Coordination Chemistry Reviews, 15 (1975) 239—278

TRANSITION METAL COMPLEXES OF CYCLIC PHOSPHINES AND THEIR DERIVATIVES

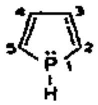
DAVID G. HOLAH, ALAN N. HUGHES AND KEN WRIGHT

Department of Chemistry, Lakehead University, Thunder Bay, Ontario, P7B 5E1 (Canada)

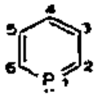
CONTENTS

A. INTRODUCTION

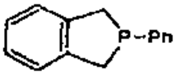
Transition metal complexes of tertiary phosphines in general have been very thoroughly studied and, during the last fifteen years, a considerable amount of research has also been carried out on the coordination chemistry of cyclic phosphines and certain of their derivatives, such as the corresponding oxides, sulfides and selenides. Systems which have received attention include three, four, five, six and seven-membered ring compounds including both saturated and unsaturated rings and some polycyclic derivatives of the larger ring systems. Some of these cyclic phosphine derivatives are of considerable interest in their own right. Thus, the chemical [1] behaviour of phosphole (I) derivatives indicates that they may have some aromatic character through delocalization of the phosphorus lone pair although the physical [2,3] evidence regarding this aromatic character is conflicting. Furthermore, the phosphorins (II) possess [4] an unusual orbital sequence which makes coordination studies particularly interesting. Other phosphines such as the dibenzophospholes are extremely rigid and bulky although they are otherwise quite good donors.



I



II



III

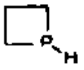
In general, the first reactions attempted with many of these systems as coordinating species have been those with metal carbonyls and, where warranted, these initial studies have been extended to include reactions with metals in a non-zero oxidation state. These cyclic phosphine derivatives form a wide variety of interesting organometallic compounds, some having unusual structures. For example, 2-phenylisophosphindoline (III) and certain phosphole derivatives are capable of causing transition metals such as Ni^{II}, Pd^{II} and Pt^{II} to adopt uncommon coordination numbers in the complexes which they form. In addition, some rhodium—phosphole complexes have proved to be active (homogeneous) catalysts for the hydrogenation of alkenes.

This review therefore surveys the major aspects of the organometallic chemistry of these cyclic phosphines and their derivatives which have been published in the chemical literature to the middle of 1974. For convenience, the discussion is organized according to increasing ring size of the ligand and the emphasis is upon synthetic aspects of the topic.

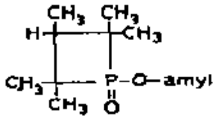
B. COMPLEXES OF THREE- AND FOUR-MEMBERED CYCLIC PHOSPHINE DERIVATIVES

Only one investigation of the coordination chemistry of the relatively little studied small-ring compound phosphirane [$(CH_2)_2PH$] (IV) appears to have been reported [5]. In this study, it was found that treatment of the *N*-methylpyridinium salt of $[Mo(CO)_5I]^-$ with (IV) in dichloromethane results in the formation of pentacarbonylphosphiranemolybdenum(0) ($[(CH_2)_2PH]Mo(CO)_5$). The compounds $[(CH_2)_2PH]_2Mo(CO)_4$ and $[(CH_2)_2PH]_3Mo(CO)_3$ have been obtained from the reaction of (IV) with tetracarbonylnorbornadienemolybdenum(0) or tricarbonylcyclohexatrienemolybdenum(0).

IV



V



VI

The pentacarbonylphosphiranemolybdenum(0) complex was found to react with KPH_2 in dimethyl ether to form a yellow crystalline salt containing the anion $[(CH_2)_2PMo(CO)_5]^-$. This result is significant in that it represents the first successful deprotonation of the phosphorus atom in the phosphirane system; previous unsuccessful attempts to deprotonate the free phosphirane have been reported [6]. The salt $[(CH_2)_2PMo(CO)_5]^-K^+$ reacts with trimethylchlorosilane to yield a white solid formulated (on the basis of IR, NMR and mass spectral data) as $[(CH_2)PSiMe_3]Mo(CO)_5$. A similar reaction occurs with monobromosilane.

There are apparently no reports in the literature regarding metal complexes of the phosphetane (V) system in which coordination occurs through the phosphorus atom. There is, however, one brief mention [7] of a uranium—phosphetane oxide complex of composition $L_2UO_2(NO_3)_2$ where L is the phosphetane oxide (VI) and where coordination occurs through the P—O link. This complex is reported [7] as one of a number of organophosphorus and organonitrogen complexes of composition $LUO_2(NO_3)_2$ (bidentate ligand) and $L_2UO_2(NO_3)_2$ (unidentate ligand) prepared by treatment of dichloromethane solutions of the appropriate ligand with uranyl nitrate. These complexes were prepared for a study of the near-visible, IR absorption, and emission spectra of uranyl nitrate complexes.

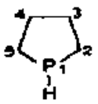
C. COMPLEXES OF FIVE-MEMBERED CYCLIC PHOSPHINE DERIVATIVES

(i) Phospholane complexes

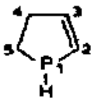
The simplest five-membered phosphorus heterocycle is phospholane (VII). However, no complexes of the parent compound have been reported and there appears to be only one brief report [8] of the direct formation of a transition metal complex of a substituted phospholane although several such complexes have been prepared by indirect methods (see later discussion). Thus, 1-phenylphospholane is reported to give with Hg^{II} chloride an adduct formulated as $(C_{10}H_{13}P)HgCl_2$ which, as Mann has pointed out [9], is almost certainly a halogen-bridged dimer of the type generally obtained from tertiary phosphines.

(ii) Phospholene complexes

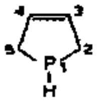
Complexes of simple derivatives of both 2-phospholene (VIII) and 3-phospholene (IX) have been the subject of several relatively brief reports in the literature.



VII



VIII



IX

The first reports of complexes of simple 2- and 3-phospholene derivatives were made in a Shell patent application [10] concerning catalytic hydroformylations of olefins at 68—81.6 atmospheres. Thus, it was found that cobalt carbonyl complexes of 1-butyl-2-phospholene, 1-phenyl-2-phospholene, 1-phenyl-3-phospholene, 3-methyl-1-phenyl-3-phospholene and 3,4-dimethyl-1-phenyl-3-phospholene all catalytically hydroformylate, for example, 1-dodecene to the corresponding primary alcohol at rates considerably greater than for the related tributylphosphine complex. Furthermore, much less saturated hydrocarbon is formed as a by-product in these reactions than is the case when other tertiary phosphine complexes are used. The complexes themselves were prepared by treatment of a cobalt alkanoate with the appropriate ligand and formaldehyde.

No other simple 2-phospholene complexes are recorded in the literature but Quin and his co-workers have reported Ni^{II} chloride complexes of various 3-phospholenes in connection with heterogeneous catalytic hydrogenation [11], X-ray crystallographic [12] and NMR [13] studies. Thus, it was found that the free phospholenes cannot be hydrogenated catalytically [11] with Pd/C under normal conditions but the corresponding Ni^{II} chloride complexes (deep purple solutions prepared *in situ* in ethanol but readily isolable) hydrogenated smoothly but slowly (several days) in the presence of 10% Pd/C. The phospholanes produced were liberated from their Ni^{II} complexes with aqueous EDTA.

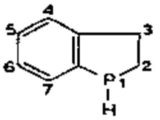
In a later paper, McPhail et al. [12] reported the synthesis and X-ray crystal and molecular structure of one of these 3-phospholene Ni^{II} complexes. Treatment of anhydrous Ni^{II} chloride in ethanol with ethanolic 1-benzyl-3-phospholene gives dark red crystals of dichlorobis(1-benzyl-3-phospholene)-nickel(II). This complex is unusual in that whereas most unidentate ligands produce a *trans* configuration in the resulting complex with Ni^{II}, 1-benzyl-3-phospholene produces a *cis* arrangement. The geometry about the nickel atom is approximately square-planar with a slight tetrahedral distortion and there are several features of the structure which are worthy of note. For example, the *trans* Cl—Ni—P angles show a considerable departure from linearity with values of approximately 165° and this is attributed to strong non-bonding interactions between the two 3-phospholene ligands. Indeed, this non-linearity, although common with bidentate ligands, was at the time of publication the greatest deviation from linearity found for unidentate ligands in square-planar Ni^{II} complexes. The severity of these ligand interactions is confirmed by the bond angles between the Ni—P bond and the two ring P—C bonds of the 3-phospholene ligand. Thus, the two Ni—P—C bond angles for each ring are far from equal and have values of 112.1° and 124.5°, i.e. there is considerable distortion in the geometry about each phosphorus atom although the two ring P—C—C angles for each of the phospholene ligands are equal.

One other feature of the structure is that the two Ni—P bonds of the complex are appreciably shorter than predictions based upon the sum of accepted values of the single bond covalent radii would suggest, while the Ni—Cl bonds are correspondingly longer than predicted. This suggests a strong *trans* influence of the phosphorus atoms.

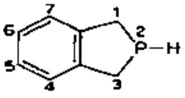
In a very recent paper devoted mainly to a phosphole—Ni^{II} complex (see later discussion), Quin et al. [13] have reported the NMR spectra of the complexes L_2NiCl_2 where L is 1-benzyl-3-phospholene, 1,3,4-trimethyl-3-phospholene or 1-benzyl-3,4-dimethyl-3-phospholene. The NMR spectra of these adducts are unusual compared with the spectra of the free ligands in that complexation removes all ^{31}P—H couplings in the ligands. For example, in 1,3,4-trimethyl-3-phospholene, the hydrogen atoms in each of the methylene groups adjacent to the phosphorus atom are magnetically non-equivalent and therefore give rise to an ABX multiplet through coupling with each other and the neighboring phosphorus atom. However, on complexation this multiplet collapses to an AB pattern. This type of decoupling on complexation has been observed previously and suggestions as to the decoupling mechanism have been made [14]. There is little difference in the chemical shifts of the various protons in the complexes compared with those in the free ligand and the decoupled signals are only very slightly broadened. Decoupling of this type may therefore prove to be of considerable value in the interpretation of the NMR spectra of certain organophosphorus heterocycles.

(iii) Phosphindoline and isophosphindoline complexes

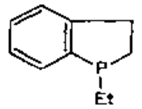
Phosphindoline (X) and isophosphindoline (XI) are fused ring derivatives of 2-phospholene (VIII) and 3-phospholene (IX) respectively. This ring fusion increases the steric bulk of these systems without greatly affecting the donor character of the phosphorus atom.



X



XI



XII

There is only one mention [15] of a phosphindoline complex in the literature in which 1-ethylphosphindoline (XII) was reported to form with palladium(II) bromide the expected complex L_2PdBr_2. However, the related isophosphindoline system (XI) (in the form of 2-phenylisophosphindoline (III)) has received considerable attention. Thus, Mann's group has made several reports, including three major studies, on the coordination chemistry of 2-phenylisophosphindoline (III). The interest shown in this particular ligand stems primarily from its ability to cause some transition metals to adopt relatively uncommon coordination numbers in the resulting complexes. Furthermore, in some cases, the complexes produced may exist in several interconvertible crystalline forms. The known coordination chemistry of (III) may be divided conveniently (as was done by Mann et al.) into three broad areas — complexes of platinum(II), palladium(II) and nickel(II) [16—18]; complexes of cobalt, rhodium and iridium halides [19]; and complexes of copper(I), silver(I) and gold halides [17,20].

