova, V. P. Plekhov, T. A. Pestova, E. S. Shcherbakova, R. R. Shifrina and A. N. Pudovik, *Zh. Obshch. Khim.*, **45**, 1685 (1975).
831. M. V. Garad, S. Gopinathan and C. Gopinathan, *Indian J. Chem., Sect. A*, **20**, 412 (1981).
832. R. Colton and D. Dakternieks, *Inorg. Chim. Acta*, **143**, 151 (1988).
833. D. Cunningham, M. Little and K. McLoughlin, *J. Organomet. Chem.*, **165**, 287 (1979).
834. C. H. Yoder, M. S. Coley, A. Grushow, B. G. Enders, S. P. Kneizys and J. N. Spencer, *J. Organomet. Chem.*, **346**, 165 (1988).
835. M. A. Wassef and S. Hessin, *Egypt, J. Chem.*, **24**, 97 (1981).
836. R. Colton and D. Dakternieks, *Inorg. Chim. Acta*, **148**, 31 (1988).
837. B. V. Liengme, R. S. Randall and J. R. Sams, *Can. J. Chem.*, **50**, 3212 (1972).
838. R. Colton and D. Dakternieks, *Inorg. Chim. Acta,* **102**, L17 (1985).
839. J. H. Holloway, G. P. McQuillan and D. S. Ross, *J. Chem. Soc. A*, 1935 (1971).
840. S. N. Bhattacharya and M. Khurana, *Indian J. Chem., Sect. A*, **16**, 988 (1978).
841. A. N. Pudovik, A. A. Muratova, M. D. Medveda, E. T. Yarkova and E. I. Loginava, *Zh. Obshch. Khim.*, **42**, 327 (1972).
842. V. G. Kumar Das, C. K. Yap and P. J. Smith, *J. Organomet. Chem.*, **327**, 311 (1987).
843. C. D. Garner, B. Hughes and T. J. King, *J. Chem. Soc., Dalton Trans.*, 562 (1975).
844. A. Midha and R. D. Verma, *J. Indian Chem. Soc.*, **62**, 421 (1985).
845. E. P. Mullins, C. Curran, *Can. J. Chem.*, **53**, 3200 (1975).
846. J. H. Holloway, G. P. McQuillan and D. S. Ross, *J. Chem. Soc. A*, 2505 (1969).
847. A. I. Tursina, L. A. Aslanov, V. V. Chernyshev, S. V. Medvedev and A. V. Yatsenko, *Koord. Khim.*, **11**, 1420 (1985).
848. A. I. Tursina, L. A. Aslanov, V. V. Chernyshev, S. V. Medvedev and A. V. Yatsenko, *Koord. Khim.*, **11**, 696 (1985).
849. J. P. Clark and C. J. Wilkins, *J. Chem. Soc. A*, 871 (1966).
850. P. G. Harrison, S. E. Ulrich and J. J. Zuckerman, *J. Am. Chem. Soc.*, **93**, 5398 (1971).
851. V. G. Kumar Das and W. Kitching, *J. Organomet. Chem.*, **13**, 523 (1968).
852. T. K. Sham, J. S. Tse, V. Wellington and G. M. Bancroft, *Can. J. Chem.*, **55**, 3487 (1977).
853. W. Kitching, V. G. Kumar Das and C. J. Moore, *J. Organomet. Chem.*, **22**, 399 (1970).
854. V. G. Kumar Das, N. S. Weng, J. Singh, P. J. Smith and R. Hill, *J. Organomet. Chem.*, **214**, 183 (1981).
855. M. Nardelli, C. Pelizzi and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 131 (1978).
856. G. M. Bancroft, V. G. Kumar Das, T. K. Sham and M. G. Clard, *J. Chem. Soc., Chem. Commun.*, 236 (1974).
857. J. C. Hill, R. S. Drago and R. H. Herber, *J. Am. Chem. Soc.*, **91**, 1644 (1969).
858. B. W. Fitzsimmons, J. Ensling, Ph. Guetlich and K. M. Hassellbach, *J. Chem. Soc. A*, 1940 (1971).
859. K. K. Bajpai and B. Bajpai, *J. Indian Chem. Soc.*, **59**, 1090 (1982).
860. J. Buckle and P. G. Harrison, *J. Organomet. Chem.*, **77**, C22 (1974).
861. A. Sau, L. A. Carpino and R. R. Holms., *J. Organomet. Chem.*, **197**, 181 (1980).
862. V. G. Kumar Das, Y. C. Keong, N. S. Weng, C. Wei and T. C. W. Mak, *J. Organomet. Chem.*, **311**, 289 (1988).
863. T. N. Srivastava and P. C. Kamboj, *Indian J. Chem,. Sect. A*, **19**, 167 (1980).
864. M. Nardelli, C. Pelizzi and G. Pelizzi, *J. Organomet. Chem.*, **112**, 263 (1976).
865. T. N. Srivastava and P. Kumar, *Indian J. Chem., Sect. A*, **22**, 878 (1983).
866. T. N. Srivastava and P. C. Kamboj, *J. Indian Chem. Soc.*, **60**, 396 (1983).
867. T. N. Srivastava and J. D. Singh, *Indian J. Chem., Sect. A*, **22**, 128 (1983).
868. T. N. Srivastava and J. D. Singh, *Indian J. Chem., Sect. A*, **22**, 674 (1983).

869. D. W. Allen, D. J. Derbyshire, I. W. Nowell and J. S. Brooks, *J. Organomet. Chem.*, **260**, 263 (1984).
870. D. W. Allen, D. J. Derbyshire, J. S. Brooks and P. J. Smith, *J. Organomet. Chem.*, **251**, 45 (1983).
871. D. W. Allen, D. J. Derbyshire, J. S. Brooks, S. J. Blunden and P. J. Smith, *J. Chem. Soc., Dalton Trans.*, 1989 (1984).
872. A. N. Pudovik, A. A. Muratova and E. P. Semkina, *Zh. Obshch. Khim.*, **33**, 3350 (1963).
873. J. N. Spencer, S. M. Coley, J. C. Otter, A. Grushow, B. G. Enders, W. L. Nachlis and C. H. Yoder, *J. Organomet. Chem.*, **346**, 161 (1988).
874. C. H. Yoder, S. M. Coley, S. P. Kneizys and J. N. Spencer, *J. Organomet. Chem.*, **362**, 59 (1989).
875. A. N. Pudovik, A. A. Muratova and M. D. Medvedeva, *Zh. Obshch. Khim.*, **42**, 1910 (1972).
876. V. G. Kumar Das. N. S. Weng, P. J. Smith and R. Hill, *J. Chem. Soc., Dalton Trans.*, 552 (1981).
877. A. J. Crowe, P. J. Smith and P. G. Harrison *J. Organomet. Chem.*, **204**, 327 (1980).
878. S. W. Ng and J. J. Nuckerman, *Organometallics*, **1**, 714 (1982).
879. H. P. Abicht and H. Weichmann, *Z. Chem.*, **28**, 69 (1988).
880. H. Clees and F. Huber, *Z. Anorg. Allg. Chem.*, **352**, 200 (1967).
881. F. Huber and M. S. A. Eel-Meligi, *Ger. Pat.*, 1 814 260 (1971); *Chem. Abstr.*, **74**, 142062y (1971).
882. H. J. Haupt and F. Huber, *J. Organomet. Chem.*, **33**, 175 (1971).
883. I. Wharf, R. Wojtowski and M. Onyszchuk, *Can. J. Chem.*, **63**, 3398 (1985).
884. M. Aritomi, K. Hashimoto and Y. Kawasaki, *J. Organomet. Chem.*, **93**, 181 (1975).
885. J. W. Aspler, R. Wojtowski, I. Wharf, R. Makhija and M. Onyszchuk, *J. Organomet. Chem.*, **205**, 53 (1981).
886. E.G. Il'in, A. P. Nazarov, M. N. Shcherbakova and Yu. A. Buslaev, *Dokl. Akad. Nauk SSSR*, **250**, 367 (1980).
887. C. D. Schmulbach, *Inorg. Chem.*, **4**, 1232 (1965).
888. H. Ishihara, *J. Sci. Hiroshima Univ., Ser. A, Phys. Chem.*, **45**, 319 (1981); *Chem. Abstr.*, **96**, 45146a (1982).
889. M. J. Gallagher, D. P. Graddon and A. R. Sheikh, *Thermochim. Acta*, **27**, 269 (1978).
890. S. Milicev and D. Hadzi, *Inorg, Chim. Acta*, **21**, 201 (1977).
891. M. Burgard, J. P. Brunette and M. J. F. Ceroy, *Inorg. Chem.*, **15**, 1225 (1976).
892. C. I. Branden and I. Lindqvist, *Acad. Chem. Scand.*, **17**, 353 (1963).
893. C. I. Branden and I. Lindqvist, *Acta Chem. Scand.*, **15**, 167 (1961).
894. I. P. Gol'dshtein, I. E. Paleeva, I. E. Cryzlov, O. V. Braverman, T. A. Pestova and E. N. Guryanova, *Zh. Fiz. Khim.*, **62**, 3333 (1988); *Chem. Abstr.*, **11**, 46007w (1989).
895. J. M. Friedt, G. K. Shenoy and M. Burgard, *J. Chem. Phys.*, **59**, 4468 (1973).
896. L. Kolditz and P. Mill, *Z. Anorg. Allg. Chem.*, **373**, 176 (1970).
897. E. G. Il'in, A. P. Na Zarov and Yu. A. Busleav, *Dokl. Acad. Nauk SSSR*, **296**, 640 (1982).
898. R. C. Paul, H. Madan and S. L. Chadha, *J. Inorg. Nucl. Chem.*, **36**, 737 (1974).
899. R. C. Paul, P. R. Sharma, L. Subbiah and S. L. Chadha, *Indian J. Chem., Sect. A*, **14**, 886 (1976).
900. R. C. Paul, D. K. Airon and S. L. Chadha, *Indian J. Chem., Sect. A*, **14**, 51 (1976).
901. P. L. Dhingra, P. Lyall and R. D. Verma, *Indian J. Chem., Sect. A*, **27**, 323 (1988).
902. S. Singh, Amita and R. D. Verma, *Indian J. Chem., Sect. A*, **22**, 814 (1983).
903. H. Teichmann, M. Jatkovsky and G. Hilgetag, *J. Prakt. Chem.*, **314**, 129 (1972).
904. R. G. Goel and H. S. Parasad, *J. Organomet. Chem.*, **59**, 253 (1973).
905. N. Nishii, Y. Matsumura and R. Okawara, *J. Organomet. Chem.*, **30**, 59 (1971).
906. V. I. Popov and N. V. Kondratenko, *Zh. Obschch. Khim.*, **46**, 2597 (1976).
907. S. Milicev and D. Hadzi, *Inorg. Nucl. Chem. Lett.*, **7**, 745 (1971).
908. R. C. Paul, C. L. Arora, R. S. Dass and K. C. Malhotra, *Indian J. Chem.*, **9**, 985 (1971).
909. F. Lazarini and S. Milicev, *Acta Crystallogr., Sect. B*, **32**, 2873 (1976).
910. R. E. Beaumont, R. G. Goel and H. S. Parsad, *Inorg. Chem.*, **12**, 944 (1973).
911. Y. Hermodsson, *Ark. Kemi*, **30**, 15 (1968); *Chem. Abstr.*, **70**, 32385r (1969).
912. T. N. Srivastava, R. C. Srivastava and M. Srivastava, *Indian J. Chem., Sect. A*, **21**, 539 (1982).
913. M. V. Garad, *Palyhedron*, **4**, 1353 (1985).
914. T. N. Srivastava, R. C. Srivastava and V. K. Srivastava, *J. Indian Chem. Soc.*, **60**, 891 (1983).
915. T. N. Srivastava and P. Kumar, *Natl. Acad. Sci. Lett. (India)*, **5**, 399 (1982).
916. M. I. Kabachnik, K. B. Yatsimirskii, Z. A. Sheka, T. Ya. Medved, Yu. M. Polikarpov and E. V. Sinyavskaya, *Redk. Shchelochnyl Elem.*, 461 (1969).
917. K. B. Ystsimirskii, M. I. Kabachnik, Z. A. Sheka, T. Ya. Medved, E. I. Sinyavskaya and Yu. M. Polikarpov, *Teor, Eksp. Khim.*, **4**, 466 (1968).

918. G. Wi Hig and G. Geissler *Justus Liebigs Ann. Chim*, **580**, 44, (1953).
919. H. Schmidbaur and J. Adekofer, *Chem. Ber.*, **105**, 1956 (1972).
920. R. D. Moulton, J. J. Chandler, A. M. Arif, R. A. Jones and A. J. Bard, *J. Am. Chem. Soc.*, **110**, 5714 (1988).
921. F. Hein, H. Plust and H. Pohlemann, *Z. Anorg. Allg. Chem.*, **272**, 25 (1953).
922. M. W. G. De Bolster, *Z. Anorg. Allg. Chem.*, **434**, 78 (1977).
923. G. B. Jameson and G. A. Rodley, *Inorg. Nucl. Chem. Lett.*, **11**, 547 (1975).
924. Y. S. Ng, G. A. Rodley and W. T. Robinson, *Acta Crystallogr., Sect. B*, **34**, 2837 (1978).
925. Y. S. Ng. G. A. Rodley and W. T. Robinson, *Acta Crystallogr., Sect. B*, **34**, 2835 (1978).
926. S. F. Lincoln, D. L. Pisaniello, T. M. Spotswood and M. N. Tkaczuk, *Aust. J. Chem.*, **34**, 283 (1981).
927. (a) S. G. Otavin, *Dopov, Akad. Nauk Ukr. RSR, Ser. B*, (2), 165 (1978); (b) S. O. Grim and S. A. Sangokoya, *J. Chem. Soc., Chem. Commun.*, 1599 (1984).
928. P. Bronzan and H. Meider, *J. Less-Common Met.*, **59**, 101 (1978).
929. J. Selbin and G. Vigee, *J. Inorg. Nucl. Chem.*, **30**, 1644 (1968).
930. P. Planinic and H. Meider, *Polyhedron*, **8**, 627 (1989).
931. J. Lewis and R. Whyman, *J. Chem. Soc.*, 6027 (1965).
932. P. Planinic and H. Meider, *Polyhedron*, **9**, 1099 (1990).
933. F. Canziani, *Ann. Chim.* (Rome), **54**, 1354 (1964).
934. W. Levason and C. A. McAuliffe, *J. Inorg. Nucl. Chem.*, **37**, 340 (1975).
935. H. Funk and H. Kreis, *Z. Anorg. Allg. Chem.*, **349**, 45 (1967).
936. T. S. Lobana and S. S. Bhatti, *Polyhedron*, **6**, 1325 (1987).
937. T. S. Lobana, H. S. Cheema and S. S. Sandhu, *Polyhedron*, **4**, 717 (1985).
938. T. S. Lobana, H. S. Cheema and S. S. Sandhu, *Indian J. Chem., Sect. A*, **24**, 516 (1985).
939. T. S. Lobana, H. S. Cheema and S. S. Sandhu, *Spectrochim. Acta, Patr. A*, **42**, 399 (1986).
940. T. S. Lobana, H. S. Cheema and S. S. Sandhu, *J. Chem. Soc., Dalton Trans.*, 2039 (1983).
941. J. A. Walmsley and S. Y. Tyree, *Inorg. Chem.*, **2**, 312 (1983).
942. T. S. Lobana, H. S. Cheema and S. S. Sandhu, *Spectrochim. Acta, Part A*, **42**, 735 (1986).
943. S. A. Cotton, *Coord. Chem. Rev.*, **8**, 185 (1972).
944. D. C. Povey, T. S. Lobana, P. K. Bhatia, *J. Cryst. Spec. Res.*, **21**, 13 (1991).
945. (a) Yu. N. Kukushkin, E. D. Ageeva, U. A. Aleshin and G. N. Sedova, *Zh. Neorg. Khim.*, **25**, 1135 (1980); (b) J. Ellermann and M. Thierling, *Z. Anorg. Allg. Chem.*, **411**, 28 (1975).
946. F. Mani and M. Bacci, *Inorg. Chim. Acta.*, **6**, 487 (1972).
947. S. S. Sandhu and R. S. Sandhu, *J. Inorg. Nucl. Chem.*, **37**, 597 (1975).
948. B. J. Brisdon, *J. Chem. Soc., Dalton Trans.*, 2247 (1972).
949. J. S. Field, P. J. Wheatley and S. Bhaduri, *J. Chem. Soc., Dalton Trans.*, 74 (1974).
950. A. Davison and E. S. Switkes, *Inorg. Chem.*, **10**, 837 (1971).
951. R. Jones, C. P. Warrens, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 907 (1987).
952. S. S. Sandhu and R. S. Sandhu, *Indian J. Chem., Sect. A*, **13**, 390 (1975).
953. B. J. Brisdon and D. Cocker, *Inorg. Nucl. Chem. Lett.*, **10**, 179 (1974).
954. W. E. Slinkard and D. W. Meek, *J. Chem. Soc., Dalton Trans.*, 1024 (1973).
955. P. B. Planinic and H. Meider, *Polyhedron*, **2**, 69 (1983).
956. Z. Zhang, H. Wang, Z. Xi, H. Wang and R. Wang, *J. Organomet. Chem.*, **352**, C22 (1988).
957. M. I. Kabachnik, E. I. Sinyavaskaya, L. V. Tsymbal, T. Ya. Medved, Yu. M. Polikarpov and G. V. Bodrin, *Zh. Neorg. Khim.*, **27**, 3111 (1982).
958. K. B. Yatsimirskii, M. I. Kabachnik, M. A. Konstantinovskaya, E. I. Sinyavaskaya, T. Ya. Medved, Yu. M. Polikarpov and G. V. Bodrin, *Zh. Neorg. Khim.*, **25**, 1586 (1980).
959. Yu. N. Kukushkin, G. N. Sedova, E. D. Ageeva, G. B. Avetikyan and P. L. Marin, *Koord. Khim.*, **5**, 244 (1979).
960. Yu. N. Kukushkin, G. N. Sedova, V. E. Aleshin, G. B. Avetikyan and E. D. Ageeva, *Zh. Neorg. Khim.*, **24**, 2425 (1979).
961. R. Uson, L. A. Oro, M. A. Ciriano and F. J. Lahoz, *J. Organomet. Chem.*, **240**, 429 (1982).
962. S. S. Sandhu and R. S. Sandhu, *Inorg. Chim. Acta*, **6**, 383 (1972).
963. C. Ercolani, J. V. Quagliano and L. M. Vallarino, *Inorg. Chim. Acta*, **7**, 413 (1973).
964. E. I. Sinyavskaya and Z. A. Shekha, *Zh. Neorg. Khim.*, **21**, 2420 (1976).
965. Yu. N. Kukushkin, G. N. Sedova and R. A. Vlasova, *Zh. Neorg. Khim.*, **25**, 495 (1980).
966. R. A. Vlasova, G. N. Sedova and M. A. Kirillova, *Koord. Khim.*, **12**, 118 (1986).