(a) Complexes of platinum(II), palladium(II), and nickel(II)

The cyclic phosphine (III) (2 mol) reacts [16] with potassium tetrachloroplatinate in aqueous ethanol to form what is probably the salt $[(C_{14}H_{13}P)_4Pt]$-$[PtCl_4]$ which rearranges to form the complex $(C_{14}H_{13}P)_2PtCl_2$ (XIII, X = Cl). Furthermore, a whole series of complexes of type (XIII) (where X = Br, I or SCN) is formed [16] by treating an aqueous acetone solution of $(C_{14}H_{13}P)_2PtCl_2$ with the appropriate sodium salt. These complexes (XIII) are colourless (X = Cl or Br) or pale yellow (X = I), are solvent-free, and give non-conducting solutions in nitrobenzene. In all respects then, they are normal four-coordinate platinum(II) complexes.

$(C_{14}H_{13}P)_2PtX_2$	$(C_{14}H_{13}P)_3PtX_2$	$[(C_{14}H_{13}P)_3PtX]^+[Y]^-$
XIII	XIV	XV

In addition, each of the complexes of type (XIII) will interact with another molecule of 2-phenylisophosphindoline (III) in hot acetone solution to form a series of compounds (XIV; X = Cl, Br, I or SCN) in which the platinum atom has a coordination number of five. The dichloro- and dithiocyanato- forms (XIV, X=Cl or SCN) exist as colourless dihydrates which decompose (lose ligand) on dehydration. The dibromide can exist both in colourless dihydrated and anhydrous forms (the latter being obtained on recrystallization of the dihydrate from benzene), while the orange diiodide (XIV, X=I) is solvent-free.

In some organic solvents, these tris(phosphine) compounds of type (XIV) behave as ionized species of formula (XV) (where X=Y=Cl, Br, I or SCN). For example, all four derivatives of type (XIV) form conducting nitrobenzene solutions. Furthermore, the three species (XIV; X=Cl, Br or I) react in ethanol solution with sodium picrate or sodium perchlorate to form salts of type (XV; X=Cl, Br or I and Y=$C_6H_2N_3O_7$ or ClO_4) which again appear to be ionized in nitrobenzene solution. On the other hand, the complexes (XIV) are apparently not ionized in dichloromethane in which they show normal molecular weights.

Palladium(II) complexes of the isophosphindoline (III) have been the subject of two brief [17,18] reports and one detailed [16] report. Thus, in a paper devoted primarily to the synthesis of the ligand (III) and various derivatives thereof [17], it was mentioned that under the appropriate conditions, the ligand forms with Pd^{II} salts normal complexes of general formula $(C_{14}H_{13}P)_2$-PdX_2 (X=Cl or I) and also what appeared to be Pd^I complexes of the type $(C_{14}H_{13}P)_2PdX$ (X=Cl or Br). Further, the chloride was stated to have two different colourless crystalline forms. In a later communication [18], it was stated that the apparently Pd^I complexes are in fact five-coordinate Pd^{II} compounds and that the dichloride and dibromide may each exist in a number of different crystalline forms.

In a more extensive account [16], Mann et al. have given full details regarding the interaction of the isophosphindoline (III) with palladium(II) compounds. Thus, palladium(II) halides and palladium(II) nitrite react [16] with 2-phenylisophosphindoline (III) (2 mol) to form a series of four-coordinate palladium(II) complexes of type (XVI) (where X=Cl, Br, I or NO_2) which are darker in colour (yellow-deep orange) than, but otherwise analogous to, the platinum(II) complexes already mentioned.

A series of tris(2-phenylisophosphindoline)palladium(II) halide complexes of type (XVII) has also been prepared [16] but the situation is greatly complicated by the fact that each of the chloride and bromide complexes may exist in any one of several readily interconvertible crystalline forms. For example, the colourless derivative $(C_{14}H_{13}P)_3PdCl_2.2H_2O$ (XVII, X=Cl) (m.p. 140°) may be prepared by the reaction of ethanolic 2-phenylisophosphindoline with K_2PdCl_4 in hot water or from the reaction of (XVI, X=Cl) with an additional molecule of the cyclic phosphine. This adduct is unaltered by dissolution in methanol, ethanol or acetone in which it forms non-conducting solutions. On the other hand, addition of ether to these solutions causes precipitation of (XVI, X=Cl) while addition of aqueous K_2PdCl_4 to solutions of the tris-adduct initially causes precipitation of $[(C_{14}H_{13}P)_3PdCl]_2[PdCl_4]$ which rapidly disproportionates to give (XVI, X=Cl). The weakly bound nature of the third cyclic phosphine ligand is also illustrated by the fact that when warmed under reduced pressure, the tris-adduct loses one molecule of 2-phenylisophosphindoline.

$(C_{14}H_{13}P)_2PdX_2$	$(C_{14}H_{13}P)_3PdX_2$	$[(C_{14}H_{13}P)_3PdCl]^+[X]^-$
XVI	XVII	XVIII

The interaction of an ethanolic solution of the adduct $(C_{14}H_{13}P)_3PdCl_2.2H_2O$ described above with ethanolic sodium perchlorate or sodium picrate gives rise to the monohydrates of (XVIII, $X=ClO_4$ or $C_6H_2N_3O_7$). These two salts and the complex $(C_{14}H_{13}P)_3PdCl_2.2H_2O$ itself form conducting solutions in nitrobenzene.

The complex $(C_{14}H_{13}P)_3PdCl_2.2H_2O$ described above is remarkable in that under certain conditions, it may be transformed into another colourless dihydrate of much higher melting point, an orange dihydrate of lower melting point and a scarlet monohydrate of higher melting point. The conditions required for the various transformations are outlined in Fig. 1.

The complex $(C_{14}H_{13}P)_3PdBr_2$ is obtained [16,18] as a deep orange crystalline solid from the reaction of K_2PdBr_4 with 2-phenylisophosphindoline or by treatment of acetone—methanol solutions of $(C_{14}H_{13}P)_3PdCl_2.2H_2O$ (m.p. 140°) with lithium bromide followed by the addition of water. The orange dibromide may be recrystallized from methanol by slow evaporation but it dissociates to give (XVI, X=Br) in hot methanol, ethanol or acetone unless a trace of free ligand is added. When cold acetone or methanol solutions of the complex (XVII, X=Br) are treated with sodium perchlorate or sodium picrate, the bromo—perchlorate (XIX, $X=ClO_4$) or the bromo—picrate (XIX, $X=C_6H_2N_3O_7$) is deposited.

$[(C_{14}H_{13}P)_3PdBr]^+[X]^-$	$(C_{14}H_{13}P)_3NiX_2$	$(C_{14}H_{13}P)_2NiX_2$
XIX	XX	XXI

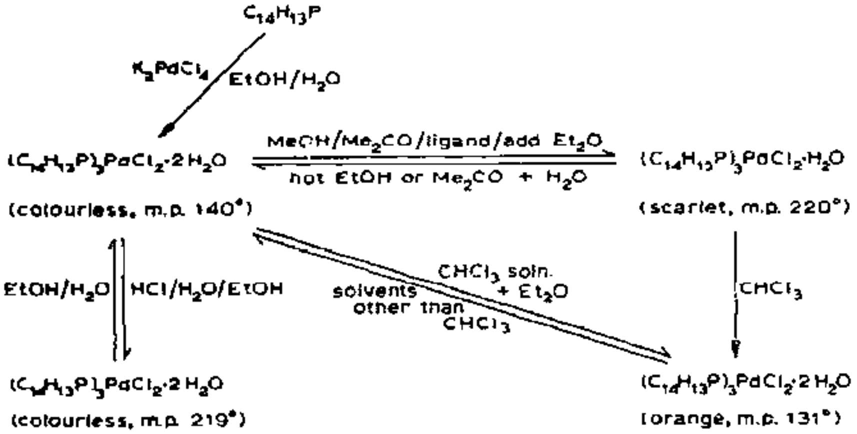


Fig. 1. The hydrates of $(C_{14}H_{13}P)_3PdCl_2$.

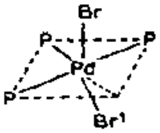
The complex $(C_{14}H_{13}P)_3PdBr_2$ apparently also exists in different crystalline forms. Thus, treatment of hot saturated solutions of the orange dibromide in acetone with free ligand gives a deep red dibromide which may also be formed by treatment of hot dilute acetone, methanol or dimethylformamide solutions of the orange dibromide with water. The structure of this red dibromide will be discussed shortly.

2-Phenylisophosphindoline (III) also reacts with palladium(II) iodide in chloroform to form the tris-adduct $(C_{14}H_{13}P)_3PdI_2$ as deep vermilion crystals. This complex is much less stable than the tris-adducts already discussed and it readily dissociates to form $(C_{14}H_{13}P)_2PdI_2$ when suspended or dissolved in organic solvents. It can, however, be recrystallized from organic solvents containing 5—10% of the free phosphine. When an acetone solution (containing some free ligand) or $(C_{14}H_{13}P)_3PdI_2$ is treated with aqueous sodium perchlorate, the salt $[(C_{14}H_{13}P)_3PdI]^+[ClO_4]^-$ is formed.

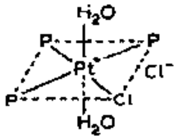
Hydrated nickel(II) chloride reacts [16] with 2-phenylisophosphindoline (III) in ethanol to give deep green crystals of tris(2-phenylisophosphindoline)-dichloronickel(II) monohydrate (XX, X=Cl). This complex is stable in chloroform solution, but in other solvents it dissociates to form the bis-complex (XXI, X=Cl). The solvent-free analogous dibromo- and diiodo-compounds (XX, X=Br or I) are readily prepared by similar methods and, when heated in ethanol, they also give the bis-phosphine adducts (XXI, X=Br or I).

It appears that some of these Pt^{II}, Pd^{II} and Ni^{II} tris(2-phenylisophosphindoline) complexes have structures in the solid state which are different from those in solution in organic solvents. In addition, the various hydrates of tris(2-phenylisophosphindoline)dichloropalladium(II) appear to have specific identities in the crystalline state, but in solution they apparently have the same structure or, possibly, an equilibrium mixture of two structures. Thus, all four forms of hydrated $(C_{14}H_{13}P)_3PdCl_2$ give similar yellow acetone or ethanol solutions from which only one chloro—perchlorate (XVIII, X=ClO_4) or chloro—picrate (XVIII, X=$C_6H_2N_3O_7$) is obtained.

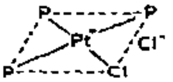
The crystal and molecular structure of the deep red form of $(C_{14}H_{13}P)_3$-$PdBr_2$ has been determined by X-ray studies. This five-coordinate palladium(II) complex has [16] a distorted square pyramidal structure (XXII) with one of the Br atoms (Br^1) depressed by 10° below the plane formed by the phosphorus atoms and the palladium atom. While this species has a covalent structure in the solid state, in ethanol solution it behaves as a salt of the type $[(C_{14}H_{13}P)_3PdBr]^+[Br]^-$ although in nitrobenzene solution, it shows a very low conductivity.



XXII



XXIII



XXIV

Since tris(2-phenylisophosphindoline)dichloroplatinum(II) dihydrate $[(C_{14}H_{13}P)_3PtCl_2.2H_2O]$ is very reluctant to undergo dehydration, Mann et al. [16] have suggested that it may have an octahedral cationic structure (XXIII) in the solid state. Evidence was put forward which indicates that in solution, the compound may exist as an equilibrium of (XXIII) and (XXIV).

Structures have also been proposed [16] for the bis(2-phenylisophosphindoline) complexes of Pt^{II}, Pd^{II} and Ni^{II}. Thus, it was suggested that the colourless $(C_{14}H_{13}P)_2PtX_2$ (X=Cl or Br) complexes have the *cis* arrangement, while the corresponding diiodo compound probably has the *trans* arrangement. Similarly, the $(C_{14}H_{13}P)_2PdX_2$ (X=Cl, Br or I) derivatives are likely to have normal *trans* arrangements as are the nickel(II) derivatives $(C_{14}H_{13}P)_2NiX_2$ (X=Cl, Br or I).

(b) Complexes of cobalt, rhodium and iridium halides

2-Phenylisophosphindoline (3 mol) reacts [19] with cobalt(II) halides in ethanol to form five-coordinate derivatives of the form $(C_{14}H_{13}P)_3CoX_2$ (X=Cl, Br or I) of which the dichloride is monohydrated and the dibromide and diiodide are solvent-free. These complexes are covalent as is indicated by the fact that they show normal molecular weights in dichloromethane solution (at 23°C), form non-conducting solutions in nitrobenzene and do not react with sodium perchlorate or sodium tetraphenylborate in ethanol. However, in boiling benzene, they dissociate to give the four-coordinate (normal) bis(2-phenylisophosphindoline) complexes $(C_{14}H_{13}P)_2CoX_2$ (X=Cl, Br or I). Of these, the dichloride and dibromide are dihydrated (after recrystallization from acetone—petroleum) and the diiodide is monohydrated (after similar recrystallization).

Reaction of 2-phenylisophosphindoline (3 mol) with a hot aqueous ethanolic solution of sodium hexachlororhodate(III) (Na_3RhCl_6) was found [19] to produce the bright yellow tris(2-phenylisophosphindoline)trichlororhodium(III) derivative (XXV, X=Cl). The corresponding tribromo- and triiodo- compounds can be prepared by treating the sodium hexachlororhodate(III) solution with sodium bromide or sodium iodide before adding the ligand. These complexes are normal six-coordinate rhodium(III) species and no rhodium(I) compounds were isolated from the reactions.

The reaction of sodium hexachloroiridate(IV) ($Na_2IrCl_6.6H_2O$) with 2-phenylisophosphindoline (3 mol) in ethanol under reflux yields [19] tris-(2-phenylisophosphindoline)dichlorohydridoiridium(III) (XXVI, X=Cl).

$(C_{14}H_{13}P)_3RhX_3$	$(C_{14}H_{13}P)_3IrHX_2$	$(C_{14}H_{13}P)_3IrX_3$
XXV	XXVI	XXVII

As with the related rhodium(III) complexes, the dibromohydrido analogue (XXVI, X=Br) is produced by treating the reaction mixture with sodium bromide before heating. When the dichlorohydrido- species (XXVI, X=Cl) is heated with 1,2-dichloroethane, carbon tetrachloride or 1-chlorobutane, or treated with chlorine or hydrogen chloride gases, the tris(2-phenylisophosphindoline)trichloroiridium(III) complex (XXVII, X=Cl) is formed. The tribromo- compound (XXVII, X=Br) is produced similarly by treating the dibromohydrido- complex (XXVI, X=Br) with the corresponding bromo-organic reagents.

In contrast, 2-phenylisophosphindoline gives a very different reaction with iridium(III) iodide in boiling ethanol and the products of this reaction have been tentatively formulated [19] as $(C_{14}H_{13}P)_3Ir(CO)I_2$ and $(C_{14}H_{13}P)_3IrI_2$.

(c) Complexes of copper(I), silver(I) and gold(I) halides

2-Phenylisophosphindoline (III) reacts with the halides of copper(I) [20], silver(I) [20] and gold(I) [17,20] to produce three types of complex (XXVIII, XXIX and XXX) while copper(I) halides also form [20] a fourth type of complex (XXXI) under the appropriate conditions.

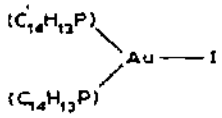
$[(C_{14}H_{13}P)MX]_n$	$(C_{14}H_{13}P)_2MX$	$(C_{14}H_{13}P)_3MX$	$[(C_{14}H_{13}P)_4Cu]^+[X]^-$
XXVIII	XXIX	XXX	XXXI

The copper(I) derivatives of type (XXVIII; M=Cu, X=Cl, Br or I) and the related silver(I) complexes (XXVIII; M=Ag, X=Cl or Br) are readily prepared [20] by normal methods and can be isolated as colourless crystals. The corresponding silver(I) iodide complex (XXVIII; M=Ag, X=I) could not be isolated and this is somewhat surprising since in related silver(I) complexes, the iodo- compounds are often more stable than the corresponding chloro- and bromo- compounds. The copper(I) iodide species (XXVIII; M=Cu, X=I) is a tetramer in dichloromethane solution and this is typical of simple trialkylphosphine and arsine complexes of this general type [21,22]. On the other hand, the silver(I) chloride complex (XXVIII; M=Ag, X=Cl), which is probably a tetramer in the solid state, gives a molecular weight in dichloromethane solution corresponding to $n=2.1$. This behaviour is believed to be due to a partial dissociation of the tetramer in solution. All of the gold(I) derivatives (XXVIII; M=Au, X=Cl, Br or I) are monomeric [17,20].

The mono(2-phenylisophosphindoline)copper(I) complexes (XXVIII; M=Cu, X=Cl, Br or I) do not oxidise to the corresponding copper(II) species when treated with chlorine gas or bromine in cold chloroform solution but, instead, undergo a general decomposition. In contrast, the gold(I) derivatives (XXVIII; M=Au, X=Cl or Br) form the corresponding stable crystalline gold(III) species when similarly treated. These complexes are of type (XXXII, X=Cl or Br) and probably have [20] the planar structure typical of four-coordinate gold(III) compounds [23].

$(C_{14}H_{13}P)AuX_3$

XXXII



XXXIII

$(C_{14}H_{13}P)_3CdX_2$

XXXIV

The bis(2-phenylisophosphindoline)copper(I) and silver(I) complexes (XXIX; M=Cu or Ag, X=Cl, Br or I) have all been isolated [20] and are all stable species. The silver(I) nitrate complex (XXIX; M=Ag, X=NO_3) can also be prepared, but it proved to be light-sensitive. Of the gold(I) compounds of this type, the iodide is stable, the chloride could not be isolated and the bromide is stable in the solid state but dissociates is hot organic solvents to form $(C_{14}H_{13}P)AuBr$ and free ligand. The compounds (XXIX; M=Cu, X=I), (XXIX; M = Ag, X = I or NO_3) and (XXIX; M = Au, X = I) all have covalent structures as indicated by the fact that they form non-conducting nitrobenzene solutions. Also, some of the compounds have molecular weights in dichloromethane solution (at 23°) which are somewhat higher than expected for monomeric species, and halogen bridging may occur [20].

The gold(I) iodide derivative (XXIX; M=Au, X=I) is particularly interesting since it is thought [20] to have a monomeric trigonal planar structure (XXXIII) in benzene solution and this suggestion is supported by dipole moment measurements. On the other hand, the compound has been shown by a partial X-ray crystal structure determination to have in the solid state the ionic structure $[(C_{14}H_{13}P)_2Au]^+[I]^-$ with a nearly linear arrangement of the P—Au—P atoms.

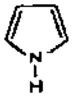
Of the tris(2-phenylisophosphindoline) complexes, the copper(I) iodide compound (XXX; M=Cu, X=I) was the only copper(I) complex of this type which could be isolated. The only similar silver(I) complex to be isolated was the perchlorate (XXX; M=Ag, X=ClO_4) which appears to be a salt of the type $[(C_{14}H_{13}P)_3Ag]^+[ClO_4]^-$. All attempts to prepare the corresponding silver(I) halide complexes (XXX; M=Ag, X=Cl, Br or I) were unsuccessful. However, all three of the related gold(I) halide derivatives (XXX; M=Au, X=Cl, Br or I) were readily prepared and probably have a tetrahedral structure [20].

Considering complexes containing four 2-phenylisophosphindoline ligands, only the two copper(I) compounds (XXXI; X=NO_3 or ClO_4) could be isolated and all attempts to prepare similar silver(I) and gold(I) complexes were unsuccessful.

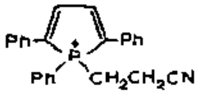
Brief mehtion has also been made [20] of the reaction of the ligand 2-phenylisophosphindoline with cadmium halides. Thus, the ligand reacts with cadmium(II) bromide or iodide to form the bis(2-phenylisophosphindoline)dihalogenocadmium(II) complexes (XXXIV, X=Br or I) of which the diiodide is the more stable. A similar reaction with cadmium(II) chloride gave a mixture from which only the bridged dimeric compound $[(C_{14}H_{13}P)CdCl_2]_2$ could be isolated.

(iv) Phosphole and phosphole derivative complexes

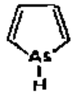
The five-membered ring systems so far discussed have been either fully saturated (phospholanes) or partly unsaturated (2-phospholenes, 3-phospholenes, phosphindolines and isophosphindolines) cyclic phosphines and, as such, they exhibit the expected phosphine-type characteristics except for the tendency of isophosphindolines to cause certain metals to adopt uncommon coordination numbers. However, the simplest five-membered fully unsaturated cyclic phosphine is phosphole (I) and it can be seen that superficially (I) is very similar to the pyrrole system (XXXV) which can be regarded as having aromatic character through $(2p{-}2p)\pi$ delocalization of the nitrogen atom lone-pair over the entire ring [24]. There is therefore the possibility that simple phosphole derivatives may also exhibit some degree of aromatic character through $(3p{-}2p)\pi$ type interactions although there may also be some *d*-orbital involvement.