967. E. I. Sinyavskaya and Z. A. Sheka, *Zh. Neorg. Khim.*, **21**, 2420 (1976).
968. K. R. Dixon, G. W. Bushnell and J. Browning, *Inorg. Chem.*, **20**, 3912 (1981).
969. J. C. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, **2**, 345 (1969).
970. P. S. Pregosin and R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Oxides*, Springer, New York, 1979.
971. E. I. Sinyavskaya, *Zh. Neorg. Khim.*, **28**, 2026 (1983).
972. E. G. Boguslavskii, A. A. Shklyaev and V. F. Anufrienko, *Teor. Eksp. Khim.*, **17**, 138 (1981).
973. K. B. Yatsimirskii, Z. A. Sheka, E. I. Sinyavskaya and M. A. Konstantinovskaya, *Zh. Neorg. Khim.*, **19**, 1180 (1974).
974. E. I. Sinyavskaya, Z. A. Sheka, T. Ya. Medved, S. A. Pisareva and M. I. Kabachnik, *Zh. Neorg. Khim.*, **18**, 2427 (1973).
975. Z. A. Sheka, K. B. Yatsimirskii and M. A. Ablova *Zh. Neorg. Khim.*, **15**, 2932 (1970).
976. M. I. Kabachnik, Z. A. Sheka, T. Ya. Medved, E. I. Sinyavskaya, K. Zh. Kulumbetova and M. A. Konstantinovskaya, *Zh. Neorg. Khim.*, **18**, 2042 (1973).
977. Z. A. Sheka, K. B. Yatsimirskii, M. A. Ablova, K. S. Yudina, T. Ya. Medved and M. I. Kabachnik, *Zh. Neorg. Khim.*, **16**, 2440 (1971).
978. M. Mathew and G. J. Palenik, *Can. J. Chem.*, **47**, 1093 (1969).
979. M. Mathew and G. J. Palenik, *Inorg. Chim. Acta*, **5**, 573 (1971).
980. B. J. Hathaway and P. G. Hodgson, *Spectrochim. Acta, Part A*, **30**, 1465 (1974).
981. B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).
982. C. A. Bates, W. S. Moore, K. J. Standley and K. W. H. Steevens, *Proc. Phys. Soc.*, **79**, 73 (1962).
983. D. W. Smith, *Struct. Bonding*, **12**, 49 (1972).
984. K. B. Yatsimirskii, U. T. Struchkov, A. S. Batsanov and A. I. Sinyavskaya, *Koord. Khim.*, **11**, 826 (1985).
985. S. S. Sandhu and G. S. Aulakh, *J. Inorg. Nucl. Chem.*, **37**, 581 (1975).
986. Z. A. Sheka and E. I. Sinyavskaya, *Zh. Neorg. Khim.*, **14**, 2083 (1969).
987. S. S. Sandhu and G. S. Aulakh, *Indian J. Chem.*, **12**, 1102 (1974).
988. Z. M. Alibaeva, N. I. Snezhko, N. I. Pechurova, T. E. Kron, E. N. Tsvetkov and L. I. Martynenko, *Zh. Neorg. Khim.*, **31**, 2780 (1986).
989. X. Chen, J. Jiang and L. Jhang *Zhonggu Xitu Xuebao*, **6**, 13 (1988).
990. M. A. Wassef, W. S. Hegazi and S. A. Ali, *Acta Chim. Acad. Sci. Hung.*, **111**, 199 (1982).
991. P. Gans and B. C. Smith, *J. Chem. Soc.*, 4172 (1964).
992. S. S. Sandhu and S. S. Sandhu, Jr, *Indian J. Chem.*, **11**, 369 (1973).
993. S. S. Sandhu and G. S. Aulakh, *J. Indian Chem. Soc.*, **51**, 717 (1974).
994. J. Selbin and J. D. Ortego, *J. Inorg. Nucl. Chem.*, **29**, 1449 (1967).
995. T. H. Siddall, R. L. McDonald and W. E. Stewart, *J. Mol. Spectrosc.*, **28**, 243 (1968).
996. M. A. Wassef, W. S. Hegazi and S. A. Ali, *J. Coord. Chem.*, **12**, 97 (1983).
997. T. Ya. Medved, N. P. Nesterova, P. V. Petrovskii, T. D. Kirillova and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1714 (1978).
998. P. A. W. Dean and G. K. Carson, *Can. J. Chem.*, **61**, 1800 (1983).
999. P. A. W. Dean and M. K. Hughes, *Can J. Chem.*, **58**, 180 (1980).
1000. P. A. W. Dean, *Can. J. Chem.*, **59**, 3221 (1981).
1001. S. A. Sangokoya, B. Lee, M. F. Self, W. T. Pennington and G. H. Robinson, *Polyhedron*, **8**, 1497 (1989).
1002. G. H. Robinson, B. Lee, W. T. Pennington and S. A. Sangokoya, *J. Am. Chem. Soc.*, **110**, 6260 (1988).
1003. M. A. Wassef and M. Gaber, *Egypt. J. Chem.*, **24**, 165 (1981).
1004. M. A. Wassef and M. Gaber, *Egypt. J. Chem.*, **25**, 505 (1982).
1005. M. V. Castano, M. R. Bermajo, M. Gayoso and J. Sordo, *An. Quim., Ser. B*, **78**, 384 (1982).
1006. S. S. Sandhu and S. S. Sandhu, Jr, *J. Inorg. Nucl. Chem.*, **31**, 1363 (1969).
1007. C. M. J. Fernandez, M. P. Pazoslerez, J. Sordo, J. S. Casas, M. R. Bermejo and M. Gayoso, *An. Quim., Ser B*, **78**, 190 (1982).
1008. S. S. Sandhu, J. K. Sandhu and G. K. Sandhu, *J. Inorg. Nucl. Chem.*, **39**, 2099 (1977).
1009. G. M. Bancroft, V. G. Kumar Das and K. D. Butler, *J. Chem. Soc., Dalton Trans.*, 2355 (1974).
1010. G. M. Bancroft, T. K. Sham, J. S. Tse and V. Wellington, *J. Chem.*, **55**, 3487 (1977).
1011. V. G. Kumar Das, N. S. Weng, P. J. Smith and R. Hill, *J. Chem. Soc., Dalton Trans.*, 552, (1981).
1012. F. P. Mullins and C. Currans, *Can J. Chem.*, **53**, 3200 (1975).
1013. P. G. Harrison, N. W. Sharpe, C. Pelizzi, G. Pelizzi and P. Tarasconi, *J. Chem. Soc., Dalton Trans.*, 1687 (1983).

1014. G. Pelizzi, P. Tarasconi, C. Pelizzi, K. C. Molloy and P. Waterfield, *Main Group Met. Chem.*, **10**, 353 (1987).
1015. G. Pelizzi, P. Tarasconi, F. Vitali and C. Pelizzi, *Acta Crystallogr., Sect. C*, **43**, 1505 (1987).
1016. (a) J. Holecek, M. Nadvornik, K. Handlir and A. Lycka, *J. Organomet. Chem.*, **315**, 299 (1986); (b) J. Holecek and A. Lycka, *Inorg. Chim. Acta*, **118**, L15 (1986).
1017. V. G. Kumar Das, *J. Inorg. Nucl. Chem.*, **38**, 1241 (1976).
1018. G. K. Sandhu, H. Singh and S. S. Sandhu, Jr, *Indian J. Chem.*, **20**, 518 (1981).
1019. V. G. Kumar Das, *Inorg. Nucl. Chem. Lett.*, **9**, 155 (1973).
1020. (a) G.Pelizzi, C. Pelizzi, P. Tarasconi, P. G. Harrison and N. W. Sharpe, *J. Chem. Soc., Dalton Trans.*, 921 (1983); (b) G. M. Bancroft, V. G. Kumar Das, T. K. Sham and M. G. Clark, *J. Chem. Soc., Dalton Trans.*, 643 (1976); (c) G. M. Bancroft, V. G. Kumar Das, T. K. Sham and M. G. Clark, *J. Chem. Soc., Chem. Commun.*, 236 (1974); (d) A. J. Crowe and P. J. Smith, *J. Organomet. Chem.*, **204**, 327 (1980).
1021. V. G Kumar Das, W. Kitching and C. J. Moore, *J. Organomet. Chem.*, **22**, 399 (1970).
1022. B. W. Fitzsimmons, N. T. Seeley and A. W. J. Smith, *J. Chem. Soc. A*, 147 (1969); 390 (1965).
1023. G. M. Bancroft, *Mössbauer Spectroscopy: an Introduction for Inorganic and Geochemists*, McGraw-Hill, London, 1973.
1024. G. M. Bancroft and R. H. Platt, *Adv. Inorg. Radiochem.*, **15**, 59 (1972).
1025. M. A. Cullins and C. Curran, *Inorg. Chem.*, **7**, 2584 (1968).
1026. A. Aslanov, V. M. Lonov, W. M. Attia, A. B. Permin and V. S. Petrosyan, *J. Organomet. Chem.*, **144**, 39 (1978).
1027. G. Pelizzi and C. Pelizzi, *J. Organomet. Chem.*, **202**, 411 (1980).
1028. G. Pelizzi and C. Pelizzi, *Inorg. Nucl. Chem. Lett.*, 451 (1980).
1029. C. Pelizzi and G. Pelizzi *Congr. Naz. Chim. Inorg.* [*Atti*], *13th, 120, 1980; Chem. Abstr.*, **95**, 81142j (1981).
1030. C. Pelizzi and G. Pelizzi, *Inorg. Nucl. Chem. Lett.*, **16**, 451 (1980).
1031. G. Pelizzi, C. Pelizzi and M. Nardelli, *Inorg. Chim. Acta*, **33**, 181 (1979).
1032. S. Dondi, M. Nardelli, C. Pelizzi, G. Pelizzi, G. Predieri, *J. Chem. Soc., Dalton Trans.*, 487 (1985).
1033. S. Dondi. M. Nardelli, C. Pelizzi, G. Pelizzi and G. Predieri, *J. Organomet. Chem.*, **308**, 195 (1986).
1034. E. G. Il'in, M. N. Shcherbakova, Yu. A. Buslaev, T. Ya. Medved, N. P. Nesterova and M. I. Kabachnik, *Dokl. Akad. Nauk SSSR*, **271**, 373 (1983).
1035. K. B. Yatsimirskii, M. I. Kabachnik, A. A. Shehka, T. Ya. Medved, E. I. Sinyavaskaya, N. P. Nestertova and M. A. Konstantinovskaya, *Dokl. Akad. Nauk SSSR*, **212**, 428 (1973).
1036. M. I. Kabachnik, K. B. Yatsimirskii, T. Ya. Medved, Z. A. Shekha, Y. M. Polikarpov and E. I. Sinyavaskaya, *Dokl. Akad. Nauk SSSR*, **171**, 619 (1966).
1037. K. B. Yatsimirskii, M. I. Kabachnik, Z. A. Sheka, T. Ya. Medved, E. I. Sinyavskaya and Yu. M. Polikarpov, *Teor. Eksp. Khim.*, **4**, 446 (1968).
1038. E. I. Sinyavskaya, Z. A. Sheka and K. B. Yatsimirskii, *Zh. Neorg. Khim.*, **14**, 940 (1969); *Chem. Abstr.*, **71**, 16433v (1969).
1039. Z. A. Sheka, E. I. Sinyavskaya and K. B. Yatsimirskii, *Zh. Neorg. Khim..*, **14**, 390 (1969).
1040. M. I. Kabachnik, Yu. M. Polikarpov, K. Kulumbetova and T. Ya. Medved, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1326 (1970).
1041. M. I. Kabachnik, K. B. Yatsimirskii, Z. A. Sheka, T. Ya. Medved, Ya. M. Polikarpov and E. V. Sinyavskaya, *Redk. Shchelochnye Elem.*, 461 (1969); *Chem. Abstr.*, **74**, 106651f (1970).
1042. K. B. Yatsimirskii, M. I. Kabachnik, E. I. Sinyavskaya, T. Ya. Medved and F. I. Belskii, *Teor. Eksp. Khim.*, **12**, 777 (1976).
1043. W. Hewertson, B. T. Kilobourn and R. H. B. Mais, *J. Chem. Soc. D*, 952 (1970).
1044. A. E. Kalinin, V. G. Andrianov and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **17**, 153 (1976).
1045. V. I. Everinov, Z. N. Vostroknutova, V. E. Baulin, N. A. Bondarenko, V. Kh. Syundyukova and E. N. Tsvetkov, *Zh. Obshch. Khim.*, **59**, 67 (1989).
1046. T. E. Kron, E. I. Sinyavskaya and E. N. Tsvetkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2451 (1986).
1047. T. E. Kron, N. A. Novikov, E. I. Sinyavskaya and E. N. Tsvetkov, *Izv. Akad Nauk SSSR, Ser. Khim.*, 810 (1986).
1048. E. I. Sinyavskaya and Z. A. Sheka, *Zh. Neorg. Khim.*, **16**, 896 (1971).
1049. W. Hewertson, *Brit. Patent*, 1, 197, 717 (Cl. Co7f), 08 July, 1970, Appl. 23 Nov. 1966, 8 pp.; *Chem. Abstr.*, **73**, 68138p (1970).

1050. V. P. Solov'ev, L. V. Govorkova, O. A. Raevskii, V. E. Baulin, V. Kh. Syundyukova and E. N. Tsvetkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 814 (1989).

1051. (a) D. J. Berg, C. J. Burns, R. A. Andersen and A. Zalkin, *Organometallics*, **8**, 1865 (1989); (b) K. Baker and G. W. A. Fowles, *J. Less-Common Met.*, **8**, 47 (1965).

1052. I. Cuadrado and M. Moises, *Transition Met. Chem.*, **9**, 96 (1984).

1053. I. Cuadrado and M. Moran, *Transition Met. Chem.*, **6**, 329 (1981).

1054. I. Lindqvist and C. I. Branden, *Acta Chem. Scand.*, **14**, 726 (1960).

1055. J. Rimbault, J. C. Pierrard and R. P. Hugel, *Nouv. J. Chim.*, **7**, 653 (1983).

1056. W. Vander Veer and F. Jellinek, *Recl. Trav. Chim. Pays-Bas*, **85**, 842 (1966).

1057. K. Behzadki and A. Thompson, *J. Less-Common Met.*, **32**, 21 (1987).

1058. D. Brown, J. Hill and C. E. F. Rickard, *J. Less-Common Met.*, **20**, 57 (1970).

1059. M. G. B. Drew, G. W. A. Fowles, R. J. Hobson and D. A. Rice, *Inorg. Chim. Acta*, **20**, L35 (1976).

1060. M. G. B. Drew and R. J. Hobson, *Inorg. Chim. Acta*, **72**, 233 (1983).

1061. E. G. Il'in, M. E. Ignatov, A. A. Shvets, Yu. A. Buslaev, *Dokl. Akad. Nauk SSSR*, **243**, 1182 (1978).

1062. R. P. Stewart, Jr., and J. J. Isbrand-Benedict, *Inorg. Chem.*, **15**, 2011 (1976).

1063. P. W. Codding and K. A. Kerr, *Acta Crystallogr., Sect. B*, **34**, 3785 (1978).

1064. M. E. Ignatov, E. G. Il'in, L. V. Gorcharova, A. A. Shvets, O. A. Osipov, V. S. Nepovezov and Yu. A. Buslaev, *Koord. Khim.*, **6**, 148 (1980).