XXXV



XXXVI



XXXVII

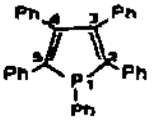
Early studies regarding the possible aromatic character of the phosphole system have been reviewed adequately elsewhere [25]. Although a detailed survey would not be appropriate here, a brief summary of the present conflicting position regarding this possible aromatic character is in order. Thus, Quin [1] et al. have found that the basicity of the phosphorus atom in 1-methylphosphole is extremely low (pK_a = 0.5) compared with experimental values for normal tertiary phosphines (pK_a = 7—8) or calculated values for divinylphosphines (pK_a = 5.2) and this was taken to indicate substantial delocalization of the phosphorus lone-pair of electrons. Similarly, Farnham and Mislow [26] have concluded from kinetic studies of retrocyanoethylation reactions of phospholium salts of type (XXXVI) that, in phospholes, there is significant delocalization of the lone-pair electrons. Also, ^{1}H and ^{31}P [1,27,28] together with ^{13}C [29] NMR measurements as well as crystallographic data [30] have been interpreted as being not inconsistent with some degree of lone-pair delocalization in simple *P*-substituted phospholes. Furthermore, Egan et al. [2] have found by NMR studies that the pyramidal inversion barrier about the phosphorus atom in simple phospholes is exceptionally low compared with such inversion barriers for normal tertiary phosphines. This, too has been taken to indicate considerable interaction of the lone-pair with the π-system and that this interaction is at a maximum in the planar transition state of the inversion.

On the other hand, Schäfer et al. [3] have recently deduced from photoelectron spectroscopic measurements that, in the ground state (pyramidal) arrangement, phospholes (and arsoles, XXXVII) consist of localized diene systems and lone-pairs of electrons and are not aromatic.

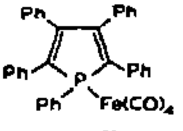
The possible interaction of the lone-pair with the π-system would clearly affect the donor character of the phosphorus atom towards transition metal systems and studies of such donor character are therefore of considerable interest. Furthermore, there is also the possibility of π-complex formation with phosphole systems. Also, various derivatives of phospholes such as the corresponding oxides, sulfides and selenides may show interesting behaviour towards transition metal systems. The following subsections are therefore an account of the coordination chemistry of phospholes and phosphole derivatives of the type mentioned above. For convenience, phosphole complexes and phosphole derivative complexes are treated separately.

(a) Complexes of phospholes

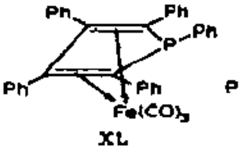
The earliest studies of the coordination chemistry of phospholes date from the first synthesis of the phosphole system and they involved reactions with metal carbonyls. Braye et al. [31] found that 1,2,3,4,5-pentaphenylphosphole (XXXVIII) reacts quantitatively with $Fe(CO)_5$ under fairly drastic conditions (refluxing isooctane for several hours) to form the monosubstituted product tetracarbonyl(1,2,3,4,5-pentaphenylphosphole)iron(0) (XXXIX) in which the ligand is bound to the iron atom through the phosphorus atom. A similar reaction between the phosphole (XXXVIII) and $Fe_3(CO)_{12}$ was found to give, in addition to (XXXIX), the complex (XL) in which the iron atom is π-bonded to the ligand through the diene system of the phosphole ring. These authors also report [31] that, occasionally, the interesting complex (XLI) may also be formed in this reaction. Thus, in these metal carbonyl reactions, the phosphole resembles both tertiary phosphines and a number of non-aromatic conjugated dienes which are known [32] to react readily with iron carbonyls.



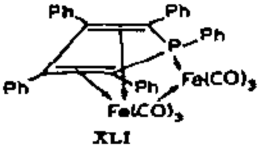
XXXVIII



XXXIX



XL

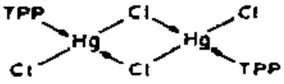


XLI

In a later investigation, Cookson et al. [33] obtained both π-complexes and normal phosphine complexes analogous to (XXXIX) and (XL) from the reactions of 1,2,5-triphenylphosphole (abbreviated here to TPP) with iron carbonyls. Similarly, the hexacarbonyls of Cr, Mo and W and $Ni(CO)_4$ all react [33] with TPP to form the monosubstituted P-bonded derivatives $(TPP)M(CO)_5$ (M=Cr, Mo or W) and $(TPP)Ni(CO)_3$. In the same investigation, it was found that the bismorpholine tetracarbonyls of Mo and W form, with TPP, complexes of the type $(TPP)_3M(CO)_4$ (M=Mo or W). These apparently contain 7-coordinate Mo or W but IR studies [33] indicate that one of the phosphole molecules is not directly coordinated to the metal atom although repeated crystallization does not change the ligand to metal ratio.

As already mentioned in an earlier section, cobalt carbonyl complexes of 2- and 3-phospholenes are efficient catalysts for the conversion [10] of 1-alkenes into 1-alkanols in the presence of CO and H_2. Similar behaviour has also been found [10] for cobalt carbonyl complexes of heavily substituted phospholes such as TPP, 1,2,3,4,5-pentaphenylphosphole (XXXVIII) and 1-styryl-2,3,4,5-tetraphenylphosphole. For the complexes of TPP and (XXXVIII), the rates of conversion of alkene into alkanol were found to be considerably faster than for the various related phospholene complexes under similar conditions while overall yields for the conversion remain about the same (ca. 90%).

The first study of the coordinating ability of a phosphole (in this instance, TPP) with transition metals in a non-zero oxidation state was carried out by Walton [34]. Thus, it was found that the chlorides and bromides of Pd^{II} and Pt^{II} react with the phosphole under mild conditions to give crystalline complexes formulated as $(TPP)_2MX_2$ (M=Pd or Pt, X=Cl or Br) while mercury(II) chloride reacts with TPP to form (regardless of reactant ratios) the halogen-bridged dimeric adduct (XLII). In similar reactions, it was found [24] that Rh^{III} chloride reacts with a twofold excess of TPP to form $(TPP)RhCl_3$. No evidence for any reduction of Rh^{III} to Rh^{I} (as readily occurs [35] in the reactions of triphenylphosphine with Rh^{III} chloride) was found although the conditions chosen for the reaction (mixing of solutions at room temperature) were very mild. In all of the above mentioned complexes, the stoichimetry indicates bonding of the ligand to the metal through the phosphorus atom.



XLII

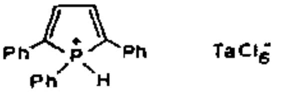
As part of a general investigation of the donor character of unsaturated phosphorus heterocycles, a detailed study of the coordinating ability of the readily available [36] 1,2,5-triphenylphosphole (TPP) has been undertaken [37—41]. Thus, preliminary studies [37] showed that TPP does not react under normal conditions with the chlorides of Ag^{I}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Th^{IV} and U^{IV} although most of these transition metal species are known [42] to form complexes easily with normal tertiary phosphines. From these observations, it appears that the lone pair of electrons of the phosphorus atom of TPP is not readily available for coordination. This conclusion is supported by Quin's observations that 1-methylphosphole is an extremely weak base ($pK_a = 0.5$) and that this simple phosphole will not form complexes with Ni^{II} chloride [1]. Quin et al. [13] have similarly found that the related structure 1-benzylphosphole also lacks donor character towards Ni^{II}. This would indicate that the reluctance of TPP to form complexes with Ni^{II} is not primarily a steric effect (a conclusion supported by Walton's observations already discussed [34]) since both 1-methylphosphole and 1-benzylphosphole are very much less bulky than TPP and still do not form Ni^{II} complexes.

In contrast, Quin et al. [13] have also observed that the relatively unhindered structure 1-benzyl-3,4-dimethylphosphole smoothly and rapidly forms a stable recrystallizable complex of the type L_2NiCl_2 with Ni^{II} chloride (L = phosphole ligand). This readiness of 1-benzyl-3,4-dimethylphosphole to form complexes has been attributed by Quin et al. [13,43] to a modification in delocalization in the phosphole ring as a result of steric interaction of the two adjacent methyl groups. Spectroscopic evidence has been put forward [43] which supports this suggestion. It is also interesting to note that, as with the phospholene—Ni^{II} complexes already discussed, complexation of 1-benzyl-3,4-dimethylphosphole with Ni^{II} chloride leads to the complete disappearance of all ^{31}P—H couplings in the NMR spectrum.

That the reluctance of TPP to form complexes with the transition metal systems mentioned above is not steric in origin is confirmed by the fact that this ligand will interact with and form complexes with quite a wide variety of other transition metal systems in addition to those investigated by Walton [34]. For example, TPP reacts smoothly [37] with Cu^{II} chloride in methanol to form a complex with the stoichiometry (TPP)CuCl — i.e. in this reaction, the phosphole apparently has both the reducing power [44] and coordinating ability of a normal tertiary phosphine although the reaction is somewhat slower than with normal phosphines. The same complex may also be prepared by direct reaction of TPP with Cu^{I} chloride. A similar reduction of Fe^{III} to Fe^{II} occurs when a methylene chloride solution of Fe^{III} chloride is treated with TPP which, during the reaction, is oxidized to 1,2,5-triphenylphosphole oxide (TPPO), presumably by hydrolysis of an intermediate *P,P*-dichlorophosphole. In this reaction, no complex is formed unless an excess of Fe^{III} chloride is used. Under these conditions, a 1,2,5-triphenylphosphole oxide complex of Fe^{III} is formed with the stoichiometry $(TPPO)_2FeCl_3.0.5\,CH_2Cl_2$.

In the same study [37], coordination of TPP with halides of transition metals in higher oxidation states, such as Ta^{V} chloride and bromide and Nb^{V} chloride, was investigated. In all cases, virtually quantitative yields of crystalline 1:1 adducts of the type $(TPP)MX_5$ (M=Ta, X=Cl or Br; M=Nb, X=Cl) are readily formed. Only oils were obtained from the reaction of TPP with Nb^{V} bromide and neither Ta^{V} iodide nor Nb^{V} iodide reacted, probably because of greater steric interactions. The phosphole ligand is only very weakly bound to the metal atom in these complexes as is evident from the fact that TPP is readily displaced from $(TPP)MX_5$ by coordinating solvents such as acetonitrile and even ether. This does not occur with the corresponding triphenylphosphine complexes. On the other hand, (TPP)$TaCl_5$ may be sublimed unchanged on heating under reduced pressure although, presumably, some dissociation must occur in the gas phase.

One very interesting and significant result obtained from this work was the determination of the site of protonation [37,38] of the phosphole ring in 1,2,5-triphenylphosphole (TPP). Since phospholes are such weak bases [1] they do not normally protonate to form stable salts such as hydrochlorides and 1-methylphosphole cannot even be extracted from pentane by 2*N* hydrochloric acid. However, it was found [38] that dry hydrogen chloride gas reacts rapidly with a benzene solution of (TPP)$TaCl_5$ or with a benzene solution of TPP in which $TaCl_5$ is suspended to give a highly crystalline orange solid analyzing for $[TPPH]^+[TaCl_6]^-$. The same compound may also be prepared [38] by exposing a benzene solution of (TPP)$TaCl_6$ to ethanol vapour or to the direct addition of small amounts of ethanol. On the basis mainly of IR spectral data and deuterium labelling experiments, this compound has been assigned [38] the *P*-protonated structure (XLIII). If protonation at this site is general for phospholes, this would be in complete contrast to the behaviour of pyrroles (the aromatic nitrogen containing analogues of phospholes) where protonation occurs at the ring carbon atoms [45]. The corresponding complex $[TPPH]^+[NbCl_6]^-$ is also easily prepared by similar methods although it is much more sensitive to atmospheric moisture than is the Ta^V adduct. Presumably the complex (XLIII) owes its stability to the strictly anhydrous conditions used, the stabilizing influence of the $[TaCl_6]^-$ ion and a favourable lattice energy for the crystalline solid.



XLIII

Attempts to replace the $[TaCl_6]^-$ ion by other potentially good stabilizing anions were largely unsuccessful although there was some evidence [37] for the formation of $[TPPH]^+[FeCl_4]^-.FeCl_3$ on treatment of Fe(III) chloride and TPP (2:1) in benzene with dry hydrogen chloride. With a 1:1 metal halide: ligand ratio, the complex salt $[(TPP)_2FeCl_2]^+[FeCl_4]^-$ was apparently formed [37].

Because of the current interest in phosphine—rhodium and phosphine—ruthenium complexes as homogeneous catalysts for various reactions, the reactions of TPP and other phosphole derivatives with rhodium [39] and ruthenium [40] systems have been investigated. Thus, it was confirmed [39] that rhodium(III) chloride trihydrate reacts almost immediately in ethanol with up to six-fold excesses of TPP and the much less hindered 1-phenylphosphole (PP) to give complexes of formula (TPP)$RhCl_3$ (as observed by Walton [34]) and $(PP)_3RhCl_3$ respectively. With TPP, longer reflux times (ca. 24 h) lead to the formation of the hydrido complex $(TPP)_2RhHCl_2$. Evidence has been put forward [39] which suggests that $(TPP)_2RhHCl_2$ is a square pyramidal structure with the hydrogen atom at the apex and with the two phosphole ligands mutually *trans.*

In the above mentioned experiments, no reduction of Rh^{III} to Rh^{I} was detected (c.f. Walton [34]). However, if the reaction is carried out under reflux in solvent systems in which the phosphole has a much greater solubility than in ethanol (e.g. chloroform—methanol), reduction of Rh^{III} to Rh^{I} does occur to give the complex (TPP)(TPPO)RhCl in which the TPP is bound to the metal atom through the phosphorus atom while the TPPO is bound through the π-diene system. More will be said about these π-coordinated systems later but it is worth noting that the Rh^{I} atom has a stronger affinity for the π-system of TPPO in the presence of an excess of TPP and this again illustrates the very weak donor character of the phosphole system.

Rhodium(I) complexes of TPP may also be prepared [39] directly by reaction with chlorobis(carbonyl)rhodium(I) dimer $[RhCl(CO)_2]_2$ in ethanol to give the monomeric square-planar complex $(TPP)_2(CO)RhCl$. On the other hand, a similar reaction between a 3:1 excess of TPP and chlorobis(ethylene)-rhodium(I) dimer $[(C_2H_4)_2RhCl]_2$ under reflux in methanol gives the dimeric complex $[(TPP)_2RhCl]_2$. Both of these complexes are air sensitive and IR evidence [39] indicates that the oxygen is taken up to oxidize the TPP in the complex to TPPO. If the reaction of chlorobis(ethylene)rhodium(I) dimer with TPP is carried out in the presence of a sixfold excess of TPP in chloroform—ethanol solution under reflux, the complex $(TPP)_3RhCl$ is formed.

The rhodium(III) and rhodium(I) complexes mentioned above are of interest because they are related to a number of catalytically active rhodium complexes of normal tertiary phosphines (e.g. $(Ph_3P)_3RhCl$ [46]). A preliminary investigation [39] has shown that several of these complexes, such as the Rh^{III} complex $(TPP)_2RhHCl_2$ in the presence of Et_3N and also, to a lesser extent, the Rh^{I} complex $[(TPP)_2RhCl]_2$, do indeed have catalytic activity in homogeneous hydrogenation reactions. For example, 1-hexene is smoothly hydrogenated in the presence of these complexes in benzene solution although the rate of hydrogenation is considerably less than has been observed [46] for $(Ph_3P)_3RhCl$.

The coordination chemistry of TPP with both ruthenium(III) and ruthenium(II) has received some attention [40]. For example, commercial ruthenium trichloride hydrate reacts smoothly with a three-fold excess of TPP in ethanol to give a complex with the stoichiometry $(TPP)_2RuCl_3$. Infrared spectroscopic studies [40] indicate that this has a halogen-bridged dimeric structure and the complex therefore contains normal six-coordinate ruthenium. No evidence was obtained for reduction of Ru^{III} to Ru^{II}.

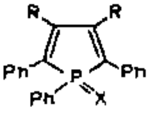
Ruthenium(II) complexes of TPP may be prepared by two methods. The first of these involves the reaction of TPP with the blue ruthenium(II) solution containing $[Ru_5Cl_{12}]^{2-}$ obtained [47,48] by reduction of alcoholic commercial ruthenium trichloride hydrate with hydrogen in the presence of Adam's catalyst. Thus, heating the ethanolic Ru^{II} blue solution under reflux for sixty hours with a three-fold excess of TPP leads [40] to the formation of a stable green complex of formula $(TPP)_3RuCl_2$. The second method involves the reaction of TPP with the ruthenium(II) red solution containing the species $Ru(CO)_nCl_m$ which is obtained [49] by passage of carbon monoxide through ethanolic commercial ruthenium trichloride hydrate under reflux. Under these conditions, the stable orange crystalline adduct *cis* $(TPP)_2Ru(CO)_2Cl_2$ is obtained [40]. This compound is analogous to the series of compounds of formula $L_2Ru(CO)_2Cl_2$ formed [49] when the red Ru^{II} solution is treated with a variety of normal phosphine and arsine ligands. However, reactions of this type with the ethanolic red $Ru(CO)_nCl_m$ solution normally give the *trans* isomers of $L_2Ru(CO)_2Cl_2$ while the corresponding *cis* isomers can be obtained from a similar yellow $Ru(CO)_nCl_m$ solution in 2-methoxyethanol [49]. The *trans* isomers of $L_2Ru(CO)_2Cl_2$ may also be converted into the *cis* isomers on heating [49] and it is possible in the reaction described above, that *trans* $(TPP)_2Ru(CO)_2Cl_2$ is initially formed and undergoes thermal isomerization.

The behaviour of phospholes (in particular TPP) towards the rhenium(III) cluster compound nonachlorotrirhenium(III) (Re_3Cl_9) is also of interest for several reasons. Thus, rhenium has only borderline "class b" acceptor characteristics [50] and, moreover, Re_3Cl_9 is a crowded system. These characteristics would seem to render unlikely any significant interaction between the bulky and apparently poor donor TPP and Re_3Cl_9 although the common tertiary phosphines form [51], with this cluster system, complexes of the type $L_3Re_3Cl_9$ in which each rhenium atom accepts one ligand molecule. Nevertheless, Re_3Cl_9 forms [41] fairly readily with TPP, under reflux in dichloromethane, the complex $(TPP)_2Re_3Cl_9.CH_2Cl_2$ from which the solvent cannot be removed by low pressure pumping. Other solvent molecules (e.g. acetone) can be incorporated into the complex in place of dichloromethane but treatment of the complex with substantial quantities of coordinating solvents such as acetone or ethanol leads to the immediate displacement of TPP from the complex. A similar phenomenon (ligand displacement by a coordinating solvent) has been observed [37] (see earlier discussion) with $(TPP)TaCl_5$ and this again illustrates the weakness of the phosphorus—metal link in these phosphole complexes.

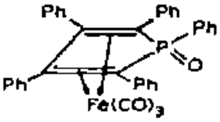
The poor donor character together with the crowded nature of Re_3Cl_9 is probably responsible for the fact that each Re_3 cluster can accommodate a maximum of two TPP ligands with the third coordination site occupied by a solvent molecule. In this connection, it should be noted that the reaction of TPP with Re_3Cl_9 in dichloromethane at room temperature leads to the formation [41] of $(TPP)Re_3Cl_9.(CH_2Cl_2)_2$ — i.e. a complex in which only one coordination site is occupied by a TPP ligand.

(b) Complexes of phosphole oxides, sulfides and selenides

In general, studies of the coordination chemistry of phosphole oxides, sulfides and selenides (e.g. XLIV, X=O, S or Se; R=H or Ph) have paralleled similar investigations of the corresponding phospholes except that phosphole oxides and sulfides with few substituents (e.g. 1-methylphosphole oxide) have received no attention, probably because of their readiness[27,52] to undergo spontaneous dimerization at room temperature via a Diels—Alder addition.



XLIV



XLV

As with the phospholes, the first such studies involved metal carbonyls. Thus, 1,2,3,4,5-pentaphenylphosphole oxide (XLIV, X=O; R=Ph) reacts [31] with $Fe(CO)_5$ to give the π-complex (XLV) and very similar behaviour has been noted [33] for 1,2,5-triphenylphosphole oxide (TPPO) (XLIV, X=O; R=H). Reactions of TPPO with the hexacarbonyls of Cr^0 and W^0 produced no identifiable compounds [33] while TPPO reacts with $Mo(CO)_6$ to give a product for which the formula $(TPPO)_2Mo(CO)_2$ was suggested. Attempts to prepare this same complex by reaction of TPPO with $(CH_2CHCN)_2$-$Mo(CO)_2$ gave only the Diels—Alder adduct of TPPO and acrylonitrile in low yield. Similar reactions [31] of 1,2,3,4,5-pentaphenylphosphole sulfide (XLIV, X=S; R=Ph) with iron carbonyls give only the pentaphenylphosphole—iron tetracarbonyl adduct (XXXIX) — i.e. the P=S link is very easily cleaved under these mild conditions.

The donor character of the oxide (TPPO), sulfide (TPPS) and selenide (TPPSe) of 1,2,5-triphenylphosphole (TPP) towards transition metal halides has received considerable attention. For example, it has been shown [37] that the donor character of the TPP system is only marginally increased by oxidation to TPPO. Thus, TPPO does not react with the chlorides of Fe^{II}, Ni^{II} and Cu^{II} even after prolonged reflux in dichloromethane or ethanol solution. Some reaction was observed under similar conditions with Mn^{II} chloride but no identifiable product could be obtained. The only divalent 3*d* metal to have any substantial degree of reactivity towards TPPO was found to be cobalt and the reaction of Co^{II} chloride hexahydrate with TPPO gives a bright green solid tentatively formulated as $(TPPO)_2CoCl_2$ mainly on the basis of the visible and near infrared reflectance spectra which showed the presence of tetrahedral cobalt. The complex itself was contaminated with appreciable amounts of unreacted ligand but all attempts to purify the adduct (recrystallization, sublimation or chromatography) led to decomposition (loss of ligand). The phosphole oxide TPPO reacts readily, however, with various transition metals in higher oxidation states to form stable complexes. In this connection, although Fe^{II} chloride does not react with TPPO, Fe^{III} chloride reacts smoothly [37] to give the complex $(TPPO)_2FeCl_3.0.5CH_2Cl_2$. As has been mentioned earlier, this same complex is produced when TPP is treated with an excess of Fe^{III} chloride in dichloromethane. In this reaction, Fe^{III} is reduced to Fe^{II}, the phosphole TPP is oxidized (probably via the *P,P*-dichloro-compound) and the resulting TPPO coordinates to the remaining Fe^{III}. Unlike the phosphole TPP, the phosphole oxide TPPO reacts [37] with both thorium(IV) and uranium(IV) chlorides to give complexes of the type $(TPPO)_2MCl_4$ (M=Th or U) and also $(TPPO)_3ThCl_4$.