1065. G. W. A. Fowles, D. A. Rice and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 2313 (1972).

1066. R. Fandos, M. Gomeza and P. Royo, *Organometallics*, **8**, 1604 (1989).

1067. E. W. Ainscough, A. M. Brodie and A. R. Furness, *Chem. Commun.*, 1357 (1971).

1068. E. W. Ainscough, A. W. Brodie and A. R. Furness, *J. Chem. Soc., Dalton Trans.*, 2360 (1973).

1069. E. N. Baker and B. R. Reay, *J. Chem. Soc., Dalton Trans.*, 2205 (1973).

1070. P. M. Boorman, S. A. Clow, D. Potts and H. Weiser, *Inorg. Nucl. Chem. Lett.*, **9**, 941 (1973).

1071. W. Ehrl and H. Vahrenkamp, *Chem. Ber.*, **103**, 3563 (1970).

1072. R. Colton and P. Panagiotidou, *Aust. J. Chem.*, **40**, 13 (1987).

1073. S. O. Grim and L. J. Matienzo, *Inorg. Chem.*, **14**, 1014 (1975).

1074. S. O. Grim and J. D. Mitchell, *Inorg. Chem.*, **16**, 1762 (1977).

1075. S. O. Grim and E. D. Walton, *Inorg. Chem.*, **19**, 1982 (1980).

1076. S. O. Grim, P. H. Smith and I. J. Colquhoun and W. McFarlane, *Inorg. Chem.*, **19**, 3195 (1980).

1077. S. O. Grim, I. J. Colquhoun, W. McFarlane, J. D. Mitchell and P. H. Smith, *Inorg. Chem.*, **20**, 2516 (1981).

1078. S. O. Grim, G. T. Andrews, I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 2353 (1982); 988 (1971).

1079. A. M. Bond, R. Colton, J. E. Kevekordes and P. Panagiotid, *Inorg. Chem.*, **26**, 1430 (1987).

1080. A. M. Bond, R. Colton and P. Panagiotidou, *Organometallics*, **7**, 1774 (1988).

1081. H. Aeper and J. Hartgerink, *J. Organomet. Chem.*, **190**, C25 (1980).

1082. C. D. Garner, P. M. Boorman and F. E. Mabbs, *J. Chem. Soc., Dalton Trans.*, 1299 (1975).

1083. C. D. Garner, P. M. Boorman, F. E. Mabbs and T. J. King, *J. Chem. Soc., Chem. Commun.*, 663 (1974).

1084. C. D. Garner, N. C. Howlader, F. E. Mabbs, P. M. Boorman and T. J. King, *J. Chem. Soc., Dalton Trans.*, 1350 (1978).

1085. C. D. Garner, P. Lambert, F. E. Mabbs and T. J. King, *J. Chem. Soc., Dalton Trans.*, 1191 (1977).

1086. P. M. Boorman and K. J. Reimer, *Can. J. Chem.*, **49**, 2926 (1971).

1087. F. A. Cotton and R. Leusar, *Acta Crystallogr., Sect. C*, **44**, 952 (1988).

1088. A. M. Bond, R. Colton and P. Panagiotidou, *Organometallics*, **7**, 1767 (1988).

1089. O. Siiman and H. B. Gray, *Inorg. Chem.*, **13**, 1185 (1974).

1090. O. Siiman and J. Vetuskey, *Inorg. Chem.*, **19**, 1672 (1980).

1091. M. Panowski and M. Bigorgue, *J. Organomet. Chem.*, **30**, 227 (1971).

1092. L. M. Hainesand M. H. B. Stiddard, *Adv. Inorg. Chem. Radiochem.*, **12**, 53 (1969).

1093. S. O. Grim, D. A. Wheatland and W. McFarlane, *J. Am. Chem. Soc.*, **89**, 5573 (1967).

1094. S. M. Grant and A. R. Manning, *J. Chem. Soc., Dalton Trans.*, 1789 (1979).

1095. F. W. Grevels, J. G. A. Reuvers and J. Takats, *J. Am. Chem. Soc.*, **103**, 4069 (1981).

1096. R. B. King, *The Organic Chemistry of Iron*, Vol. I, Academic Press, New York, 1978.

1097. S. Vancheesan, *Indian J. Chem., Sect. A*, **22**, 54 (1983).

1098. W. Hieber and H. Fuehrling, *Z. Anorg. Allg. Chem.*, **373**, 48 (1970).
1099. I. Ya. Kuramshin, N. R. Safiullina, L. A. Zhelonkina, A. S. Khramov and A. N. Pudovik, *Zh. Obshch. Khim.*, **48**, 2179 (1978).
1100. T. S. Lobana and P. K. Sharma, *Indian J. Chem., Sect. A*, **26**, 784 (1987).
1101. T. S. Lobana and P. K. Sharma, *Indian J. Chem., Sect. A*, **27**, 732 (1988).
1102. T. S. Lobana and V. Sharma, *Indian J. Chem., Sect. A*, **25**, 615 (1986).
1103. W. Saak, D. Haase and S. Pohl, *Z. Naturforsch., Teil B*, **43**, 289 (1988).
1104. W. Saak and S. Pohl, *Z. Naturforsch, Teil B*, **43**, 813 (1988).
1105. A. Davison and D. L. Reger, *Inorg. Chem.*, **10**, 1967 (1971).
1106. M. R. Churchill amd J. Wormald, *Inorg. Chem.*, **10**, 1778 (1971).
1107. N. Kuhn and H. Schumann, *J. Organomet. Chem.*, **304**, 181 (1986).
1108. M. Moran, I. Cuadrado, C. Pascual, J. R. Masaguer and J. Losada, *Inorg. Chim. Acta*, **132**, 257 (1987).
1109. H. Schumann, *J. Organomet. Chem.*, **320**, 145 (1987).
1110. W. Hieber and P. John, *Chem. Ber.*, **103**, 2161 (1970).
1111. P. John, *Chem. Ber.*, **103**, 2178 (1970).
1112. U. C. Aggarwala and S. Datta, *Indian J. Chem., Sect. A*, **20**, 1153 (1981).
1113. U. C. Aggarwala, S. Datta and S. K. Shukla, *Indian J. Chem., Sect. A*, **20**, 985 (1981).
1114. A. M. Brodie, S. H. Hunter, G. A. Rodley and C. J. Wilkins, *J. Chem. Soc. A*, 2039 (1968).
1115. A. M. Brodie, G. A. Rodley and C. J. Wilkins, *J. Chem. Soc. A*, 2927 (1969).
1116. W. E. Slinkard and D. W. Meek, *J. Chem. Soc., Dalton Trans.*, 1024 (1973).
1117. J. Rimbault, J. C. Pierrard and R. P. Hugel, *J. Chem. Res.* (*S*), 74 (1978).
1118. G. P. McQuillan and I. A. Oxton, *Inorg. Chim. Acta*, **29**, 69 (1978).
1119. K. Nakamoto, E. Maslowsky and R. Czernuszewicz, *Spectrochim. Acta*, **40**, 199 (1980).
1120. A. A. M. Aly, M. M. Kamal, S. S. El-Meligy and A. I. El-Said, *Z. Naturforsch., Teil B*, **42**, 233 (1987).
1121. M. R. Churchill, J. Cooke, J. Wormald, A. Davison and E. S. Switkes, *J. Am. Chem. Soc.*, **91**, 6518 (1969).
1122. T. M. Dunn, *J. Chem. Soc.*, 623 (1959).
1123. J. Owen, *Discuss. Faraday Soc.*, **19**, 127 (1955).
1124. H. R. Weaklien, *J. Chem. Phys.*, **36**, 2177 (1962).
1125. U. C. Aggarwala, S. Datta and K. K. Pandey, *Inorg. Chim. Acta*, **40**, 65 (1980).
1126. L. Dahlenburg, N. Hoeck and H. Berke, *Chem. Ber.*, **121**, 2083 (1988).
1127. S. D. Robinson and E. B. Boyar, *J. Chem. Soc., Dalton Trans.*, 629 (1985).
1128. E. W. Ainscough, A. M. Brodie and E. Mantzer, *J. Chem. Soc., Dalton Trans.*, 2167 (1973).
1129. C. Claver, F. Gili, J. Vinas and A. Ruiz, *Polyhedron*, **6**, 1329 (1987).
1130. A. Christofides and A. S. Kourakou, *Inorg. Chim. Acta*, **141**, 161 (1988).
1131. C. Claver, A. Ruiz, A. M. Masdev, J. Vinas, T. Saballs, F. J. Lahoz and F. J. Plou, *J. Organomet. Chem.*, **373**, 269 (1989).
1132. B. R. James and L. F. T. Ng, *J. Chem. Soc., Dalton Trans.*, 355 (1972).
1133. J. Browning, K. R. Dixon and R. W. Hilts, *Organometallics*, **8**, 552 (1989).
1134. R. Usón, L. A. Oro, D. Carmona and M. A. Estervelas, *J. Organomet. Chem.*, **263**, 109 (1984).
1135. V. F. Kober and B. C. Pham, *Z. Anorg. Allg. Chem.*, **466**, 183 (1980).
1136. V. F. Kober and B. C. Pham, *Z. Anorg. Allg. Chem.*, **477**, 139 (1981).
1137. M. R. Churchill, J. Cooke, J. P. Fennessey and J. Wormald, *Inorg. Chem.*, **10**, 1031 (1971).
1138. A. Schmidpeter, H. Groeger and R. Bohn, *Angew. Chem.*, **3**, 704 (1964).
1139. F. Carballero and P. Royo, *J. Organomet. Chem.*, **137**, 229 (1977).
1140. N. Kuhn and M. Winter, *J. Organomet. Chem.*, **239**, C31 (1982).
1141. N. Kuhn and M. Winter, *J. Organomet. Chem.*, **246**, C83 (1983).
1142. N. Kuhn, N. Hauser and M. Winter, *J. Organomet. Chem.*, **267**, 221 (1984).
1143. C. K. Jorgensen, *Inorg. Chim. Acta Rev.*, **2**, 65 (1968).
1144. G. Peyronel and A. Pignedoli, *Acta Crystallogr.*, **23**, 398 (1967).
1145. R. J. H. Clark, R. S. Nyholm and F. B. Taylor, *J. Chem. Soc.*, 1802 (1967).
1146. B. N. Figgis, *Introduction to Ligand Fields*, Interscience, New York, 1966, p. 240.
1147. B. N. Figgis, J. Lewis, F. E. Mabbs and G. A. Webb, *J. Chem. Soc. A*, 1141 (1966).
1148. D. M. L. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **82**, 5774 (1960).
1149. A. Schmidpeter, H. Groeger and R. Bohn, *Angew. Chem.*, **76**, 860 (1964).
1150. A. M. Mazany and J. P. Fackler, Jr, *Organometallics*, **1**, 752 (1982).

1151. C. A. Chilardi, P. Innocenti, S. Midollini and A. Arlandini, *J. Chem. Soc., Dalton Trans.*, 1063 (1988).
1152. T. S. Lobana and K. B. Sharma, *Transition Met. Chem.*, **7**, 333 (1982).
1153. G. P. McQuillan and M. G. King, *J. Chem. Soc. A*, 898 (1967).
1154. M. F. Richardson, *Acta Crystallogr., Sect. C*, **41**, 27 (1985).
1155. L. C. Satek, H. L. Ammon and J. M. Stewart, *Acta Crystallogr., Sect. B*, **31**, 2691 (1975).
1156. R. K. Singh, S. K. Singh and E. B. Singh, *Indian J. Chem., Sect. A*, **19**, 1212 (1980).
1157. E. W. Ainscough, H. A. Mergen and A. M. Brodie, *J. Chem. Soc., Dalton Trans.*, 1649 (1976).
1158. E. W. Ainscough, A. M. Brodie, H. A. Bergen and K. L. Brown, *J. Inorg. Nucl Chem.*, **38**, 337 (1976).
1159. S. S. Sandhu and T. Singh, *Transition Met. Chem.*, **1**, 155 (1976).
1160. S. S. Sandhu and T. Singh, *Transition Met. Chem.*, **2**, 195 (1977).
1161. D. A. Wheatland, C. H. Clapp and R. W. Waldron, *Inorg. Chem.*, **11**, 2340 (1972).
1162. M. G. King, G. P. McQuillan and R. Milne, *J. Inorg. Nucl. Chem.*, **35**, 3039 (1973).
1163. G. P. McQuillan and I. A. Oxton, *Spectrochim. Acta, Part A*, **33**, 233 (1977).
1164. S. Datta and U. C. Aggarwala, *Indian J. Chem., Sect. A*, **20**, 1190 (1981).
1165. R. Uson, J. Fornies, P. Espinet and M. P. Garcia, *Rev. Acad. Cienc. Exactas Fis.-Quim. Nat., Zaragoza*, **32**, 193 (1977).
1166. P. G. Eller, R. R. Ryan and D. C. Moody, *Inorg. Chem.*, **15**, 2442 (1976).
1167. J. J. Levison and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 2013 (1972).
1168. F. C. March, R. Mason and G. R. Scollary, *Aust. J. Chem.*, **30**, 2407 (1977).
1169. C. Pecile, *Inorg. Chem.*, **5**, 210 (1966).
1170. S. O. Grim, S. A. Sangokoya, I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Chem. Commun.*, 930 (1982).
1171. J. Browning, K. A. Beveridge, G. W. Bushnell and K. R. Dixon, *Inorg. Chem.*, **25**, 1987 (1986).
1172. C. A. Grygon, W. C. Fultz, A. L. Reingold and J. L. Burmeister, *Inorg. Chim. Acta*, **141**, 205 (1988).
1173. P. Nicpon and D. W. Meek, *Inorg. Chem.*, **6**, 145 (1967).
1174. P. Paul and J. Schwald, *J. Chem. Soc., Chem. Commun.*, 1625 (1986).
1175. R. Colton, J. Ebner and B. F. Hoskins, *Inorg. Chem.*, **27**, 1993 (1988).
1176. R. Colton and J. Ebner, *Inorg. Chem.*, **28**, 1559 (1989).
1177. D. J. Gulliver and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1895 (1982).
1178. E. W. Ainscough, A. M. Brodie and K. L. Brown, *J. Chem. Soc., Dalton Trans.*, 1042 (1980).
1179. G. A. Bowmaker, R. Whiting, E. W. Ainscough and A. M. Brodie, *Aust. J. Chem.*, **28**, 1431 (1975).
1180. P. G. Eller and P. W. R. Corfield, *J. Chem. Soc., Chem. Commun.*, 105 (1971).
1181. J. D. Graybeal, C. F. Shoemaker and T. Gallaher, *J. Magn. Reson.*, **20**, 372 (1975).
1182. K. Nakamoto and J. Kincaid, *Spectrochim. Acta, Part A*, **30**, 2091 (1974).
1183. J. Philip and C. Curran, *Abstracts, 147th ACS Meeting, Philadelphia*, 1964, p. 28.
1184. J. A. Tiethof, A. T. Hetey and D. W. Meek, *Inorg. Chem.*, **13**, 2505 (1974).
1185. J. A. Tiethof, A. T. Hetely, P. E. Nicpon and D. W. Meek, *Inorg. Nucl. Chem. Lett.*, **8**, 841 (1972).
1186. E. W. Ainscough, A. M. Brodie and K. C. Palmer, *J. Chem. Soc., Dalton Trans.*, 2375 (1976).
1187. J. A. W. Dalziel, A. F. le C. Holding and B. E. Watts, *J. Chem. Soc. A*, 358 (1967).
1188. J. A. Tiethof, J. K. Stalick and D. W. Meek, *Inorg. Chem.*, **12**, 1170 (1973).
1189. M. Arshad, A. Beg and S. H. Khaweja, *Spectrochim. Acta, Part A*, **24**, 1031 (1968).
1190. K. L. Brown, *Acta Crystallogr., Sect. B*, **35**, 462 (1979).
1191. F. A. Cotton, B. A. Frenzy, D. L. Hunter and Z. C. Mester, *Inorg. Chem. Acta*, **11**, 111 (1974).
1192. F. A. Cotton, B. A. Frenzy, D. L. Hunter and Z. C. Mester, *Inorg. Chim. Acta*, **11**, 119 (1974).
1193. C. P. McQuillan and I. A. Oxton, *J. Chem. Soc., Dalton Trans.*, 895 (1979).
1194. T. S. Lobana, *Transition Met. Chem.*, **16**, 57 (1991).
1195. K. Krause, R. A. Krause and S. Lamtruong, *J. Coord, Chem.*, **19**, 91 (1988).
1196. G. M. Sheldrick, K. K. Pandey, M. Noltemeyer and H. W. Roesky, *Acta Crystallgr Sect. C*, **40**, 1555 (1984).
1197. J. A. Tiethof, J. K. Stalick, P. W. R. Corfield and D. W. Meek, *J. Chem. Soc., Chem. Commun.*, 1141 (1972).
1198. P. W. R. Corfield, Personal communication, 1973; cf. ref. 1184.
1199. G. H. Faye, *Can. J. Chem.*, **44**, 1643 (1966).

1200. R. D. Bereman, F. T. Wang, J. Najdzionek and D. M. Braitsch, *J. Am. Chem. Soc.*, **98**, 7266 (1976).
1201. O. Siiman, *Inorg. Chem.*, **20**, 2285 (1981).
1202. O. Siiman, C. D. Huber and M. L. Post, *Inorg. Chim. Acta*, **25**, L11 (1977).
1203. R. D. Bereman, S. N. Choi and J. R. Wasson, *J. Inorg. Nucl. Chem.*, **37**, 2087 (1975).
1204. M. D. Joesten, R. C. Koch, T. W. Martin and J. H. Venable, Jr, *J. Am. Chem. Soc.*, **93**, 1138 (1971).
1205. R. C. Koch, M. D. Joesten and J. H. Venable, Jr, *J. Chem. Phys.*, **59**, 6312 (1973).
1206. P. W. Lau and W. C. Lin, *J. Chem. Phys.*, 3981 (1973).
1207. J. Pelsach and W. E. Blumberg. *Arch. Biochem. Biophys.*, **165**, 691 (1974).
1208. R. C. Rosenberg, C. A. Root, P. K. Bernstein and H. B. Gray, *J. Am. Chem. Soc.*, **97**, 2092 (1975).
1209. F. G. Moers, P. J. W. M. Muskens and J. Francot, *J. Inorg. Nucl. Chem.*, **41**, 759 (1979).
1210. R. Uson, A. Laguna, M. Laguna, B. R. Manzano, P. G. Jones and G. M. Shaldrick, *J. Chem. Soc., Dalton Trans.*, 285 (1984).
1211. S. O. Grim, Phosphorus Sulphur, **18**, 283 (1983).
1212. M. S. Hussain, *J. Crystallogr. Spectrosc. Res.*, **16**, 91 (1986).
1213. P. G. Jones, A. G. Maddock, M. J. Mays, M. M. Muir and A. F. Williams, *J. Chem. Soc., Dalton Trans.*, 1434 (1977).
1214. P. G. Jones and A. F. Williams, *J. Chem. Soc., Dalton Trans.*, 1430 (1977).
1215. I. M. Keen. *J. Chem. Soc.*, 5751 (1965).
1216. R. A. Potts and A. L. Allred, *J. Inorg. Nucl. Chem.*, **28**, 1479 (1966).
1217. H. Schmidbauer, D. Koth and P. E. Wagner, *Z. Naturforsch.*, **318**, 1607 (1976).
1218. H. M. Sakhwat and E. O. Schlemper, *Acta Crystallogr., Sect. C*, **43**, 450 (1987).
1219. A. Laguna, M. Laguna, A. Rojo and M. N. Fraile, *J. Organomet. Chem.*, **315**, 269 (1986).
1220. R. Uson, A. Laguna, M. Laguna, M. N. Fraile, P. G. Jones and C. F. Erdbruegger, *J. Chem. Soc., Dalton Trans.*, 73 (1989).
1221. R. Uson, A. Laguna, M. Laguna, M. N. Fraile, I. Lazaro, M. C. Gimeno, P. G. Jones, C. Reihs and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 333 (1990).
1222. R. Uson, A. Laguna, M. Laguna, I. Lazaro, P. G. Jones and C. Fittschen, *J. Chem. Soc., Dalton Trans*, 2323 (1988).
1223. H. N. Murray, D. A. Briggs, G. Garzon, R. G. Raptis, L. C. Porter and J. P. Fackler, Jr, *Organometallics*, **6**, 1992 (1987).
1224. C. King, D. D. Heinrich, J. C. Wang, J. P. Fackler, Jr, and G. Garzon, *J. Am. Chem. Soc.*, **111**, 2300 (1989).
1225. H. H. Murray, G. Garzon, R. G. Raptis, A. A. Mazany, L. C. Porter and J. P. Fackler, Jr, *Inorg. Chem.*, **27**, 836 (1988).
1226. A. M. Brodie, S. H. Hunter, G. A. Rodley and C. J. Wilkins, *J. Chem. Soc. A*, 987 (1968).
1227. T. S. Lohana, T. R. Gupta and S. S. Sandhu, *Polyhedron*, **1**, 781 (1982).
1228. K. C. Malhotra, *Indian J. Chem.*, **12**, 823 (1974).
1229. G. P. McQuillan and A. J. Blake, *J. Chem. Soc., Dalton Trans.*, 1849 (1984).
1230. D. W. Meek and P. Nicpon, J. Am. Chem. Soc., **87**, 4951 (1965).
1231. G. Eastland, Jr, *Inorg. Nucl. Chem. Lett.*, **11**, 373 (1975).
1232. G. P. McQuillan, L. S. D. Glasser, L. Ingram and M. G. King, *J. Chem. Soc. A*, 2501 (1969).
1233. T. S. Lobana and K. B. Sharma, *Indian J. Chem., Sect. A*, **22**, 710 (1983).
1234. S. S. Sandhu and T. Singh, *Indian J. Chem., Sect. A*, **15**, 829 (1977).
1235. S. S. Sandhu and T. Singh, *Indian J. Chem., Sect. A*, **15**, 831 (1977).
1236. S. S. Sandhu and T. Singh, *J. Inorg. Nucl. Chem.*, **39**, 1086 (1977).
1237. A. J. Blake, G. P. McQuillan and I. A. Oxton, *Spectrochim. Acta, Part A*, **36**, 501 (1980).
1238. G. P. McQuillan and I. A. Oxton, *J. Mol. Struct.*, **64**, 173 (1980).
1239. G. P. McQuillan and I. A. Oxton, *Spectrochim. Acta, Part A*, **35**, 865 (1979).
1240. C. J. Wilkins, W. T. Robinson and P. C. Tellinghuisen, *J. Chem. Soc., Dalton Trans.*, 1289 (1985).
1241. P. A. W. Dean and D. C. Ibbott, *Can, J. Chem.*, **54**, 177 (1976).
1242. C. I. Branden, Ark, Kemi, **22**, 488 (1964).
1243. T. S. Lobana and M. K. Sandhu, *Chem. Ind. (London)*, 106 (1986).
1244. K. C. Malhotra, G. Mehrotra and S. C. Chaudhry, *Indian J. Chem., Sect. A*, **16**, 905 (1978).
1245. E. C. Alyea, K. J. Fisher, R. P. Shakya and A. E. Vougioukas, *Synth. React. Inorg. Met.–Org. Chem.*, **18**, 163 (1988).

1246. S. Wang and J. P. Fackler, Jr, *Organometallics*, **7**, 2415 (1988).
1247. (a) T. S. Lobana, M. K. Sandhu, M. J. Liddell and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 691 (1990); (b) T. S. Lobana, R. Singh, M. K. Sandhu and E. R. T. Tiekink, *J. Coord. Chem.*, in Press.
1248. M. Lusser and P. Peringer, *Inorg. Chim. Acta*, **127**, 151 (1987).
1249. S. O. Grim, P. H. Smith, S. Nittolo, H. L. Ammon, I. J. Colquhoun, W. McFarlane and J. R. Holden, *Inorg. Chem. Acta*, **77**, L241 (1983).
1250. S. O. Grim, P. H. Smith, L. C. Satek, I. J. Colquhoun and W. McFarlane, *Polyhedron*, **1**, 137 (1982).
1251. T. S. Lobana and M. K. Sandhu, *Indian J. Chem., Sect. A*, **29**, 349 (1990).
1252. T. N. Srivastava and M. N. Pande, *J. Indian Chem. Soc.*, **60**, 914 (1983).
1253. T. S. Lobana, M. K. Sandhu and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 1401 (1988).
1254. T. S. Lobana and M. K. Sandhu, *Indian J. Chem., Sect. A*, **29**, 806 (1990).
1255. P. A. W. Dean and L. Polensek, *Can. J. Chem.*, **58**, 1627 (1980).
1256. S. O. Grim, E. D. Walton and L. C. Satek, *Can. J. Chem.*, **58**, 1476 (1980).
1257. S. O. Grim, E. D. Walton and L. C. Satek, *Inorg. Chim. Acta*, **27**, L115 (1978).
1258. R. Colton and D. Dakternieks, *Aust. J. Chem.*, **33**, 1463 (1980).
1259. I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 658 (1981).
1260. C. K. Jorgensen, *Inorg. Chem.*, **3**, 1201 (1964).
1261. A. M. Bond, R. Colton, J. Ebner and S. R. Ellis, *Inorg. Chem.*, **28**, 4509 (1989).
1262. A. M. Bond, R. Colton and J. Ebner, *Inorg. Chem.*, **27**, 1697 (1988).
1263. P. M. Boorman and D. Potts, *Can. J. Chem.*, **52**, 2016 (1974).
1264. M. L. Denniston and D. R. Martin, *J. Inorg. Nucl. Chem.*, **36**, 1461 (1974).
1265. M. Schmidt and H. D. Block, *Chem. Ber.*, **103**, 3705 (1970).
1266. L. Maier, *Z. Anorg. Allg. Chem.*, **345**, 29 (1966).
1267. G. H. Robinson, M. F. Self, W. T. Pennington and S. A. Sangokoya, *Organometallics*, **7**, 2424 (1988).
1268. W. T. Robinson, C. J. Wilkins and Z. Zhang, *J. Chem. Soc., Dalton Trans.*, 2187 (1988).
1269. G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, **24**, 1125 (1968).
1270. K. C. Malhotra and Balkrishan, *Indian J. Chem., Sect. A*, **14**, 869 (1976).
1271. T. N. Srivastava and M. V. Pande, *Indian J. Chem., Sect. A*, **22**, 344 (1983).
1272. P. A. W. Dean, *Can. J. Chem.*, **60**, 2921 (1982).
1273. R. G. Kidd and R. J. Goodfellow, *NMR and the Periodic Table*, Academic Press, London, 1978.
1274. R. A. Manapov, I. Ya. Kuramshin, A. A. Muratova and A. N. Pudovik, *Zh. Obshch. Khim.*, **45**, 1975 (1975).
1275. L. E. Orgel, *Mol. Phys.*, **1**, 322 (1958).
1276. L. H. Piette and H. E. Weaver, *J. Chem. Phys.*, **28**, 735 (1958).
1277. A. F. Wells, *Structural Inorganic Chemistry*, 3rd ed., Oxford University Press, London, 1962, p. 527.
1278. M. J. FernandezCid, M. P. Pazos Parez, J. Sordo, J. S. Casas, M. R. Bermejo and M. Gayoso, *Ann. Quim., Ser., B*, **78**, 190 (1982).
1279. E. G. Amarskii, A. A. Shvets, O. A. Osipov and U. A. Likhovidov, *Koord. Khim.*, **1**, 1323 (1975).
1280. H. Teichmann, *Angew. Chem.*, **77**, 809 (1965).
1281. L. V. Kucheruk, I. P. Gol'dshtein, I. Ya. Kuramshin, E. N. Gur'yanova and A. N. Pudovik, *Zh. Obshch. Khim.*, **47**, 2386 (1977).
1282. T. N. Srivastava and P. C. Kamboj, *Indian J. Chem., Sect. A*, **19**, 167 (1980).
1283. T. N. Srivastava and P. C. Kamboj, *J. Indian Chem. Soc.*, **56**, 857 (1979).
1284. P. Mill and L. Kolditz, *Z. Anorg. Allg. Chem.*, **373**, 176 (1980).
1285. D. J. Williams, C. O. Quicksall and K. M. Barkigia, *Inorg. Chem.*, **21**, 2097 (1982).
1286. S. Bjornevag, S. Husebye and K. Maartmann-Moe, *Acta Chem. Scand., Ser. A*, **36**, 195 (1982).
1287. E. I. Rybalkina, D. Ya. Movshovich, S. B. Bulgarevich, V. A. Kogan, I. D. Sadekov and A. A. Shvets, *Zh. Obshch. Khim.*, **58**, 1561 (1988).
1288. T. N. Srivastava, J. D. Singh and S. K. Srivastava, *Polyhedron*, **6**, 219 (1987).
1289. R. A. Zingaro, *J. Organomet. Chem.*, **1**, 200 (1963).
1290. R. A. Zingaro, B. H. Steeves and K. Irgolic, *J. Organoment. Chem.*, **4**, 320 (1965).
1291. W. W. DuMont, *Z. Naturforsch., Teil B*, **40**, 1453 (1985).
1292. W. W. DuMount and H. J. Kroth, *J. Organomet. Chem.*, **113**, C-35 (1976).
1293. N. Kuhn, H. Schumann, and G. Wolmershaeuser, *Z. Naturforsch., Teil B*, **42**, 674 (1987).

1294. T. Austad, T. Rod, K. Ase, J. Songstad and A. H. Norbury, *Acta Chem. Scand.*, **27**, 1939 (1973).
1295. E. V. Ryl'tsev, I. E. Boldeskii, A. F. Pavlenko, Yu. P. Egorov and V. P. Akkerman, *Zh. Prikl. Spektrosk.*, **16**, 513 (1972); *Chem. Abstr.*, **77**, 26907r (1972).
1296. I. A. Nuretdinov and E. I. Loginova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 2827 (1973).
1297. N. Kuhn and H. Schumann, *Phosphorus Sulphur*, **26**, 199 (1986).
1298. J. Von Windheim and M. Cocivera, *J. Electrochem. Soc.*, **134**, 440 (1987); *Chim. Abstr.*, **106**, 109891z (1987).
1299. M. L. Steigerwald and C. R. Sprinkle, *Organometallics*, **7**, 245 (1988).
1300. M. L. Steigerwald and C. E. Rice, *J. Am. Chem. Soc.*, **110**, 4228 (1988).
1301. M. L. Steigerwald, *Chem. Mater.*, **1**, 52 (1989); *Chem. Abstr.*, **110**, 68438u (1989).
1302. N. Kuhn, H. Schumann and R. Boese, *J. Chem. Soc., Chem. Commun.* 1257 (1987).
1303. H. F. Klein, M. Gass, U. Koch, B. Eisenmann and H. Schaefer, *Z. Naturforsch., Teil B*, **43**, 830 (1988).
1304. J. G. Brennan, R. A. Andersen and A. Zalkin, *Inorg. Chem.*, **25**, 1761 (1986).
1305. N. Kuhn and H. Schuman, *J. Chem. Soc., Dalton Trans.*, 541 (1987).
1306. L. Lewman and P. Klotz, *J. Phys. Chem.*, **67**, 205 (1963).
1307. H. Akaiwa and H. Kawamoto, *Rev. Anal. Chem.*, **6**, 65 (1982).
1308. T. Shigematsu, M. Tabushi, M. Matsui and T. Honjyo, *Bull. Chem. Soc. Jpn.*, **39**, 165 (1966).
1309. A. M. Rozen and A. I. Mikhailichenko, *Zh. Neorg. Khim.*, **12**, 741 (1967).
1310. T. V. Healy, *J. Inorg. Nucl. Chem.*, **31**, 499 (1969).
1311. T. V. Healy, *J. Inorg. Nucl. Chem.*, **30**, 1025 (1968).
1312. F. G. Seeley and W. H. Baldwin, *J. Inorg. Nucl. Chem.*, **38**, 1049 (1976).
1313. T. V. Healy, *Solv. Extn. Chem., Proc. Int. Conf. Goteborg*, 119 (1966); *Chem. Abstr.*, **69**, 90367b (1969).
1314. E. Kunugita, J. H. Kim and I. Komasawa, *Kagaku Kogaku Ronbunshu*, **15**, 504 (1989).
1315. H. Mukai, S. Miyazaki, S. Umetani, S. Kihara and M. Matsui, *Anal. Chim. Acta*, **220**, 111 (1989).
1316. M. Tanigawa, S. Nishiyama, S. Tsuruya and M. Masai, *Chem. Eng. J.* (*Lausanne*), **39**, 157 (1988).
1317. F. Persin and G. Durand, *Bull. Soc. Chim. Fr.*, 21 (1987).
1318. T. V. Healy, *J. Inorg. Nucl. Chem.*, **19**, 314 (1961).
1319. T. V. Healy, *J. Inorg. Nucl. Chem.*, **19**, 328 (1961).
1320. G. V. Volkova, S. V. Kachin, D. G. Brinblat and P. P. Smimov, *Debosited Doc.* 1975, VINIT 3–76, 9 pp. *Chem. Abstr.*, **88**, 55556h (1977).
1321. J. Minczewski, Z. Boguszewska and Z. Skorko-Trybula, *Chem. Anal.* (*Warsaw*), **17**, 899 (1972).
1322. Y. Akama, K. Sato, T. Nakai, M. Kajitani and S. Kishimoto, *Anal. Sci.*, **3**, 141 (1987).
1323. Y. Takeda, *Bull. Chem. Soc. Jpn.*, **56**, 2589 (1983).
1324. Y. Yamashoji, T. Matsushita and T. Shono, *Anal. Sci.*, **4**, 43 (1981).
1325. Y. Yamashoji, T. Matsushita and T. Shono, *Anal. Sci.*, **3**, 327 (1987).
1326. T. Sato, *J. Radioanal. Nucl. Chem.*, **101**, 77 (1986).
1327. Y. Le Quesne, *Eur. Pat. Appl.*, EP 318 383 (1989); *Chem. Abstr.*, **111**, 199085v (1989).
1328. O. Navratil, J. Meindl and J. Kos, *Collect. Czech. Chem. Commun.*, **46**, 1906 (1981).
1329. J. S. Preston and A. C. Dupreez, *Report Mintek*, M228, 43 (1985); *Chem. Abstr.*, **104**, 190228s (1986).
1330. R. DuPreez and J. S. Preston, *S. Afr. J. Chem.*, **39**, 89 (1986).
1331. H. H. Tsien and M. J. F. Leroy, *K'uang Yeh*, **29**, 125 (1985).
1332. J. P. Brunette, M. Taheri, G. Goetz- Grandmont and M. J. F. Leroy, *Solvent Extr. Ion Exch.*, **3**, 309 (1985).
1333. E. C. Lee and M. S. Lee, *Taehan Kumsok Hakhoe Chi.*, **26**, 454 (1988).
1334. L. K. Chuchalin, S. P. Khranenko and Z. N. Mironova, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 61 (1973).
1335. M. L. P. Reddy, B. Rangamannar and A. S. Reddy, *Radioisotopes*, **34**, 675 (1985).
1336. V. I. Aleinikov and A. I. Gorbanev, *Dokl. Akad. Nauk SSSR*, **236**, 1394 (1977).
1337. W. A. Rickelton and R. J. Boyle, *Eur. Pat. Appl.*, EP 299 169 (1989); *Chem. Abstr.*, **110**, 235058d (1989).
1338. S. Ignacy, *Inst. Nucl. Phys. Cracow, Rep.*, No. 427-C, 119 (1965); *Chem. Abstr.*, **64**, 11939e (1966).
1339. S. Umetani, M. Matsui, T. Kuzunishi and Y. Nishikawa, *Bull. Inst. Chem. Res. Kyoto Univ.*, **60**, 254 (1982).
1340. M. Spankova, L. Smirnova and J. Durcanska, *Acta Fac. Rerum Nat. Univ. Comenianae, Chim.*, **31**, 73 (1984).