The phosphole sulfide (TPPS) (XLIV, X=S; R=H) and the corresponding selenide (TPPSe) (XLIV, X=Se; R=H) do not react with any of the divalent *3d* metals mentioned previously nor do they react with Th^{IV} and U^{IV} chlorides. However, TPPS does react with $FeCl_3$ to give the unstable adduct $(TPPS)_2$-$FeCl_3$ but attempts to recrystallize this complex led to the formation of $(TPPO)_2FeCl_3$. This P=S bond cleavage is reminiscent of the formation [31] of (XXXIX) on treatment of 1,2,3,4,5-pentaphenylphosphole sulfide with iron carbonyls.

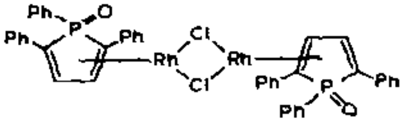
Considering transition metals in even higher oxidation states, the interaction of TPPO, TPPS and TPPSe with Nb^V and Ta^V halides has been thoroughly investigated [37] since these reactions allow direct comparison with similar reactions [53] of triphenylphosphine oxide, sulfide and selenide. In this study, it was found that TPPO, TPPS and TPPSe all react quite readily, but under strictly anhydrous conditions, with halides of Nb^V and Ta^V to give adducts (sometimes solvated) with the general formula LMX_5 (L=ligand, M=metal, X=halogen) although some of these complexes may exist in any one of several crystalline forms. For example, TPPO reacts with $TaCl_5$ in dichloromethane under reflux to give the solvated complex $(TPPO)TaCl_5$-$(CH_2Cl_2)_n$. The solvent can be removed from this product by two methods. Thus, washing the solvated adduct with anhydrous acetonitrile leads to α-$(TPPO)TaCl_5$ as a crystalline solid. On the other hand, sublimation of the solvated adduct leads to a different crystalline form β-$(TPPO)TaCl_5$ and this β-phase may also be prepared directly by treatment of TPPO with $TaCl_5$ under reflux in benzene. Similar reactions of TPPO occur with $NbCl_5$ and with the bromides of both Nb^V and Ta^V.

Exposure of $(TPPO)TaCl_5(CH_2Cl_2)_n$ to trace amounts of moisture causes formation of $(TPPO)TaOCl_3$ and it has been shown that the additional oxygen atom is indeed derived from the moisture and not from TPPO [37]. Oxygen abstraction might have been expected in view of Fairbrother's observations [53] that reaction of $NbCl_5$ with Ph_3PO gives $(Ph_3PO)_2NbOCl_3$ with the additional oxygen atom being derived from Ph_3PO, and Millar's findings [54] from thermochemical measurements that the P=O bond strength in phosphole oxides (e.g. 1,2,3,4,5-pentaphenylphosphole oxide (XLIV, X=O; R=Ph)) is considerably less than in most tertiary aryl phosphine oxides. However, even prolonged reflux of $TaCl_5$ or $NbCl_5$ with large excesses of TPPO under strictly anhydrous conditions showed no oxygen abstraction from TPPO.

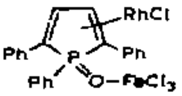
The phosphole sulfide TPPS and the selenide TPPSe both react with Nb^V and Ta^V chlorides. For example, TPPS reacts with a slight excess of $TaCl_5$ in benzene to give $(TPPS)TaCl_5.C_6H_6$. Removal of the solvent (low pressure pumping) leads to the formation of α-$(TPPS)TaCl_5$. A solvated β-phase of this complex may be prepared by heating TPPS and $TaCl_5$ in an exactly 1:1 molar ratio in benzene or dichloromethane. In contrast, similar reactions of TPPSe give only a solvated β-phase regardless of the nature of the solvent and the ratios of the reactants.

Infrared examination of the various adducts described above showed [37] that the P=O, P=S and P=Se stretching vibrations are shifted on coordination to lower values and this confirms that the ligands are linked to the metal atoms through the O, S or Se atoms. However, the shifts are very much smaller (particularly for TPPSe) than for the corresponding triphenylphosphine oxide, sulfide and selenide adducts. This again emphasises that these phosphole derivatives are much weaker σ donors than the corresponding triphenylphosphine derivatives.

In other investigations, studies of the donor character of TPPO, TPPS and TPPSe towards rhodium [39,55], ruthenium [40] and rhenium [41] systems have also been carried out, usually in connection with similar studies of TPP. Thus, treatment of TPPO with rhdoium(III) chloride hydrate in ethanol causes reduction of Rh^{III} to Rh^{I} and yields [55] the interesting dimeric complex $[(TPPO)RhCl]_2$ in which the TPPO ligand, unlike that in the adducts discussed above, is π-bonded to the metal as shown in (XLVI). Other π-complexes of phosphole oxides (e.g. XLV) are known [31,33] but these involve metal carbonyls. The same complex may prepared directly [55] from the rhodium(I) compound $Rh_2Cl_2(CO)_4$ by treatment with TPPO in ethanol



XLVI



XLVII

The wide variety of reactions entered into [55] by (XLVI) is of some interest and the reactions may be divided into those in which the TPPO is retained as a π-complexing ligand on rhodium and those in which the TPPO is displaced. For example, (XLVI) reacts smoothly with $FeCl_3$ to give the monomeric complex (XLVII) which apparently contains three-coordinate rhodium. However, it has been suggested that the fourth coordination site of the rhodium atom is occupied by a chlorine atom of the $FeCl_3$ grouping. No products could be isolated from reactions of (XLVI) with the divalent chlorides of other 3*d* metals.

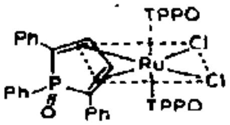
The dimer (XLVI) also reacts [55] with *o*-phenanthroline, pyridine and carbon monoxide to give complexes of the type (TPPO)RhCl.L (bidentate ligand) or $(TPPO)RhCl.L_2$ (monodentate ligand) in which the TPPO remains π-complexed to the rhodium atom. With the monodentate ligands Me_2S and Ph_3P (1:1 in methanol), only the mono-adducts (TPPO)RhCl.L are formed, with potassium acetate the acetate-bridged dimer $[(TPPO)Rh(OAc)]_2$ is obtained and with methanolic triphenylphosphine in the presence of formaldehyde, formation of the mixed ligand adduct $(TPPO)(Ph_3P)RhCl(CO)$ occurs [55]. This last compound is also obtained by treatment of (XLVI) with triphenylphosphine in tetrahydrofuran containing diethyl ether. Reaction of TPP (six-fold excess) with $RhCl_3.3H_2O$ in methanol—chloroform under reflux leads directly [39] to the Rh^I π-complex (TPPO)(TPP)RhCl analogous to (TPPO)(Ph_3P)RhCl mentioned above. In all of these complexes, the ligand TPPO is clearly very strongly bound to the Rh^I atom.

Reactions of (XLVI) in which the π-bonded TPPO ligand is lost include [55] treatment of (XLVI) with diphos where $(diphos)_2RhCl$ is obtained or with a large excess of triphenylphosphine in methanol under reflux where $(Ph_3P)_3RhCl$ is formed.

Relatively little attention has been paid to reactions between rhodium compounds and TPPS. In one study [39] it was found that TPPS reacts with rhodium(III) chloride hydrate in ethanol under reflux to give the Rh^I adduct $(TPPS)RhCl.CH_2Cl_2$ in which, unlike the corresponding TPPO adduct, the phosphole sulfide is σ-bonded to the metal through the sulfur atom. This difference in behaviour between two very similar systems has been attributed [39] to the fact that rhodium is a "class b" acceptor and hence should react more readily with sulfur donors than with oxygen donors. TPPS will also react directly [39] with Rh^I in the form of $Rh_2Cl_2(CO)_4$ to give $(TPPS)RhCl(CO)_2$ which apparently has a square-planar arrangement about the rhodium atom.

Turning to ruthenium systems, the ligands TPPO, TPPS and TPPSe all react [40] smoothly with Ru^{III} chloride hydrate to give adducts of the form L_3RuCl_3 in which the ligand is bound to the metal via the O, S or Se atom — i.e., unlike the Rh^{III} system, no reduction of Ru^{III} occurs and also no cleavage of the P═X bond (X=O, S, Se) occurs, as has been observed [31] in the reactions of phosphole sulfides with iron carbonyls.

Although Ru^{III} is not reduced to Ru^{II} by TPPO, Ru^{II} complexes of this ligand can be formed by direct reaction of TPPO with the blue Ru^{II} methanol solution [47,48] already mentioned to give $(TPPO)_3RuCl_2.EtOH$. This adduct is of some interest since IR spectral data indicate that two of the TPPO ligands are σ-bonded to the ruthenium atom while the third is π-bonded to give a normal 6-coordinate Ru^{II} system as in (XLVIII). Similar experiments [40] with TPPS and TPPSe gave only the L_3RuCl_3 adducts mentioned above. This oxidation of Ru^{II} to Ru^{III} has also been previously observed [48] with other sulfur-containing ligands although the reasons for this behaviour are not clear.



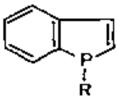
XLVIII

In other attempts [40] to form Ru^{II} complexes of TPPO and TPPS using the red ethanolic ruthenium(II) carbonyl chloride solution [49] previously mentioned, no characterizable compounds could be obtained although, as already mentioned, TPP itself readily forms the adducts *cis* $(TPP)_2Ru(CO)_2Cl_2$.

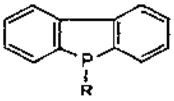
Finally, a brief study [41] of the interaction of phosphole derivatives with the cluster compound rhenium(III) chloride has shown that, as with TPP, both TPPO and TPPSe react with Re_3Cl_9 in dichloromethane without destroying the cluster to give adducts of the type $L_2Re_3Cl_9.CH_2Cl_2$. Thus, only two coordination sites are occupied on the Re_3 cluster while the third is occupied by solvent although Re_3Cl_9 usually forms [51] complexes of the form $L_3Re_3Cl_9$ with a wide variety of ligands. As with TPP, this behaviour presumably reflects the borderline "class b" acceptor nature of rhenium and the steric bulk and weak donor character of the ligands. Rather surprisingly, a similar reaction with TPPS gives no identifiable product.

(v) Dibenzophosphole complexes

Although there have been no reports of complexes of the phosphindole (benzophosphole) system (XLIX), the dibenzophosphole system (L) has received considerable attention during recent years.