1341. S. Kusakabe and T. Sekine, *Bull. Chem. Soc. Jpn.*, **54**, 2533 (1981).
1342. H. Moriya and T. Sekine, *Bull. Chem. Soc. Jpn.*, **45**, 1626 (1972).
1343. N. V. Shakhova, I. P. Alimarin and Yu. A. Zolotov, *Radiokhimiya*, **10**, 467 (1968).
1344. R. DuPreez and J. S. Preston, *S. Afr. J. Chem.*, **39**, 137 (1986).
1345. M. A. Quereshi and M. Ejaz, *Arabian J. Sci. Eng.*, **8**, 9 (1983).
1346. I. N. Popkov, I. N. Tselik, L. P. Chernega, T. A. Pentkovskaya, T. I. Burova and B. N. Laskorin, *Dokl. Akad Nauk SSSR*, **173**, 1351 (1967).
1347. W. J. Ross and J. C. White, *Anal. Chem.*, **31**, 1847 (1959).
1348. S. Li, G. Dai, Z. Zou and G. Xu, *Yingyong Huaxue*, **2**, 71 (1985).
1349. Y. Ding, W. Wang and M. Yi, *Youkuangye*, **5**, 21 (1986).
1350. H. Zhang, J. Le and H. Zhang, *Wuji Huaxue*, **2**, 70 (1986).
1351. W. Wang, Y. Din, M. Yi, D. Chen, X. Li, and X. Feng, *He Huaxue Yu Fangshe Huaxue*, **8**, 1 (1986).
1352. E. G. Goryacheva and N. M. Aksenova, *Nauch. Tr. N.-i. i. Proekt. In-t Redkomet. Prom-sti Giredmet* (125), 23 (1984); *Chem. Abstr.*, **103**, 25511a (1985).
1353. T. Delloye, J. L. Sabot, *Eur. Pat. Appl.*, EP 284 503, 1987.
1354. T. Delloye and J. L. Sabot, *Eur. Pat. Appl.*, EP 284 504, 1987.
1355. J. P. Young and J. C. White, *Anal. Chem.*, **31**, 393 (1959).
1356. J. C. White, *Am. Soc. Test. Mater. Spec. Tech. Publ.*, No. **238**, 27 (1958).
1357. M. Watanabe and R. Sei, *Eur. Pat. Appl.*, EP 298 763, 1989; *Chem. Abstr.*, **110**, 139120x (1989).
1358. J. P. Young and J. C. White, *Talanta*, **1**, 263 (1958).
1359. E. A. Pepelaeva, O. A. Sinegribova, N. A. Shostenko and G. A. Yagodin, *Zh. Prikl. Khim.*, **46**, 1301 (1973).
1360. G. Y. Yagodin, O. A. Sinegribova and A. M. Chekmarev, *Proc. Int. Solvent Extn. Conf.*, **3**, 2209 (1974).
1361. M. A. Awwal, K. M. Idriss and S. M. Ali, *At. Energy Centre Rep.*, AECD/CH-12 (1968); *Chem. Abstr.*, **71** 74774t (1969).
1362. J. C. White and W. J. Ross, *US Atomic Energy Comm.*, ORNL-2498 (1958).
1363. H. Saisho, *Bull. Chem. Soc. Jpn.*, **35**, 514 (1962).
1364. L. S. Scherff and H. Gunter, *Z. Electrochem.*, **64**, 1022 (1960).
1365. M. Mrnka, J. Sladkovska and O. Hinterhozinger, *Sb. Vys. Sk. Chem.-Technol. Praze, Anorg. Chem. Technol.*, **B25**, 147 (1980).
1366. V. G. Timoshev, K. A. Petrov, A. V. Radionov, V. V. Balandina, A. A. Volkova, A. V. El'kina and Z. I. Nagnibeda, *Ekst. Teoriya, Primenenie, Apparatura, Sb. Statei*, 88 (1962); *Chem. Abstr.*, **59**, 5850d (1963).
1367. O. Navratil and R. Kolouch, *Hydrometallurgy*, **7** 289 (1981); *Chem. Abstr.*, **96**, 55839t (1982).
1368. O. Navratil, J. Smola and R. Kolouch, *Collect. Czech. Chem. Commun.*, **44**, 3656 (1979).
1369. H. Akaiwa and H. Kawamoto, *Nippon Kagaku Kaishi*, 90 (1973).
1370. H. Irving and D. N. Edgington, *Chem. Ind.* (*London*)., 77 (1961).
1371. H. Akaiwa, H. Kawamoto and E. Hiyamuta, *Bull. Chem. Soc. Jpn.*, **54**, 3409 (1981).
1372. H. Akaiwa, H. Kawamoto and E. Hiyamuta, *Chem. Lett.*, 793 (1979).
1373. V. L. Bykhovtos and G. N. Melikhone, *Zh. Prikl. Khim.*, **43**, 954 (1970).
1374. J. P. Bonsack, *Ind. Eng. Chem., Prod. Res. Dev.*, **10**, 396 (1971).
1375. R. Haehn and H. J. Retelsdorf, *Erzmetall*, **37**, 444 (1984); *Chem. Abstr.*, **102**, 29162q (1985).
1376. A. Ohki, Y. Fujino, K. Ohmori and M. Takagi, *Solvent Extr. Ion Exch.*, **4**, 639 (1986).
1377. C. K. Mann and J. C. White, *Anal. Chem.*, **30**, 989 (1958).
1378. M. Niitsu and T. Sekine, *J. Inorg. Nucl. Chem.*, **38**, 1057 (1976).
1379. T. Mikalauskas and G. G. Shemelva, *Zh. Prikl. Khim.* **54**, 1815 (1981).
1380. Y. Yamoshoji, T. Matsushita and T. Shono, *Polyhedron* **5**, 1291 (1986).
1381. B. N. Laskorin, V. A. Kuznetsov and I. F. Egorov, *Ekstr. Sorbtsiya Met. Molibdena, Vol'frama Reniya*, 118 (1971); *Chem. Abstr.*, **76**, 28255e (1972).
1382. E. Oezensoy and A. R. Burkin, *US, Pat.*, 4 275 039, 1981; *Chem. Abstr.*, **96**, 9940w (1982).
1383. B. N. Laskorin, V. A. Kuznetsov and K. K. Osokina, *Ekstr. Sorbtsiya Met. Molibdena Vol'frama Reniya*, 100-5 (1971).
1384. R. Shabana, S. M. Khalifa and S. Abdalla, *J. Radioanal. Nucl. Chem.*, **106**, 55 (1986).
1385. T. Sekine, R. Murai, K. Takashashi and S. Iwahori, *Bull. Chem. Soc. Jpn.*, **50**, 3415 (1977).
1386. S. Nakamura, H. Imura and N. Suzuki, *J. Radioanal. Nucl. Chem.* **82**, 33 (1985).
1387. T. Aoki, *Bull. Inst. Chem. Res. Kyoto Univ.*, **59**, 195 (1981).

1388. R. Shankar and K. S. Venkateswarlu, *J. Inorg. Nucl. Chem.*, **32**, 229 (1970).
1389. G. E. Boyd and Q. V. Larson, *J. Phys. Chem.*, **64**, 988 (1960).
1390. K. A. Bol'shakov, N. M. Sinitsyn, V. F. Travkin and L. N. Antimonova, *Dokl. Akad. Nuck SSSR*, **198**, 614 (1971).
1391. J. J. Bucher and R. M. Diamond, *J. Inorg. Nucl. Chem.*, **34**, 3531 (1972).
1392. J. J. Bucher, M. Zirin, R. C. Laugen and R. M. Diamond, *J. Inorg. Nucl. Chem.*, **33**, 3869 (1971).
1393. V. F. Travkin, V. V. Borisov, K. A. Bol'shakov and N. M. Sinitsyn, *Zh. Neorg. Khim.*, **20.**, 2541 (1975).
1394. J. Kaehler and E. Gock, *Erzmetall*, **41**, 132 (1988).
1395. W. J. Ross and J. C. White, *US Atomic Energy Comm.*, ORNL 2382 (1957); *Chem. Abstr.*, **52**, 2631d (1958).
1396. A. G. Maddock and L. O. Maderios, *J. Chem. Soc. A*, 1946 (1969).
1397. A. Textoris, G. Lyaudet and A. Bathelier, *Eur. Pat. Appl.*, EP 239 501 1987; *Chem. Abstr.*, **108**, 79282y (1988).
1398. S. Yu, Z. Wu and C. Chen. *Iron Control Hydrometall. (Int. Symp).* 334 (1986); (Eds J. E. Dutrizac and A. J. Monheniius), *Chem. Abstr.*, **106**, 21467e (1987).
1399. S. Kikuchi, *Jpn. Kokai Tokkyo Koho*, 79 119 331, 1979; *Chem. Abstr.*, **92**, 26186q (1980).
1400. G. Michel, E. DeGoyet and G. Duyckaerts, *Anal. Chim. Acta*, **72**, 97 (1974).
1401. T. Sekine and T. Tetsuka, *Bull. Chem. Soc. Jpn.*, **45**, 1620 (1972).
1402. T. Sekine and H. Honda, *J. Inorg. Nucl. Chem.*, **38**, 1347 (1976).
1403. R. Shankar and K. S. Venkateswarlu, *J. Inorg. Nucl. Chem.*, **32**, 2369 (1970).
1404. H. Akaiwa, H. Kawamoto and E. Hiyamuta, *Bunseki Kagaku*, **28**, 477 (1979).
1405. J. Agett, *J. Inorg. Nucl. Chem.*, **32**, 2767 (1970).
1406. A. J. Fischman, H. L. Finston and D. E. Goldberg, *J. Inorg. Nucl. Chem.*, **35**, 2497 (1973).
1407. H. L. Finston and Y. Inoue, *J. Inorg. Nucl. Chem.*, **29**, 2431 (1967).
1408. H. L. Finston and Y. Inoue, *J. Inorg. Nucl. Chem.*, **29**, 199 (1967).
1409. W. A. Rickelton, *Fr. Demande*, 2 481 941; *Chem. Abstr.*, **96**, 145318b (1982).
1410. N. M. Sinitsyn, V. N. Pichkov and O. E. Zvyagintsev, *Zh. Neorg. Khim.*, **13**, 1469 (1968).
1411. (a) T. S. Lobana and A. Sharma, *Indian J. Environ. Protect.*, **9**, 447 (1989); (b) T. S. Lobana and P. V. K. Bhatia, *Talanta*, in press, C 90140.
1412. N. M. Sinitsyn, V. F. Travkin and V. V. Boriosov, *Radiokhimiya*, **14**, 686 (1972).
1413. V. N. Saraiya, K. S. Venkateswarlu and J. Shankar, *Indian J. Chem.*, **11**, 490 (1973).
1414. H. Meier, E. Zimmerhackl, W. Albrecht, W. Hecker, D. Boesche, P. Menge, A. Ruckdeschel, E. Unger and G. Zeitler, *Mikochim. Acta*, 573 (1969).
1415. E. A. Belousov, V. M. Kirillov and V. I. Zubeiko, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Technol.*, **15**, 161 (1972).
1416. G. L. DeLong and U. A. Brinkman, *Fresenius' Z. Anal. Chem.*, **289**, 358 (1978).
1417. M. Wada, K. Iwabuchi and H. Tsumaki, *Jpn. Kokai Tokkyo Koho*, 63 275 595, 1988; *Chem. Abrst.*, **110**, P 231887a (1989).
1418. Yu. A. Zolotov and L. G. Gavrilova, *Radiokhimiya*, **11**, 389 (1969).
1419. A. T. Kandil and A. Ramadan, *J. Radioanal. Chem.*, **52**, 15 (1979).
1420. T. Shigematsu, T. Honjyo, M. Tabushi and M. Matsui, *Bull. Chem. Soc. Jpn.*, **43**, 793 (1970).
1421. S. M. Khalifa, H. F. Aly, N. Zakaria and J. A. Daoud, *Solvent Extr. Ion Exch.*, **3**, 473 (1985).
1422. R. Murai, T. Sekine and M. Iguchi, *Nippon Kagaku Tasshi*, **92**, 967, (1971).
1423. (a) T. Shigematsu and T. Honjyo, *Bunseki Kagaku* **18**, 68 (1969); (b) S. O. Umetani, S. Kihara and M. Matsui, *Anal Chim. Acta*, **232**, 293 (1990).
1424. H. Akaiwa, H. Kawamoto and T. Saito, *Nippon Kagaku Zasshi*, **92**, 1156 (1971).
1425. J. M. Castresana, M. P. Elizalde, M. Aguilar and M. Cox, *Anal. Chim. Acta*, **198**, 315 (1987).
1426. A. T. Rane and D. R. Nepali, *J. Radional. Nucl. Chem.*, **120**, 147 (1988).
1427. V. F. Travkin, V. Ya. Semenii, L. Yu. Izvekova, V. V. Yakshin, V. P. Lanin, A. L. Sirkis and A. Yu. Lapin, *USSR Pat.*, 1 227 704; *Chem. Abstr.*, **105**, 46758t (1986).
1428. T. S. Lobana and P. V. K. Bhatia, *Indian J. Chem., Sect. A*, **29**, 933 (1990).
1429. P. Beneitez, S. J. Ortiz and J. Ortega, *An. Quim., Ser. A*, **81**, 65 (1985).
1430. N. Suzuki, H. Takahashi and H. Imura, *Kakuriken Kenkyu Hokoku*, **21**, 57 (1988).
1431. H. Imura, H. Takahashi, Y. Ueki and N. Suzuki, *Proc. Symp. Solvent Extr.*, 1 (1988); *Chem. Abstr.*, **111**, 203002k (1989).
1432. Y. Zhang, C. Wang, P. Wang and M. Fan, *Gaodeng Xuexiao Huaxue Xuebao*, **6**, 126 (1985).

1433. R. Murai, S. Iwahori and T. Sekine, *Bull. Chem. Soc. Jpn.*, **50**, 1315 (1977).
1434. T. Sekine, R. Murai and M. Iguchi, *Nippon Kagaku Zasshi*, **92**, 412 (1971).
1435. H. Hoshino and T. Yotsuyanagi, *Bull. Chem. Soc. Jpn.*, **58**, 1037 (1985).
1436. S. Ide and M. Takagi, *Anal. Sci.*, **2**, 265 (1986).
1437. T. Sekine, S. Iwahori and R. Murai, *J. Inorg. Nucl. Chem.*, **39**, 363 (1977).
1438. T. Sekine and N. Ihara, *Bull. Chem. Soc. Jpn.*, **44**, 2642 (1971).
1439. R. Murai, T. Sekine and M. Iguchi, *Nippon Kagaku Zasshi*, **92**, 967 (1971).
1440. T. Sekine, R. Murai, M. Niitsu and N. Ihara, *J. Inorg. Nucl. Chem.*, **36**, 2569 (1974).
1441. R. Murai, K. Kurakane and T. Sekine, *Bull. Chem. Soc. Jpn.*, **49**, 355 (1976).
1442. R. Murai, T. Sekine and M. Iguchi, *Nippon Kagaku Zasshi*, **92**, 1019 (1971).
1443. M. Mojski, *J. Radioanal. Chem.*, **46**, 239 (1978).
1444. B. P. Blednov, G. N. Shivrin, B. N. Laskorin, A. F. Pavlenko and V. E. Dul'neva, *Zhidk. Ekrts., Tr. Vses. Nanch.-Tekh. Soveshch.*, 3rd 1967 (Pub. 1969), 356; *Chem. Abstr.*, **73**, 90239u (1970).
1445. G. L. Grigor'ev, A. V. Mozzhukhin, L. N. Moskvin and A. M. Orlov, *Dokl. Akad. Nauk SSSR.*, **292**, 884 (1987).
1446. Y. Shigetomi, T. Kojima, E. Iwamoto and Y. Yamamoto, *Anal. Chim. Acta*, **152**, 301 (1983).
1447. V. S. Shmidt, N. A. Shorokhov and E. G. Teterin, *Zh. Neorg. Khim.*, **30**, 3152 (1985).
1448. (a) Y. Baba, K. Inoue, K. Yoshizuka and I. Nagamatus, *Proc. Symp. Solvent Extr.*, 37 (1988); *Chem. Abstr.*, **111**, 181950p (1989); (b) R. J. Casey, J. J. M. Fardy and W. R. Walker, *J. Inorg. Nucl. Chem.*, **29**, 1139 (1967).
1449. S. M. Wang, W. R. Walker and N. C. Li, J. Inorg. Nucl. Chem., **28**, 875 (1966).
1450. N. C. Li, S. M. Wang and W. R. Walker, *J. Inorg. Nucl. Chem.*, **27**, 2263 (1965).
1451. C. H. Ke and N. C. Li, *J. Inorg. Nucl. Chem.*, **28**, 2255 (1966).
1452. E. B. Jacobs, *At. Energy Aust.*, **18**, 13 (1975); *Chem. Abstr.*, **84**, 50469q (2976).
1453. Y. Akama, K. Sato, M. Ukaji, T. Kawata and M. Kajitani, *Polyhedron*, **4**, 59 (1985).
1454. A. T. Kandil, A. M. El-Atrash and S. M. El-Medani, *Solvent Extr. Ion Exch.*, **3**, 453 (1985).
1455. T. S. Lobana and P. V. K. Bhatia, *Indian J. Chem., Sect. A*, **29A**, 93 (1990).
1456. Y. Hasegawa, K. Suzuki and T. Sekine, *Chem. Lett.*, 1075 (1981).
1457. Y. Gong, S. Xia and J. Yang, *Hangzhou Daxue Xuebao, Ziran Kexueban*, **12**, 363 (1985).
1458. Y. Gong. S. Xia and J. Yang, *Kexue Tongbao*, **31**, 1112 (1986).
1459. M. I. Tocher, D. C. Whitney and R. M. Diamond, *J. Phys. Chem.*, **68**, 368 (1964).
1460. Yu. M. Yukhin, T. A. Udalova, V. G. Tsimbalistand S. S. Shatskaya, *Zh. Anal. Khim.*, **43**, 1020 (1988).
1461. H. Moriya and T. Sekine, *Bull. Chem. Soc. Jpn.*, **44**, 3347 (1971).
1462. M. Billon and G. Durand, *C.R. Acad. Sci., Ser. C*, **277**, 961 (1973).
1463. C. Rozycki, *Chem. Anal.* (*Wassaw*)., **29**, 169 (1984); *Chem. Abstr.*, **102**, 68158n (1985).
1464. C. Rozycki, *Chem. Anal.* (*Wassaw*)., **29**, 169 (1984).
1465. S. Kikuchi, *Jpn. Kokai*, 76,75617, 1976; *Chem. Abstr.*, **85**, 111244g (1976).
1466. S. Kikuchi, T. Goto and A. Nakayama, *Nippon Kogyo Kaishi*, **101**, 381 (1985).
1467. M. Matsui, H. Doe, T. Hirade and T. Shigematsu, *Anal. Lett.*, **12**, 1385 (1979).
1468. H. Doe, M. Matsui and T. Shigematsu, *Bull. Inst. Chem. Res. Kyoto Univ.*, **57**, 343 (1979).
1469. T. Shigematsu, M. Tabushi, M. Matsui and K. Utsunomiya, *Bull. Inst. Chem. Res. Koyoto Univ.*, **45**, 290 (1967).
1470. W. R. Walker and M. S. Farrell, *J. Inorg. Nucl. Chem.*, **28**, 1483 (1966).
1471. K. Ueda, T. Aoki, M. Matsui and T. Shigematsu, *Bull. Inst. Chem. Res. Kyoto Univ.*, **50**, 653 (1972).
1472. T. Aoki, E. Deguchi, M. Matsui and T. Shigematsu, *Bull. Inst. Chem., Res. Kyoto Univ.*, **49**, 307 (1971).
1473. G. N. Rao and V. S. Chouhan, *Indian J. Chem., Sect. A*, **17**, 154 (1979).
1474. Y. Goto and T. Sekine, *Proc. Symp. Solvent Extr.*, 55 (1988); *Chem. Abstr.*, **111**, 181953s (1989).
1475. K. Sato, Y. Akama and T. Nakai, *Anal. Chim. Acta*, **207**, 367 (1988).
1476. Yu. A. Zolotov and L. G. Gavrilova, *J. Inorg. Nucl. Chem.*, **31**, 3613 (1969).
1477. M. Sudersanan and Pushparaja, *Indian J. Chem., Sect. A*, 998 (1980).
1478. T. V. Healy, D. F. Peppard and G. W. Mason, *J. Inorg. Nucl. Chem.*, **24**, 1429 (1962).
1479. S. M. Wang and N. C. Li, *J. Inorg. Nucl. Chem.*, **28**, 1091 (1966).
1480. J. M. Castresana, A. Gonzalez de la Presa and M. P. Elizalde, *Quim. Anal.* (*Barcelona*), **7**, 184 (1985).

1481. S. Iwahori, R. Miura and R. Mural, *Bunseki Kagaku*, **34**, 727 (1985).
1482. M. Sudersanan and A. K. Sundaram, *Proc. Indian Acad. Sci., Sect. A*, **85**, 75 (1977); *Chem. Abstr.*, **87**, 29728a (1977).
1483. R. Lahiri and G. N. Rao, *Croat. Chem. Acta*, **58**, 29 (1985).
1484. I. Casas, N. Miralles, A. M. Sastre and M. Aguilar, *Polyhedron*, **8**, 2535 (1989).
1485. V. A. Mikhailov, N. A. Korol and D. D. Bogdanova, *Zh. Neorg. Khim.*, **33**, 176 (1988).
1486. F. H. Al-Dabbagh and J. I. Bullock, *J. Less-Common Met.* **125**, 75 (1986).
1487. A. Alian and Z. Moustapha, *Indian J. Chem.*, **3**, 390 (1965).
1488. A. S. Reddy and L. K. Reddy, *J. Inorg. Nucl. Chem.*, **39** 1683 (1977).
1489. I. N. Popkov, I. N. Tselik, T. A. Pentkovskaya and I. D. Sokolova, *Ukr. Khim. Zh.*, **34**, 1066 (1968).
1490. O. Vittori and M. Porthault, *C. R. Acad Sci., Ser. C*, **269**, 967 (1969).
1491. Yu. S. Kuznetsova, N. A. Suvorovskaya, *Tr. Inst. Obogashch. Tverd. Goryuch. Iskop*, **21**, 143 (1972).
1492. G. Duyckerts and J. Goffart, *US At. Energy Comm.*, EUR- 437f (1964); *Chem. Abstr.*, **62**, (1965).
1493. T. Cecconie and H. Freiser, *Anal. Chem.*, **62**, 622 (1990).
1494. Z. Zhov and Y. Gao, *Yuanzineng Kexue jitshu*, **22**, 470 (1988).
1495. C. T. Rhee, *Daehan Hawhak Hwoejee*, **7**, 245 (1963).
1496. H. D. Harmon, J. R. Peterson, W. J. McDowell and C. F. Cokeman, *J. Inorg. Nucl. Chem.*, **38**, 155 (1976).
1497. K. Watanabe and R. Ono, *J. Nucl. Sci. Technol*, **1**, 75 (1964).
1498. K. Watanbe, *J. Nucl. Sci. Technol.*, **1**, 39 (1964).
1499. E. B. Mikhlin, A. I. Mikhailichenko and M. A. Khmuran, *Radiokhimiya*, **28**, 42 (1986).
1500. J. J. Fardy and J. M. Pearson, *J. Inorg. Nucl. Chem.*, **35**, 2513 (1973).
1501. X. Zhang, *Huaxue Xuebao*, **42**, 183 (1984).
1502. A. K. More, M. Sundernanan and A. K. Sundaram, *Indian J. Chem., Sect. A*, **19**, 926 (1980).
1503. T. V. Healy and J. R. Ferraro, *J. Inorg. Nucl. Chem.*, **24**, 1449 (1962).
1504. T. Taketatsu and C. V. Banks, *Anal. Chem.*, **38**, 1524 (1966).
1505. T. Taketatsu and N. Okhura, *Bull. Chem. Soc. Jpn.*, **44**, 2430 (1971).
1506. H. F. Aly and H. A. El-Naggar, *Microchem. J.* **18**, 405 (1973).
1507. T. Lengyel, *Radiochem. Radioanal. Lett.*, **27**, 199 (1976).
1508. T. Taketatsu and N. Toriumi, *J. Inorg. Nucl. Chem.*, **31**, 2235 (1969).
1509. H. F. Aly, S. M. Khalifa and N. Zakareia, *Solvent Extr. Ion Exch.*, **2**, 887 (1984).
1510. S. Nakamura, Y. Surakitbanharn and K. Akiba, *Proc. Symp. Solvent Extr.*, 31 (1987).
1511. T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **29**, 1475 (1967).
1512. J. N. Mathur, S. A. Pai, P. K. Khopkar and M. S. Subramanian, *J. Inorg. Nucl. Chem.*, **39**, 653 (1977).
1513. H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, **21**, 169 (1961).
1514. M. A. Carey and C. V. Banks, *J. Inorg. Nucl. Chem.*, **31**, 533 (1969).
1515. P. K. Khopkar and P. Narayanankutty, *J. Inorg. Nucl. Chem.*, **34**, 3233 (1972).
1516. K. Akiba, M. Wada and T. Kanno, *J. Inorg. Nucl. Chem.*, **43**, 1031 (1981).
1517. N. Zakareia, S. M. Khalifa, J. A. Daoud and H. F. Aly, *Radiochim Acta*, **39**, 89 (1986).
1518. T. Shigematsu and T. Honjyo, *Bull. Chem. Soc. Jpn.*, **43**, 796 (1970).
1519. T. Honjyo, *Bull. Chem. Soc. Jpn.*, **42**, 995 (1969).
1520. St. Ahrland, *Struct. Bonding*, **5**, 118 (1968).
1521. K. Akiba, *J. Radioanal. Chem.*, **36**, 153 (1977).
1522. J. F. Desreux, J. Massaux and G. Duyckaerts, *J. Inorg. Nucl. Chem.*, **40**, 1159 (1978).
1523. S. Umetani, H. Freiser, S. Kihara and M. Matsui, *Proc. Symp. Solvent Extr.*, 13 (1986); *Chem. Abstr.*, **107**, 16277m (1987).
1524. S. Umetani and H. Freiser, *Inorg. Chem.*, **26**, 3179 (1987).
1525. O. Tochiyama and H. Freiser, *Anal. Chim. Acta*, **131**, 233 (1981).
1526. Q. Meng, and X.Ma, *Hebei Daxue Xuebao Ziran Kexueban*, (4), 25 (1987).
1527. X. Mou and D. Chen, *Beijing Daxue Xuebao, Ziran Kexueban*, **24**, 150 (1988).
1528. B. F. Smith, G. D. Jarvinen, G. G. Miller, R. R. Ryan and E. J. Peterson, *Solvent. Extr. Ion Exch.*, **5**, 895 (1987).
1529. T. Sato and S. Ban, *Proc. Symp. Solvent Extr.*, 49 (1988); *Chem. Abstr.*, **111**, 181952r (1989).
1530. I. B. Kvasnitskii, B. N. Zaitsev and V. P. Popik, *Radiokhimiya*, **27**, 761 (1985).

1531. R. Wen and J. Chen, *He Huaxue Yu Fangshe Huaxue*, **11**, 102, 112 (1989).
1532. G. W. Mason, S. McCarty and D. M. Peppard, *J. Inorg. Nucl. Chem.*, **24**, 967 (1962).
1533. K. L. and H. Freiser, *Solvent Extr. Ion Exch.*, **4**, 739 (1986).
1534. K. Li, C. Qu and H. Freiser, *Solvent Extr. Ion. Exch.* **5**, 1045 (1987).
1535. C. Qu and H. Freiser, *Solv. Extr. Ion Exch.*, **7**, 31 (1989).
1536. A. Chatt and R. R. Rao, *Mater. Res. Soc. Symp. Proc.*, **127**, 897 (1989).
1537. J. N. Mathur and P. K. Mathur, *J. Radioanal. Nucl. Chem.*, **109**, 329 (1987).
1538. S. Al-Fared, F. Zantuti, Yu. S. Krylov, *J. Radioanal Nucl. Chem.*, **125**, 381 (1988).
1539. H. M. N. H. Irving and S. P. Sinha, *Anal. Chim. Acta*, **51**, 39 (1970).
1540. M. K. Chmutova, B. F. Myasoedov, B. Ya. Spivalov, N. E. Kochetkova and Yu. A. Zolotov, *J. Inorg. Nucl. Chem.*, **35**, 1317 (1973).
1541. Z. K. Karolova, L. M. Radionova, Z. I. Pyzhova and B. F. Myasoedov, *Radiokhimiya*, **19**, 42 (1977).
1542. W. J. Ross and J. C. White, *US At. Energy Comm.*, ORNL 2627, 31 (1958); *Chem. Abstr.*, **53**, 6553 (1959).
1543. A. Alin, M. Miloud, A. El Hassadi and M. Khaliquzzaman, *J. Radioanal. Nucl. Chem.*, **116**, 271 (1987).
1544. M. Mojski, *J. Radioanal. Chem.*, **35**, 303 (1977).
1545. V. S. Shmidt and S. D. Nikitin, *Radiokhimiya*, **27**, 175 (1985); *Chem. Abstr.*, **103**, 27725x (1985).
1546. V. G. Torgov, M. K. Drozdova, Z. A. Larionova and G. A. Mardezhova, *Izv. Sib. Otd. Acad. Nauk SSSR, Ser. Khim. Nauk*, (1), 81 (1978).
1547. J. Li, *Yankuang Ceshi*, **5**, 246 (1986).
1548. T. V. Healy, D. F. Peppard and G. W. Mason, *J. Inorg. Nucl. Chem.*, **24**, 1429 (1962).
1549. H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, **20**, 321 (1961).
1550. S. Singh, V. Chakravorty and K. C. Dash, *J. Radioanal. Nucl. Chem.*, **127**, 349 (1988).
1551. D. T. Nguyen, S. Mareva and N. Iordanov, *Izv. Otd. Khim. Nauki, Bulg. Akad. Nauk*, **3**, 671 (1970).
1552. A. T. Kandil and S. M. El-Medani, *Radiochim. Acta*, **46**, 109 (1989).
1553. H. B. Maghrawy, S. A. El-Reefy and H. F. Aly, *Radiochim. Acta*, **46**, 127 (1989).
1554. R. Von Ammon, P. Dressler and W. Troye, *Kernforschungszentrum Rep.*, KFK-958, 30 (1969); *Chem. Abstr.*, **72**, 125594q (1970).
1555. B. N. Laskorin, D. I. Skorovarov and V. V. Shatalov, *Ekstr. Teoriya, Primenenie, Appatura, Sb. Statei*, 163 (1962); *Chem. Abstr.*, **59**, 3601b (1963).
1556. B. N. Laskorin, D. I. Skorovarov, L. A. Fedorova and V. V. Shatalov, *At. Energ.* (*USSSR*), **28**, 383 (1970).
1557. A. M. Rozen, P. M. Boredin, Yu. I. Mitchenko and Z. I. Nikolotova, *Radiokhimiya*, **12**, 510 (1970).
1558. J. Sladkovskaya and M. Mrnka, *Sb. Vys. Sk. Chem. -Technol. Praze, Anorg. Chem. Technol*, **B26**, 71 (1981).
1559. M. F. Pushlenkov, G. P. Nikitina and V. G. Voden, *Radiokhimiya*, **2**, 215 (1960).
1560. L. L. Burger, *J. Phys. Chem.*, **62**, 590 (1958).
1561. W. D. Shultz and L. B. Dunlap, *Anal. Chim. Acta*, **20**, 254 (1963).
1662. Y. Shigetomi, T. Kojima and H. Kamba, Anal. Chim. Acta, **116**, 199 (1980).
1563. G. Wang, J. Niu, X. Jhou and F. Zhao, *Fushe Fanghu*, **5**, 154 (1985).
1564. H. Liu, *Yankuang Ceshi*, **5**, 186 (1986).
1565. J. Sun and X. Jia, *Fenxi Shiyanshi*, **7**, 63 (1988).
1566. C. A. Blake, K. B. Brown and C. F. Coleman, US At. Energy Comm., ORNL 1964 (1965).
1567. A. H. A. Heny and G. Banerjee, *US At. Energy Comm.*, NYO 7568 (1959).
1568. T. Yanagi, H. Mukai and M. Shinagawa, *Bunseki Kagaku*, **26**, 313 (1977).
1569. A. W. Nobrega, I. A. Sachet and E. C. B. Hespanhol, *Quim. Nova*, **10**, 175 (1987).
1570. A. V. Nikolaev, V. B. Durasov and Z. N. Mironova, *Dokl. Akad. Nauk SSSR*, **186**, 603 (1969).
1571. J. Chen and W. Wang, *Youkuangyl*, **3**, 30 (1984).
1572. C. Chin, Z. Zhou, J. Mao, Z. Liu and W. Zhang, *Radiochim. Acta*, **36**, 201 (1984).
1573. Y. Ding, W. Wang and M. Yi, *He Huaxue Yu Fangshe Huaxue*, **8**, 65 (1986).
1574. H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, **15**, 158 (1960).
1575. H. Irving and D. N. Edington, *Proc. Chem. Soc.*, 360 (1959); *Chem. Abstr.*, **54**, 11649g (1960).
1576. H. F. Aly, H. B. Maghrawy, S. A. El-Reefy, *Lanthanide Actinide Res.*, **3**, (1989).
1577. M. S. Subramanian and S. A. Pai, *J. Inorg. Nucl. Chem.*, **32**, 3677 (1970).