XLIX



L

Thus, in a series of four papers, Allen and co-workers [56—59] have thoroughly investigated reactions of dibenzophosphole derivatives with Ni^{II}, Co^{II}, Pd^{II} and Pt^{II} halides and cyanides. In a preliminary report [56] on the first of these studies, it was shown that whereas 5-phenyl-5*H*-dibenzophosphole (L, R=Ph) forms only normal four-coordinate complexes of type L_2MX_2 with NiX_2 (X=Cl, Br, I), $PdBr_2$ and $PtBr_2$, the corresponding 5-alkyl-derivatives (L, R=Me or Et) readily give five-coordinate complexes of the type L_3MX_2 (M=Ni, X=Cl, Br, I; M=Co, Pd, Pt, X=Br). These five-coordinate complexes are all stable in the solid state and many of them are stable in dichloromethane solution while others dissociate according to the equilibrium $L_3MX_2 \rightleftharpoons L_2MX_2 + L$. These complexes therefore strongly resemble in behaviour the analogous complexes of 2-phenylisophosphindoline(III) which have already been discussed at length.

In a later full report on this work [57], the study was extended to include the cyanides and thiocyanates of Ni^{II} and Pt^{II} and the cyanide of Pd^{II}, and it was confirmed that, in general, simple 5-alkyl-5*H*-dibenzophospholes (L, R=Me or Et) readily form with most of these divalent metal salts five-coordinate complexes of the type L_3MX_2, although four-coordinate complexes may be formed in certain instances. It was also reported [57] that although some of these complexes dissociate in dichloromethane solution as mentioned above, as a general rule they do not ionize according to the equilibrium $L_3MX_2 \rightleftharpoons [L_3MX]^+[X]^-$ in polar solvents such as nitrobenzene or ethanol. In this respect, they differ from the corresponding 2-phenylisophosphindoline(III) complexes. The exceptions to this behaviour are the complexes L_3PtX_2 (L=5-ethyl- or 5-methyl-5*H*-dibenzophosphole, X=Br or SCN) where ionization readily occurs in nitrobenzene solution to give solutions of partially ionized complexes for which the conductivity is concentration dependent and approaches that of a 1:1 electrolyte at infinite dilution.

The five-coordinate nickel complexes are of particular interest. For example, it was noted [57] that although most known five-coordinate Ni^{II} complexes (including those involving phosphorus ligands) are diamagnetic, some such complexes containing donor atoms which do readily take part in metal π-bonding are high spin arrangements with magnetic moments of the order of 3.1—3.4 B.M. However, most of the five-coordinate complexes reported in this study [57] (L_3NiX_2, L=5-alkyl-5*H*-dibenzophosphole, X=Cl, Br, I, SCN) have magnetic moments of 0.65—1.5 B.M. These values are intermediate between those expected for a high spin and a low spin arrangement but, as the magnetic moments are independent of temperature, it appears that these intermediate values are not a result of an equilibrium between high spin and low spin forms. On the other hand, the related dicyanato complexes $L_3Ni(CN)_2$ are diamagnetic. The corresponding Co^{II} complexes have normal low spin arrangements since they show magnetic moment values in the range 1.95—2.0 B.M.

Another point of interest regarding the five-coordinate nickel complexes is that two geometrical arrangements (trigonal bipyramidal and tetragonal pyramidal) are possible and, in other known five-coordinate Ni^{II} complexes, both arrangements have been observed [57]. In this connection, it was observed [57] that the visible and near infrared solution spectra of the paramagnetic Ni^{II} complexes of 5-alkyl-5*H*-dibenzophospholes (L_3NiX_2, X=Cl, Br, I, SCN) differ considerably from the solid state spectra (which are very similar for all of the paramagnetic complexes) indicating that the complexes have different structures in solution from those in the solid state. Indeed, the complexity of the solution spectra was taken to indicate [57] that a complex equilibrium involving square planar, five coordinate and tetrahedral complexes operates with the five-coordinate species dominating the equilibrium at lower temperatures. This supports the dissociation in solution inferred from molecular weight studies.

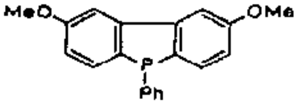
The structures of the related diamagnetic dicyanatotris(5-methyl-) and dicyanatotris(5-ethyl-5*H*-dibenzophosphole)nickel(II) complexes ($L_3Ni(CN)_2$) show several noteworthy characteristics. Thus, the solid state spectra of the two complexes are totally different whereas the dichloromethane solution spectra (where no dissociation occurs) are identical. This suggests that the two complexes have different solid state structures which become identical in solution. This indeed has proved to be the case and, in structural studies, Allen et al. have shown in a brief preliminary report [57] that dicyanatotris-(5-methyl-5*H*-dibenzophosphole)nickel(II) crystallizes from ethanol in a distorted tetragonal pyramidal arrangement. A later, slightly more detailed, communication by the same group [58] confirmed this assignment and showed also that one of the dibenzophosphole ligands occupies the apical position with the two cyano groups mutually *trans* at the base of the pyramid. This communication also reported that the corresponding 5-ethyl-5*H*-dibenzophosphole Ni^{II} complex exists in the solid state in the trigonal bipyramidal arrangement with the two cyano groups occupying the apical positions.

In a still later and much more detailed report, Powell et al. [60] have shown, again by X-ray methods, that the dicyanototris(5-methyl-5*H*-dibenzophosphole)nickel(II) complex can exist in either the tetragonal pyramidal form or the trigonal bipyramidal form depending upon the crystallizing solvent. Thus, crystallization of the complex from chloroform—methanol leads to a trigonal bipyramidal form (with the cyanide groups in the apical positions) in which a molecule of methanol of crystallization interacts weakly with one of the cyanide groups. Furthermore, in both forms of the 5-methyl-5*H*-dibenzophosphole Ni^{II} complex and also the corresponding 5-ethyl- complex, two of the dibenzophosphole ligands are arranged such that the plane of the two ring systems are almost parallel and are overlapping. The degree of overlap varies. For example, with the tetragonal pyramidal 5-methyl- complex, the overlap is almost complete so that one of the ligands almost completely eclipses a second such ligand when viewed from a point above the ring system and perpendicular to the plane of the ligand. With the other (trigonal bipyramidal) 5-methyl- complex and the similar 5-ethyl- complex, the overlap is very much less (only one of the outer benzenoid rings overlaps with a similar ring in the second ligand) although the planes of the two systems are still almost parallel. The authors state [60] that there is no steric requirement for this plane to plane overlap.

Turning to other metal complexes of dibenzophosphole ligands, both five-coordinate complexes analogous to those described above and also some four-coordinate complexes can be obtained [57] from suitable reactions with platinum(II) and palladium(II) halides using 5-methyl- or 5-ethyl-5*H*-dibenzophosphole (L, R = Me or Et) as ligand. However, Pt^{II} and Pd^{II} cyanides will form only the four-coordinate complexes and this has been related [57] to the stabilization of the square planar state by the π-bonding cyanide groups. NMR studies of L_2PtCl_2 (L = 5-methyl-5*H*-dibenzophosphole) have shown that it has the *cis* arrangement in trifluoroacetic acid solution whereas the corresponding Pt^{II} and Pd^{II} cyanide complexes have the *trans* configuration.

It has been suggested [57] that the formation of five-coordinate complexes of divalent Ni, Co, Pt and Pd with 5-alkyl-5*H*-dibenzophosphole (L, R = Me or Et) is due to a favourable combination of both steric and electronic factors which are not present in 5-phenyl-5*H*-dibenzophosphole (L, R = Ph) which will only form four-coordinate complexes. In particular, the steric requirement at the phosphorus atom is stated to be critical and it has been noted [57] that, in general, in those unidentate phosphorus ligands which will form five-coordinate complexes, the substituents on the phosphorus atom provide a favourable balance between σ and π-bonding character. In a later paper, Allen et al. [59] reported the results of an investigation of the effects of variation of the steric and electronic properties of dibenzophosphole ligands of type (L) in reactions with Ni^{II}, Pd^{II} and Pt^{II} dihalides. It was found for example that in 5-alkyl-5*H*-dibenzophospholes (L, R = alkyl), increasing the steric bulk of the alkyl substituent leads to the formation of only four-coordinate complexes as also occurs with the corresponding 5-phenyl- derivative (L, R=Ph). Thus, whereas the 5-methyl- and 5-ethyl- derivatives readily form five-coordinate complexes, the 5-isopropyl- and 5-*tert*-butyl- derivatives will only form four-coordinate complexes. The four-coordinate Ni^{II} chloride complexes are tetrahedral while the square planar $PdBr_2$ complexes of both 5-isopropyl- and 5-*tert*-butyl-5*H*-dibenzophosphole have the *trans* configuration. With the Pt^{II} chloride complexes, that formed with (L, R=isopropyl) has the *cis* configuration while that formed with (L, R=*tert*-butyl) takes up the *trans* arrangement.

In considering electronic effects, these workers suggested [59] the readiness of the simple 5-alkyl-5*H*-dibenzophospholes (L, R=alkyl) to form five-coordinate complexes could at least in part be due to the electron releasing nature of the alkyl substituent. This would make the 5-alkyl- derivatives better donors than 5-phenyl-5*H*-dibenzophosphole (L, R=Ph) which forms only four-coordinate complexes. With this in mind, the donor properties of 2,8-dimethoxy-5-phenyl-5*H*-dibenzophosphole (LI), where the electron density at the phosphorus atom should be appreciably higher than in (L, R=Ph), were studied. However, again only four-coordinate complexes could be obtained and the authors concluded [59] that the steric bulk of the 5-substituent in the dibenzophospholes is of overriding importance in determining which type of complex is formed.



LI

In the most recent study of these five-coordinate complexes of 5-alkyl-5*H*-dibenzophospholes (L, R=Me or Et), Powell and Chui [61] have observed that the plane to plane parallel overlap of two of the dibenzophosphole ligands discussed earlier for the Ni^{II} cyanide complexes is general for the complexes L_3MX_2 (M=Ni, X=CN, L=5-methyl- or 5-ethyl-5*H*-dibenzophosphole; M=Pd, X=Br, L=5-ethyl-5*H*-dibenzophosphole; M=Pt, X=Br, L=5-methyl- or 5-ethyl-5*H*-dibenzophosphole) although the degree of overlap varies according to the complex. These workers also report that the interplanar distance between the two almost parallel dibenzophosphole units is in the range 3.57—3.79 Å which is very similar to that in crystalline aromatic compounds and in related crystalline molecular compounds.

Furthermore, of the six such complexes for which data are reported, one ($L_3Ni(CN)_2$, L=5-methyl-5*H*-dibenzophosphole) exists as a distorted tetragonal pyramid with one of the interacting phosphorus ligands in the apical position, two other complexes (an allogon isomer of the first complex and $L_3Ni(CN)_2$, L = 5-ethyl-5*H*-dibenzophosphole) adopt a distorted trigonal bipyramidal arrangement with all phosphorus ligands disposed equatorially, while the three Pd^{II} and Pt^{II} complexes adopt a distorted tetragonal pyramidal arrangement in which all of the phosphorus ligands are basal. It follows therefore that plane to plane interaction of two of the dibenzophosphole ligands does not dictate any particular geometry for the complexes. However, this interaction does ensure that in the trigonal bipyramidal complexes the P—M—P bond angle for the two interacting phosphorus ligands is much less than the ideal 120° although such an angle could be achieved without difficulty if there were no attractive interaction between the two dibenzophosphole units. Indeed, this interaction leads to bond angle distortions at the metal atom in all of these complexes.