1578. S. A. Pai, M. S. Subramanian, *J. Radional. Nucl. Chem.*, **89**, 423 (1985).
1579. L. Fu and J. J. Mao, *J. Radioanal. Nucl. Chem.*, **131**, 181 (1989).
1580. S. K. Mundra, S. A. Pai, and M. S. Subramanian, *Lanthanide Actinide Res.*, **2**, 323 (1988).
1581. H. L. Nekimken, B. F. Smith, G. D. Jarvinen, E. J. Petrson and M. M. Jones, *Anal. Chem.*, **60**, 1390 (1988).
1582. J. Mao, G. Zhang and Y. Chen, *Fudan Xuebao Ziran Kexueban*, **25**, 51 (1986).
1583. F. Bonus and P. Dumitrescu, *Hydrometallurgy*, **16**, 167 (1986).
1584. V. G. Torgov, T. V. Us, M. K. Drozdova and S. V. Tkachev, *Izv. Sib. Otd. Akad, Nauk SSSR, Ser. Khim. Nauk*, (6), 133 (1987).
1585. M. Zhang, J. Chen and D. Xiao, *He Huaxue Yu Fangshe Huaxue*, **8**, 162 (1986).
1586. C. A. Blake, C. F. Baes, Jr, and K. B. Brown, *Ind. Eng. Chem.*, **50**, 1763 (1958).
1587. C. A. Blake, D. F. Horner and J. M. Schmitt, *US At. Energy Comm.*, ORNL 2259; *Chem. Abstr.*, **53**, 13738c (1959).
1588. D. H. Liem, *Acta Chem. Scand.*, **22**, 773 (1968).
1589. M. Yi, Y. Zhang, D. Chen and W. Wang, *Jinshu Xuebao*, **23**, 3108 (1987).
1590. (a) T. K. S. Murthy, V. N. Pai and R. A. Nagle, *Recovery Uranium, Proc. Symp.*, 341 1971; *Chem. Abstr.*, **75**, 91741e (1971); (b) M. Konstantinova, *Anal. Chim. Acta*, **90**, 185 (1977).
1591. M. Konstantinova and S. Mareva, *Dokl. Bolg. Akad. Nauk*, **30**, 1289 (1977).
1592. St. Mareva, N. Jordanov and M. Konstantinova, *Anal. Chim. Acta*, **59**, 319 (1972).
1593. B. Hok-Bernstrom, *Acta Chem. Scand.* **10**, 163 (1956).
1594. M. Konstantinova, St. Mareva and N. Jordanov, *Anal. Chim. Acta*, **68**, 237 (1974).
1595. T. K. Wiewiorowski and L. W. Thornsberry, Jr, *US Pat.*, 4 105 741, 1978; *Chem. Abstr.*, **90**, 74911 (1979).
1596. M. A. Awwal, S. Z. Haider and R. Sultana, *Nucl. Sci. Appl., Ser. B*, **8**, 53 (1975).
1597. I. Brcic, E. Polla and M. Radosevic, *Analyst*, **110**, 1463 (1985).
1598. F. J. Hurst and D. J. Grouse., *Hydrometallurgy*, **13**, 15 (1984).
1599. F. J. Hurst, *Hydrometallurgy*, **16**, 197 (1986).
1600. I. Fatovic, S. Meles, E. Polla and J. Romano, *Inst. Chem. Eng. Symp. Ser.* **103**, 29 (1987).
1601. C. D. A. Figueiredo, *Report*, INIS-BR-395, (1984) p.188, Part. From *INIS Atomindex.* 16, 1985, *Abstr.* No. 16: 080057;*Chem. Abstr.*, **104**, 190194c (1986).
1602. B. C. Lawes, *Can. Pat.*, 1 187 293; *Chem. Abstr.*, **103**, p218866k (1985).
1603. Y. Shigetomi, T. Kojima, I. Nouma and S. Hirono, *Okayama Rika Daigakukiyo, A*, **20**, 19 (1985).
1604. C. D. A. Figueiredo and N. J. Duarte, *Report*, INIS-BR-412, 12 (1984); Port. From *INIS Atomindex* 16, (1985), *Abstr.* No. 16: 080203; *Chem. Abstr.*, **104**, 190189e (1986).
1605. N. J. Duarte, *Report*, INIS-BR-416, 6 (1984); Port. From *INIS Atomindex*, 16 (1985), *Abstr.* No. 16: 080205 *Chem. Abstr.*, **104**, 190188d (1986).
1606. H. Gorecki, H. Gorecka, J. Schroeder, A. Kuzko, J. Perka and E. Mularczyk, *Pol. Pat.*, 127 814; *Chem. Abstr.*, **104**, 153193f (1986).
1607. H. J. Chen, Y. M. Tsai and G. Ting, *J. Chin. Inst. Chem. Eng.*, **16**, 317 (1985).
1608. T. You, Z. Zhou and Q. Qin, *He Huaxue Yu Fangshe Huaxue*, **10**, 207 (1988).
1609. A. G. Godbole, R. Swarup and S. K. Patil, *J. Radioanal. Nucl. Chem.*, **94**, 321 (1985).
1610. C. Ginisty, M. Marteau and B. Mauborgne, *Eur. Pat. Appl.*, EP 53 054, 1980; *Chem. Abstr.*, **97**, p186058f (1982).
1611. A. Maher and D. Pareau-Zveguintzoff, *Bull. Soc. Chim. Fr.*, 718 (1985).
1612. W. A. Rickelton, *US Pat.*, 4 778 663, 1987; *Chem. Abstr.*, **110**, 10644s (1989).
1613. X. Xu, T. Ouyan and Y. Yang, *He Huaxue Yu Fangshe Huaxue*, **10**, 124 (1988).
1614. A. Warshawsky, N. Kahana and R. Arad-Yellin, *Hydrometallurgy*, **23**, 91 (1988).
1615. H. Gorecki, M. Lewandowski, K. Grabas, J. Schroeder, H. Gorecka, Z. Wiese, A. Kuzko, T. Pozniak and J. Perka, *Pol. Pat.*, 141 351; *Chem. Abstr.*, **109**, 77148f (1988).
1616. H. A. El-Naggar, M. K. Shehata and A. S. Abdel-Gawad, *Z. Anorg. Allg. Chem.*, **383**, 191 (1971).
1617. G. A. Pribylova, M. K. Chmutova and B. F. Myasoedov, *Radiokhimiya*, **29**, 621 (1987).
1618. D. Martin, D. W. Ockenden and J. K. Foreman, *J. Inorg. Nucl. Chem.*, **21**, 96 (1961).
1619. H. Umezawa, *Nippon Genshiryoku Gokkaishi*, **2**, 478 (1960).
1620. K. H. Leiser, B. Stojanik and H. D. Greiling, *Radiochim. Acta*, **37**, 41 (1984).
1621. E. G. Chudinov and E. P. Derevyanko, *Radiokhimiya*, **20**, 14 (1978).
1622. J. Goffart and G. Duykckaerts, *Anal. Chim. Acta*, **46**, 91 (1969).
1623. D. G. Kalina and E. P. Horwitz, *Solvent Extr. Ion Exch.*, **3**, 235 (1985).

1624. M. K. Chmutova, G. A. Pribylova, N. P. Nesterova, B. F. Myasoedov and M. I. Kabachnik, *Radiokhimiya*, **31**, 73 (1989).
1625. H. Ihle, H. Michael and A. P. Murrenhoff, *AEC Accession*, No. 18561, *Report* No. EUR-2635.d, p. 18, 1966; *Chem. Abstr.*, **65**, 17774e (1966).
1626. P. K. Khopkar and J. N. Mathur, *J. Inorg. Nucl. Chem.*, **41**, 391 (1979).
1627. J. J. Fardy and J. M. Buchanan, *J. Inorg. Nucl. Chem.*, **38**, 149 (1976).
1628. B. F. Myasoedov, N. P. Molochnikova and I. A. Lebedev, *Zh. Anal. Khim.*, **26**, 1984 (1971).
1629. M. K. Chmutova, B. F. Myasoedov, N. E. Kochetkova, B. Ya. Spivakov and Yu. A. Zolotov, *Proc. Moscow Symp. Chem. Transuranium Elem.*, 157 (1972); *Chem. Abstr.*, **85**, 68967f (1976).
1630. W. Bacher and C. Keller, *J. Inorg. Nucl. Chem.*, **35**, 2945 (1973).
1631. J. N. Mathur and P. K. Khopkar, *Polyhedron*, **3**, 1125 (1984).
1632. V. F. Smirnov, E. K. Gorlov, A. P. Zefirov and B. N. Laskorin, *Zh. Prikl. Khim.*, **42**, 2147 (1969).
1633. V. F. Smirnov and V. I. Nikonov, *Radiokhimiya*, **12**, 85 (1970).
1634. M. E. Kochetkova, M. K. Chmutova and B. F. Myasoedov, *Radiokhimiya*, **25**, 435 (1983).
1635. D. K. Kalina, E. P. Horwitz, L. Kaplan and A. C. Muscatello, *Sep. Sci. Technol.*, **16**, 1127 (1981).
1636. J. Mesplede and M. Porthault, *J. Inorg. Nucl. Chem.*, **33**, 4275 (1971).
1637. N. A. Suvorovskaya and Yu. S. Kuznetsov, *Izv. Akad. Nauk SSSR, Met.*, 88 (1970).
1638. A. M. Rozen, Z. A. Berkman, L. E. Bertina, V. G. Kossykh and K. S. Yudina, *Zh. Neorg. Khim.*, **23**, 2474 (1978).
1639. J. W. Ferguson and C. V. Banks, *US At. Energy Comm.*, IS 777, 1 (1963).
1640. P. Bronzan and H. Meider-Gorican, *J. Less-Common Met.* **29**, 407 (1972).
1641. H. Meider-Gorican *Solvent Extr. Chem., Proc. Int. Conf., Goteberg*, 278 (1966); *Chem. Abstr.*, **69**, 80917s (1968).
1642. D. Sevdic and H. Meider-Gorican, *J. Less-Common Met.*, **27**, 403 (1972).
1643. B. N. Laskorin, V. F. Smirnov, E. K. Gorlov and A. P. Zefirov, *Radiokhimiya*, **9**, 435 (1967).
1644. J. Mesplede *Nucl. Sci. Abstr.*, **28**, 20736 (1973); *Report*, FRNCTH-368, p.108, (1972); *Chem. Abstr.*, **80**, 52793g (1974).
1645. J. Mesplede and M. Porthault, *Bull. Soc. Chim. Fr.*, 3771 (1971).
1446. J. Foos and J. Mesplede, *J. Inorg. Nucl. Chem.*, **34**, 2051 (1972).
1647. J. W. O'Laughlin and D. F. Jensen, *Anal. Chem.*, **41**, 2010 (1969).
1648. J. E. Morchek and C. V. Banks, *J. Inorg. Nucl. Chem.*, **27**, 589 (1965).
1649. J. E. Mrochek, J. W. O'Laughlin, H. Sakurai and C. V. Banks, *J. Inorg. Nucl. Chem.*, **25**, 955 (1963).
1650. K. E. Burke, H. Sakurai, J. W. O'Laughlin and C. V. Banks, *US At. Energy Comm.*, IS 284, 20 (1961).
1651. J. E. Mrochek and C. V. Banks, *Nucl. Sci. Abstr.*, **19**, 43 (1965); *AEC Accession* No. 277, *Report* No. IS-827, p. 193 (1964); *Chem. Abstr.*, **62**, 13921d (1965).
1652. K. A. Kraus, G. E. Moore and F. Nelson, *J. Am. Chem. Soc.*, **78**, 2692 (1956).
1653. V. M. Vdovenko, A. A. Lipovskii and S. A. Nikitina, *Russ. J. Inorg. Nucl. Chem.*, **4**, 391 (1959).
1654. A. M. Rozen, Z. I. Nikolotova, N. V. Kartasheva and A. S. Bol'shakova, *Dokl. Akad. Nauk SSSR*, **237**, 148 (1977).
1655. A. M. Rozen, L. I. Nikolotova, N. A. Kartasheva and A. S. Bol'shakova, *Radiokhimiya*, **20**, 725 (1978).
1656. M. N. Litvina, M. S. Milyukova and B. F. Myasoedov, *Radiokhimiya*, **22**, 374 (1980).
1657. M. K. Chmutova, N. E. Kochetkova and B. F. Myasoedov, *J. Inorg. Nucl. Chem.*, **42**, 897 (1980).
1658. A. M. Rozen, Z. I. Nikolotova, N. A. Kartasheva and K. S. Yudina, *Radiokhimiya*, **19**, 709(1977).
1659. A. M. Rozen, Z. I. Nikolotova and N. A. Kartasheva, *Radiokhimiya*, **17**, 772 (1975).
1660. Z. A. Berkman, L. E. Bertina, M. I. Kabachnik, V. G. Kossykh, T. Ya. Medved, N. P. Nesterova, A. M. Rozen and K. S. Yudina, *Radiokhimiya*, **17**, 210 (1975).
1661. B. F. Myasoedov, T. Ya. Medved, A. A. Nemodruk, N. P. Nesterova, O. E. Koiro and M. I. Kabachnik, *Dokl. Akad. Nauk SSSR*, **217**, 1087 (1974).
1662. M. K. Chmutova, N. E. Kochetkova and B. F. Myasoedov, *Radiokhimiya*, **20**, 713 (1978).
1663. B. F. Myasoedov, M. K. Chmutova, T. Ya. Medved and V. I. Vernadskii, *CIM Spec. Vol.* 1979, 21 (2, *Proc. Int. Solvent Extr. Conf., 1977*), 630; *Chem. Abstr.*, **92**, 65406f (1980).
1664. M. I. Kabachnik, O. E. Koiro, T. Ya. Medved, B. F. Myasoedov, N. P. Nesterova and M. K. Chmutova, *Dokl. Akad. Nauk SSSR*, **222**, 1346 (1975).

1665. M. K. Chmutova, N. P. Nesterova, O. E. Koiro and B. F. Myasoedov, *Zh. Anal. Khim.*, **30**, 1110 (1975).
1666. M. I. Kabachnik, G. V. Bordin, N. E. Kochetkova, T. Ya. Medved, Y. M. Palikarpov and M. K. Chmutova, *Izv. Akad. Nauk SSSR, Ser, Khim.*, **11**, 2572 (1979).
1667. A. M. Rozen, Z. I. Nikolotova and N. A. Kartasheva, *Radiokhimiya*, **25**, 609 (1983).
1668. J. R. Parkar and C. K. Banks, *J. Inorg. Nucl. Chem.*, **27**, 631 (1965).
1669. A. M. Rozen, Z. I. Nikolotova, N. A. Kartasheva and K. S. Yudina, *Radiokhimiya*, **17**, 237 (1975).
1670. J. Goffart, G. Duychaerts, *Anal. Chim. Acta*, **48**, 99 (1969).
1671. E. E. Gorlov, V. F. Smirnov, A. P. Zefirov and B. N. Laskorin, *ZH. Neorg. Khim.*, **12**, 2866 (1967).
1672. L. I. Arkhipova, Z. A. Berkman, L. E. Bertina, M. I. Kabachnik, V. C. Kossykh, T. Ya. Medved, N. P. Nesterova, Yu. M. Polikarpov, V. M. Rozen and K. S. Yudina, *Dokl. Akad. Nauk SSSR*, **209**, 1093 (1973).
1673. A. M. Rozen, A. S. Nikiforov, Z. I. Nikolotova and N. A. Kartasheva, *Dokl. Akad. Nauk SSSR*, **286**, 667 (1986).
1674. Z. A. Berkman, L. E. Bertina, G. M. Vol'dman, A. N. Zelikman, M. I. Kabachnik, V. G. Kossykh, T. Ya. Medved, N. P. Nesterova, A. M. Rozen and K. S. Yudina, *Zh. Neorg. Khim.*, **19**, 2839 (1974).
1675. A. M. Rozen, Z. I.Nikolotova, N. A. Kartasheva, T. Ya. Medved, N. P. Nesterava, K. S. Yudina and M. I. Kabachnik, *Radiokhimiya*, **18**, 846 (1976).
1676. G. A. Pribylova, M. K. Chmutova and B. F. Myasoedov, *Radiokhimiya*, **20**, 719 (1978).
1677. G. V. Bodrin, M. I. Kabachnik, N. E. Kochetkiva, T. Ya. Medved, B. F. Myasoedov, Yu. N. Polikarpov and M. K. Chmutova, *Izv. Akad. Nauk SSSR, Ser. Shim.*, 2572 (1979).
1678. M. K. Chmutova, G. V. Bodrin, M. N. Litvina, A. G. Matveeva, E. I. Matrosov, Yu. M. Polikarpov, P. L. Khizhnyak, B. F. Myasoedov and M. I. Kabachnik, *Radiokhimiya*, **31**, 83 (1989).
1679. M. A. Carey, *US At. Energy Comm.*, IS 7-197, 138 (1967); *Chem. Abstr.*, **69**, 13381z (1968).
1680. J. Targhetta, J. Mesplede and M. Porthault, *J. Inorg. Nucl. Chem.*, **36**, 445 (1974).
1681. A. M. Rozen, Z. I. Nikolotova, J. A. Kartasheva and K. S. Yudina, *Dokl. Akad. Nauk SSSR*, **222**, 1151 (1975).
1682. B. N. Laskorin, D. I. Sko rovarov, L. A. Fedorova and V. V. Shatalov, *At. Energ. (USSR)*, **28**, 383 (1970).
1683. M. I. Kabachnik, B. N. Laskorin, L. E. Bertina, T. Ya. Medved, V. G. Kossykh, K. S. Yudina, Z. A. Berkman and A. M. Nepryakhin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **4**, 65 (1972).
1684. M. I. Kabachnik, B. N. Laskorin, L. E. Bertina, R. Ya. Medved, V. G. Kossykh, K. S. Yudina, Z. A. Berkman and A. M. Naprya- Khim., *Khim. Protsessov Ekstr., Mater. Konf. Khim. Ekstr.*, 3rd, 81 (1969); *Chem. Abstr.*, **78**, 48627x (1973).
1685. N. E. Kochetkova, M. K. Chmutova and B. F. Myasoedov, *Radiokhimiya*, **25**, 599 (1983).
1686. V. M. Nikolaev, B. F. Myasoedov, E. A. Filippov, V. V. Yakshin, V. T. Filimonov and B. N. Laskorin, *Radiokhimiya*, **28**, 99 (1986).
1687. I. K. Shvetsov, P. S. Trukhlyaev, V. A. Kalistratov, V. P. Kulazhko, A. V. Kharitonov, A. E. Antoshin and E. N. Tsvetkov, *Radiokhimiya*, **31**, 63 (1989).
1688. P. Bronzan and H. Meider-Gorican., *Proc. Int. Solvent Extr. Conf.*, **3** 2235 (1974).
1689. P. Bronzan and H. Meider, *J. Less-Common Met.*, **59**, 101 (1978).
1690. R. B. Hitchcock, J. A. Dean and T. H. Handley, *Anal. Chem.*, **35**, 254 (1963).
1691. R. W. Cattrall, R. R. Martin and S. Tribuzio, *J. Inorg. Nucl. Chem.*, **40**, 687 (1978).
1692. M. Suzuki, K. Inoue, Y. Baba and Y. Umezadki, *Jpn. Kokai Tokkyo Koho*, 62 57 689; *Chem. Abstr.*, **107**, 81564q (1987).
1693. Y. Baba, T. Ueda and K. Inoue, *Solvent Extr. Ion Exch.*, **4**, 1223 (1986).
1994. D. E. Elliott and C. V. Banks, *Anal. Chim. Acta*, **33**, 237 (1965).
1695. W. A. Rickelton, *Eur. Pat. Appl.*, 113 454 (1984); *Chem. Abstr.*, **101**, 114631r (1984).
1696. Y. Baba, Y. Umezaki and K. Inoue, *J. Chem. Eng. Jpn.*, **19**, 270 (1986).
1697. W. A. Rickelton and A. J. Robertson, *Miner. Metall. Process.*, **4**, 7 (1987).
1698. A. F. Lee, *Report*, NIM-2105, Order No. DE 82902943, 33 (1981), (Eng.). Avail NTIS, US Sales only: from *Energy Res. Abstr.*, **7**, 47518 (1982); *Chem. Abstr.*, **98**, 27032x (1983).
1699. Y. Baba, M. Oshima and K. Inoue, *Bull. Chem. Soc. Jpn.*, **59**, 3829 (1986).
1700. S. Daamach, G. Cote and D. Bauer, *C. R.* (*Dokl.*) *Acad. Sci. URSS*, **304**, 889 (1987).

1701. T. Ichiishi, *Jpn. Kokai Tokkyo Koho*, 63 243 227 (1988); *Chem. Abstr.*, **110**, 79939j (1989).
1702. A. Okuda and T. Ichiishi, *Jpn. Kokai Tokkyo Koho*, 63 286 528 (1987); *Chem. Abstr.*, **110**, 99385d (1989).
1703. T. Ichiishi, *Jpn Kokai Tokkyo Koho*, 63 230 831; *Chem. Abstr.*, **110**, 139100r (1989).
1704. V. F. Borbat, N. G. Feshchenko, V. I. Dolgikh, E. F. Kouba, A. F. Ravlenko, G. K. Fedorova, V. P. Akkerman, I. K. Mazepaad and A. P. Merchinko, *Ukr. Khim. Zh.*, **36**, 1068 (1970) *Chem. Abstr.*, **74**, 80401x (1971).
1705. I. Longden, N. M. Patel, J. R. Thornback and J. H. Miles, *Solvent Extr. Ion Exch.*, **4**, 421 (1986).
1706. V. F. Travkin, V. V. Borisov, K. A. Bol'shakov and N. M. Sinitsyn, *Zh. Neorg. Khim.*, **20**, 2541 (1975).
1707. J. W. O.'Laughlin and C. V. Banks, *Anal. Chem.*, **36**, 1222 (1964).
1708. N. G. Vanifatova, Y. A. Zolotov and T. Y. Medved, *Zh. Neorg. Khim.*, **22**, 3103 (1977).
1709. G. A. Yagodin, V. I. Savel'eva, G. N. Kireeva, I. D. Pokidysheva, Yu. F. Korovin and Yu. I. Kuzovov, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, **27**, 1179 (1984); *Chem. Abstr.*, **102**, 65346m (1985).
1710. M. Watanabe and Y. Nishimura, *Jpn. Kokai Tokkyo Koho, JP* 62, 185, 841 (1987); *Chem. Abstr.*, **108**, 9255t (1988).
1711. L. Li and P. Di, *Huaxue Shiji*, **10**, 8 (1988).
1712. L. L. Borin and O. L. Zadesentseva, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, **19**, 169 (1976).
1713. R. B. Heddur and S. M. Khopkar, *Chem. Anal.* (*Warsaw*), **31**, 201 (1986).
1714. R. B. Heddur and S. M. Khopkar, *Talanta*, **35**, 594 (1988).
1715. J. W. O. Laughlin and C. V. Banks, *US At. Energy Comm.*, IS 373 (1963).
1716. B. N. Zaitsev, I. B. Kvasnitskii, V. A. Korolev, V. P. Popik, Yu. I. Kuzovov and Yu. F. Korivin, *Radiokhimiya*, **27**, 445 (1985).
1717. J. W. O. Laughlin, J. W. Fergusson, J. J. Richard and C. V. Banks, *J. Chromatogr.*, **24**, 376 (1966).
1718. L. Li, J. Ma and G. Jin, *Fenxi Huaxue*, **16**, 357 (1988).
1719. X. Xu, J. Liao and Y. Yang, *Fenxi Huaxue*, **16**, 354 (1988).
1720. S. Pearson and H. J. M. Bowen, *J. Radioanal. Nucl. Chem.*, **96**, 499 (1985).
1721. W. C. Dietrich, J. D. Taylor and E. C. Johnson, *US At. Energy Comm.*, TID 7606, 195 (1960).
1722. K. Akiba and H. Hashimoto, in *Chemical Aspects of the Down Stream Thorium Fuel Cycle* (Ed. S. Suzuki), Atomic Energy Society of Japan, Tokyo, 1987, p. 65.
1723. A. C. Muscatello, M. T. Saba and J. D. Navratil, *Report*, REP-4009, Order No. DE 87009471 (1986); (Eng.), Avail NTIS. From Energy Res. Abstr., **12**, 28913 (1987); *Chem. Abstr.*, **108**, 79189y (1988).
1724. A. C. Muscatello and J. D. Navratil, *Report*, REP-3965, Order No. DE 86010810 (1986) (Eng.); From *Gov. Rep. Announce Index (V.S.)*, **11**, 33826 (1986); *Chem. Abstr.*, **106**, 92095 (1987).
1725. A. C. Muscatello and J. D. Navratil, *J. Radioanal. Nucl. Chem.*, **128**, 463 (1988).
1726. C. Testa, D. Desideri, M. A. Meli and S. Bazzari, *J. Radioanal. Nucl. Chem.*, **129**, 191 (1989).
1727. W. Jin and M. Yao, *Youkuang Dizhi*, **2**, 119 (1986).
1728. U. Niese, *Zentralinst. Kernforsch. Rossendrof Dresden*, (Ber.), ZfK, ZfK-599, 83 (1986); *Chem. Abstr.*, **108**, 12790u (1988).
1729. N. Dickens, M. Rose and G. A. Davies, *Inst. Chem. Eng. Symp. Ser.*, 88 (Extr. 84), 69 (1984); *Chem. Abstr.*, **103**, 40362w (1985).
1730. S. Belfer and E. Korngold, *Isr. J. Chem.*, **26**, 71 (1985).
1731. K. W. Kim, J. H. Yoo and H. S. Park, *Hwahak Konghak*, **23**, 263 (1985).
1732. L. Pietrelli, A. Salluzzo and F. Troiani, *J. Radioanal. Nucl. Chem.*, **141**, 107 (1990).
1733. R. Y. Xie and G. D. Christian, *Analyst*, **112**, 61 (1987).
1734. T. Okada, K, Hiratani and H. Sugihara, *Analyst*, **112**, 587 (1987).
1735. A. S. Attiyat and G. D. Christian, *J. Flow-Injection Anal.*, **4**, 103 (1987).
1736. A. F. Zhukov, A. B. Koldaev, N. P. Nesterova, T. Ya. Medved and M. I. Kabachnik, *Anal. Chem. Symp. Ser.*; **22**, 711 (1985); *Chem. Abstr.*, **104** 122037d (1986).
1737. S. M. Bessis, A. F. Zhukov, Yu. I. Urusov, O. M. Petrukhin, G. V. Bodrin, N. P. Nesterova, Yu. M. Polikarpov and M. I. Kabachnik, *Zh. Anal. Khim.*, **43**, 1769 (1988).
1738. O. M. Petrukhim, E. N. Avdeeva, A. F. Zhukov, I. B. Polosukhina and G. V. Bodrin, in *Ion-Selective Electrodes, Proceedings of 5th Symposium, 1988* (Ed. E. Pungor), Pergamon, Press Oxford, 1989, p. 529. *Chem. Abstr.*, 3113, 164521y (1990).

1739. T. Xu, J. Zhu, Z, Bei and L. Jin, *Fenxi Shiyanshi*, **7** (9), 1 (1988).

1740. Y. Fang, R. Wei, P. He and L. Jin, *Fenxi Shiyanshi*, **7** (3), 1 (1988).

1741. J. Lexa, K. Stulik, *Talanta*, **36**, 843 (1989).

1742. J. M. Torres Llosa, H. Ruf, K. Schorb and H. J. Acha, *Kernforschungzent. Karlsruhe* [*Ber.*], *KfK*, KfK 4299 (1987); *Chem. Abstr.*, **108**, 15416n (1988).

1743. J. M. Torres Llosa, H. Ruf, K. Schorb and H. J. Ache, *Anal. Chim. Acta*, **211**, 317 (1988).

1744. N. Kato and T. Hidaka, Denki, *Kagaku Oyobi Kogyo Bustsuri Kagaku*, **57**, 326 (1989).

1745. K. Izutsu, T. Nakamura and T. Oku, *Nippon Kagaku Kaishi*, 1656 (1980).

1746. T. Lexa and K. Stulik, *Talanta*, **33**, 11 (1986).

1747. R. L. Cook, R. C. Maduff and A. F. Sammells, *Anal. Chim. Acta*, **217**, 101 (1989).

1748. L. N. Lomakina, T. I. Ignateva, S. A. Pisareva, T. Ya Medved and M. I. Kabachnik, *Zh. Anal. Khim.*, **35**, 86 (1980).

1749. T. Lavric, A. Osojnik and Z. Kristan, *Zelezarski Zb.*, **22**, 159 (1988).

1750. G. Staats, *Proc. Chem. Conf., 39th*, 105 (1986); *Chem. Abstr.*, **108**, 15429u (1988).

1751. K. Ueda, K. Kubo, O. Yoshimura and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **61**, 2791 (1988).

1752. M. Sugiyama, H. Mukai, N. Yasuda, S. Kihara and M. Matsui, *Bull. Inst. Chem. Res. Kyoto Univ.*, **65**, 197 (1987).

1753. (a) F. G. Seeley, W. J. McDowell and L. K. Felker, *J. Chem. Eng. Data.*, **31** , 136 (1986); (b) G. Zhu, Z. Si, J. Yang and J. Ding, *Anal. Chim. Acta*, **231**, 157 (1990); (c) D. Weiss, T. Paukert and I. Rubeska, *J. Anal. At. Spectrom.*, **5** 371 (1990).

1754. S. Liu and L. Dong, *Fenxi Huaxue*, **15**, 1086 (1987).

1755. H. G. Huang, K. Hiraki and Y. Nishikawa, *Nippon Kagaku Kaishi*, 66 (1981).

1756. M. Aihara, M. Arai and T. Tomitsuger, *Anal. Lett.*, **19**, 1907 (1986).

1757. R. Mitsui and K. Kawasaki, *Jpn. Kokai Tokkyo Koho*, 63 150 358 (1986).

1758. (a) J. Stedefeder and H. Mueller, *Ger. Offen.*, 2 005 9 66 (1971); *Chem. Abstr.*, **76**, 25992g (1972); (b) N. K. Skvortsov, N. F. Voloshina, N. A. Moldavskaya and V. O. Reikhsfel'd, *Zh. Obshch. Khim.*, **58**, 1831 (1988).

1759. E. A. Zuech, *US, Pat.* 3 726 939, 1973; *Chem. Abstr.*, **79**, 19035f (1973).

1760. E. A. Zuech, *US Pat.*, 3 627 700, 1971; *Chem. Abstr.*, **76**, 126356h (1972).

1761. (a) E. A. Zuech, *J. Polym. Sci., Polym. Chem. Ed.*, **10**, 3665 (1972). (b) K. Seyferth and R. Taube, *J. Mol. Catal.*, **28**, 53 (1985).

1762. K. Seyferth and R. Taube, *J. Organomet. Chem.*, **262**, 179 (1984).

1763. K. Seyferth and R. Taube, *J. Organomet. Chem.*, **262**, 191 (1984).

1964. K. Seyferth and R. Taube, *J. Organomet. Chem.*, **268**, 115 (1984).

1765. R. Taube and K. Seyferth, *Z. Chem.*, **14**, 410 (1974).

1766. R. Taube abd K. Seyferth, *Z. Chem.*, **14**, 284 (1974).

1767. D. Schnurpfeil, G. Lauterbach, K. Seyferth and R. Taube, *J. Prakt. Chem.* **326**, 1025 (1984).

1768. O. Gonzales, R. Schaefer, D. Schnurpfeil, K. Seyferth, R. Taube and B. Mohai, *J. Prakt. Chem.*, **325**, 981 (1983).

1769. C. C. Su, C. H. Ueng, W. H. Lin, M. J. Gu, K. H. Lii, J. S. Ting, S. C. Jan and K. O. Hodgson, *Proc. Natl. Sci. Counc., Repub. China, Part B*, **6**, 45 (1982); *Chem. Abstr.*, **96**, 180230p (1982).

1770. I. Ondrejkovicova and G. Ondrejkovic, *Czech. Pat.*, 245, 541 1987; *Chem. Abstr.*, **109**, 211222f (1988).

1771. I. Ondrejkovicova, V. Vancova, G. Ondrejovic, *Collect. Czech. Chem. Commun.*, **48**, 254 (1983).

1772. I. Onderjkovicova, V. Vancova and G. Onderjovic, *Czech. Pat.*, 205, 483, 1984; *Chem. Abstr.*, **103**, 54282g (1985).

1773. I. Ondrejkovicova, V. Vancova and G. Ondrejovic, *Proc. Conf. Coord. Chem., 9th*, 321 (1983); *Chem. Abstr.*, **99**, 70871c (1983).

1774. I. Ondrejkovicova, V. Vancova and G. Ondrejovic, *Proc. Conf. Coord. Chem., 8th*, 309 (1980); *Chem. Abstr.*, **95**, 6129g (1981).

1775. I. Ondrejkovicova and G. Ondrejovic, *Czech. Pat.*, 238 919, 1987; *Chem. Abstr.*, **109**, 47366h (1988).

1776. R. W. Wegmann and D. C. Busby, *J. Mol. Catal.*, **32**, 125 (1985); *Chem. Abstr.*, **105**, 42291n (1986).

1777. B. G. Rogachev, M. V. Klyuev and M. L. Khidekel, *USSR Pat.*, 552 994, 1975; *Chem. Abstr.*, **87**, 29692j (1977).

1778. M. V. Klyuev, B. G. Rogachev and M. L. Khidelkel, *Izv. Akad, Nauk SSSR, Ser. Khim.*, 2620 (1978).

1779. Y. Tajima and E. Kunioka, *J. Catal.*, **11**, 83 (1968); *Chem. Abstr.*, **70**, 3163m (1969).
1780. R. A. Fiato and R. L. Pruett, *Eur. Pat. Appl.*, 26990 1981; *Chem. Abstr.*, **95**, 80182k (1981).
1781. N. K. Skvortsov, N. F. Voloshina, N. A. Maldavskaya and V. O. Reikhsfel'd *Zh. Obshch. Khim.*, **55**, 2323 (1985).
1782 E. A. Zuech, *US Pat.*, 3485881, 1969; *Chem. Abstr.*, **72**, 99989a (1970).
1783. N. A. Moldvskaya, N. K. Skvortsov, N. F. Voloshina and V. O. Reikhsfel'd, *Zh. Obshch. khim.*, **51**, 1621 (1981).
1784. D. J. Strope, *US Pat.*, 4144378, 1979; *Chem. Abstr.*, **90**, 203560p (1979).
1785. N. A. Moldavskaya, N. K. Skvortsov, V. O. Reikshfel'd, V. E. Alshin, E. D. Ageeva, N. F. Voloshina and Yu. N. Kukushkin, *USSR Pat.*, 891 676, 1981; *Chem. Abstr.*, **96**, 199871v (1982).
1786. W. Gaenzler, K. Kabs and G. Schrieder, *Ger. Offen.*, 2431 330, 1976; *Chem. Abstr.*, **84**, 105019a (1976).
1787. A. Sendijarevic, V. Sendijaravic and K. C. Frisch, *J. Polym. Sci., Part A*, **25**, 151 (1987); *Chem. Abstr.*, **106**, 156901 (1987).
1788. A. Sendijarevic, V. Sendijaravic and K. C. Frisch, *Polymeri*, **7**, 159 (1986); *Chem. Abstr.*, **106**, 5515p (1987).
1789. R. V. Russo, *Ger. Offen.*, 2657412, 1977; *Chem. Abstr.*, **87**, 69231q (1977).
1790. A. Baba, H. Kashiwagi and H. Matsuda, *Organometallics*, **6**, 137 (1987); *Chem. Abstr.*, **106**, 32177m (1987).
1791. (a) W. Hewertson, *Ger. Offen.*, 1960732, 1970; *Chem. Abstr.*, 89035t (1970); (b) W. Hewertson *Ger. Offen.*, 1, 960, 731, (1970); *Chem. Abstr.*, **73**, p 56570k (1970).
1792. B. Rickborn and R. M. Gerkin, *J. Am. Chem. Soc.*, **90**, 4193 (1968).

Author index

This author index is designed to enable the reader to locate an author's name and work with the aid of the reference numbers appearing in the text. The page numbers are printed in normal type in ascending numerical order, followed by the reference numbers in parentheses. The numbers in *italics* refer to the pages on which the references are actually listed.

The chemistry of organophosphorus compounds, Volume 2, Phosphine oxides, sulphides, selenides and tellurides
Edited by Frank R. Hartley. ISBN: 0-471-93056-3

Index compiled by K. Raven

Subject index

The chemistry of organophosphorus compounds, Volume 2, Phosphine oxides, sulphides, selenides and tellurides
Edited by Frank R. Hartley. ISBN: 0-471-93056-3

Index compiled by P. Raven