In all such complexes, a plane to plane arrangement of all three phosphorus ligands is sterically impossible.

In other studies, the reactions of 5-phenyl-5*H*-dibenzophosphole (L, R = Ph), abbreviated here to DBP, with a variety of transition metal systems have been investigated. For example, it has been found [39] that DBP (six-fold excess) reacts almost instantaneously with $RhCl_3$ in ethanol to give $(DBP)_3RhCl_3$. In this reaction, the DBP appears to have donor character intermediate between that of triphenylphosphine where rapid formation of the Rh^I species $(Ph_3P)_3RhCl$ (Wilkinson's catalyst) occurs [46], and that of 1,2,5-triphenylphosphole (TPP) where a slower reaction to give the Rh^{III} complex $(TPP)RhCl_3$ takes place [34,39] as already discussed. In this respect then, DBP resembles some tertiary alkyl or aryl alkyl phosphines which readily form [62] complexes of the type L_3RhCl_3 without reduction of the metal. Rh^I complexes of DBP are, however, formed by direct interaction of DBP with suitable Rh^I species. Thus, DBP reacts smoothly [39] with both alcoholic $[RhCl(CO)_2]_2$ and $[RhCl(C_2H_4)_2]_2$ to give $(DBP)RhCl(CO)_2$ and $[(DBP)_2RhCl]_2$ respectively and reaction of the latter complex with a large excess of DBP leads to the formation of the monomeric complex $(DBP)_3RhCl$.

Hydrido—Rh^I complexes of DBP have also been prepared by several methods. For example, reduction of $(DBP)_3RhCl_3$ or $(DBP)RhCl(CO)_2$ with sodium tetrahydroborate in the presence of an excess of DBP gives [63] the orange complex $(DBP)_4RhH$ which is air stable in the solid state although benzene solutions are very oxygen sensitive. Recrystallization of this complex from benzene—ethanol (inert atmosphere) may be carried out with loss of one molecule of ligand to give $(DBP)_3RhH$ which slowly decomposes in air.

Because so many Rh^I—phosphine complexes (notably Wilkinson's catalyst $(Ph_3P)_3RhCl$ [46]) have shown promising homogeneous catalytic activity in a variety of organic reactions such as hydrogenations and hydroformylations, and because DBP is essentially a rigid and flattened form of triphenylphosphine, the homogeneous catalytic activity of these Rh^I—DBP complexes has received considerable attention [39,63]. It has been found that all of the complexes mentioned above do, in fact, show some catalytic activity in hydrogenation reactions but, for most of the complexes, this activity is relatively minor. For example, although $(DBP)_3RhCl$ apparently closely resembles Wilkinson's catalyst, it catalyzes the hydrogenation of *1*-hexene at only about one tenth of the rate of Wilkinson's catalyst. The dimeric complex $[(DBP)_2$-

$RhCl]_2$ is even less active although the activity is easily measurable.

On the other hand, the hydrido complex $(DBP)_4RhH$ is an extremely efficient catalyst [63] for the homogeneous hydrogenation of olefins in oxygen-free benzene at below atmospheric pressure and at room temperature and it is selective for terminal olefins. Thus, in the homogeneous hydrogenation of 1-hexene, $(DBP)_4RhH$ is about seven times as active as Wilkinson's catalyst. The activity is not significantly affected by the chain length of the hydrocarbon and detailed kinetic studies suggested [63] that the reaction proceeds by the following mechanism.

$$
\begin{array}{lcl}
(DBP)_4RhH & \xrightarrow{\text{benzene}} & (DBP)_3RhH + DBP \\
(DBP)_3RhH & \rightleftharpoons & (DBP)_2RhH + DBP \\
(DBP)_2RhH + \text{olefin} & \rightleftharpoons & (DBP)_2(\text{alkyl})Rh \\
(DBP)_2(\text{alkyl})Rh + H_2 & \longrightarrow & (DBP)_2RhH + \text{alkane}
\end{array}
$$

It is also of interest to note that $(DBP)_4RhH$ is considerably more active [63] than the corresponding triphenylphosphine complex $(Ph_3P)_4RhH$. This difference in reactivity has been attributed to the steric bulk and rigid nature of DBP and this in turn strongly suggests that quite minor changes in the nature of the ligand in suitable Rh^{I}—phosphine complexes can cause major changes in catalytic activity.

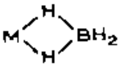
The closely related complex $(DBP)_3RhH$, which is formed by precipitation from a benzene solution of $(DBP)_4RhH$ on addition of ethanol (under N_2), appears [64] (as might be expected from the above hydrogenation mechanism for $(DBP)_4RhH$) to be an even more efficient homogeneous hydrogenation catalyst.

The reactions of DBP with both Ru^{III} and Ru^{II} have also been briefly studied [40] and DBP has been found to react rapidly with $RuCl_3$ hydrate to give the air stable monomeric complex $(DBP)_3RuCl_3$. As with the Rh^{III} reactions already reported, DBP exhibits donor character intermediate between that of triphenylphosphine (which, with an excess of ligand, reduces Ru^{III} to Ru^{II} [65] and that of 1,2,5-triphenylphosphole (TPP) which not only will not reduce Ru^{III} but also reacts very slowly to give $(TPP)_2RuCl_3$ (i.e. one less ligand than with the corresponding DBP reaction). Again, as with the case of Rh^{III}, it has been pointed out [40] that in this respect, the behaviour of DBP (and, for that matter, of TPP) resembles that of some tertiary alkyl phosphines and it has been suggested [40] that the steric factors which apparently normally govern [62c,66] the reduction of Rh^{III} and related systems by tertiary aryl phosphines may not be the only factors involved in the cases of DBP and TPP and that electronic effects may also have to be taken into consideration.

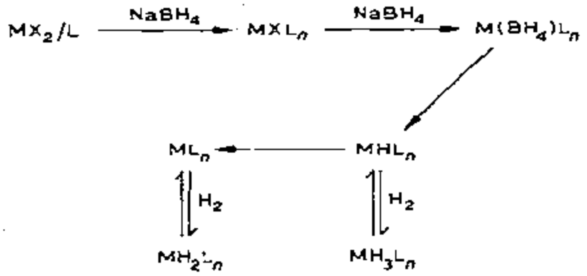
Although Ru^{III} is not reduced by DBP, a variety of Ru^{II}—DBP complexes may be prepared [40] by several methods. Thus, DBP reacts with the methanolic Ru^{II} blue solution [47,48] containing $[Ru_6Cl_{12}]^{2-}$ (already mentioned in connection with phosphole complexes) to give $(DBP)_3RuCl_2$. If the reaction is carried out in ethanol, $(DBP)_4RuCl_2$ is obtained. Similar reactions of DBP with the red ethanolic Ru^{II} carbonyl solution [49] (again already mentioned in connection with TPP complexes) give $(DBP)_3RuCl_2(CO)$. The air sensitive hydrido—Ru^{II} complex $(DBP)_4RuH_2$ is formed when boiling ethanolic $RuCl_3$ hydrate is treated with DBP (six-fold excess) followed by addition of $NaBH_4$. Further reaction of this complex with dry HCl gives the chloro—hydrido Ru^{II} complex $(DBP)_3RuHCl$ and the closely related compound $(DBP)_3RuHCl(CO)$ may be prepared by prolonged reflux of ethanolic $(DBP)_4$-$RuCl_2$ with $NaBH_4$. There appears to be nothing remarkable about any of these Ru^{II}—DBP complexes, which are quite similar to Ru^{II} complexes of other ligands [40].

In related studies, brief mention has been made [41] of the reaction of Re^{III} chloride with DBP. Reaction of the DBP ligand with Re_3Cl_9 in dichloromethane gives $(DBP)_2Re_3Cl_9.CH_2Cl_2$ — i.e. a complex in which only two of the three possible coordination sites are occupied by DBP ligands. This behaviour is virtually identical to that of TPP, TPPO and TPPSe already discussed.

Finally, the reactions of DBP (together with those of triphenylphosphine and other phosphines) with several transition metal halides in the presence of sodium tetrahydroborate ($NaBH_4$) or sodium cyanotrihydroborate ($NaBH_3CN$) have also received some attention [67—69] in attempts to stabilize uncommon oxidation states of these metals. Thus, it was shown in a series of studies [67—69] devoted mainly to inert atmosphere (N_2) reactions of triphenylphosphine with transition metal systems under mild conditions in the presence of BH_4^- or BH_3CN^-, that Ph_3P and DBP will enter into a wide variety of reactions leading to complexes in which the oxidation state of the metal remains unchanged, complexes in which the metal has been reduced and complexes which contain coordinated BH_4 or BH_3CN as well as the phosphine ligand. The results obtained with DBP are summarized in Fig. 2. It was also found that direct reaction of DBP/BH_4^- or DBP/BH_3CN^- with the chlorides of Fe^{III}, Rh^{III}, Ir^{IV}, Pd^{II}, Pt^{II} and Cr^{III} gives no identifiable product. Furthermore, infrared spectroscopic evidence indicates [67,69] that in the tetrahydroborate complexes, the BH_4 grouping is, as expected, chelated to the metal to give units of the type



Numerous other complexes of Ph_3P and diphos, mainly closely related to the DBP complexes recorded in Fig. 2 but also including Ni^I—BH_4—phosphine and Co^I—BH_4—phosphine complexes, were also obtained under various carefully controlled conditions [67—69]. Details of these other reactions are outside the scope of this review but, on the basis of the results obtained with Ph_3P and DBP, the following mechanism for the stepwise reduction of divalent transition metal halides by BH_4^- in the presence of phosphines was proposed [68,69].



Steric requirements in some of these reactions appear to be critical. For example, although triphenylphosphine and DBP have very similar donor character, under appropriate conditions Ph_3P will form tetrahydroborate complexes of the type $L_3M(BH_4)$ ($L=Ph_3P$, M=Cu, Ni, Co) which are isolable whereas in the corresponding DBP reactions, the Ni^I—BH_4—phosphine and Co^I—BH_4—phosphine complexes are highly unstable and only $(DBP)_3Cu(BH_4)$ can be isolated. In the DBP reactions, zero-valent or hydrido-metal species (such as $(DBP)_4Ni$) appear to be formed more readily. These differences in stability of the various intermediates in these reactions have been attributed [69] to the somewhat rigid geometry of DBP. Also, whereas two isomeric forms of $(Ph_3P)_3Cu(BH_3CN)$ in which the BH_3CN grouping is bonded to the Cu^I atom either through one hydrogen atom (L_3Cu—H—BH_2CN) or through the nitrogen atom (L_3Cu—$NCBH_3$) are readily prepared [69], only the *N*-

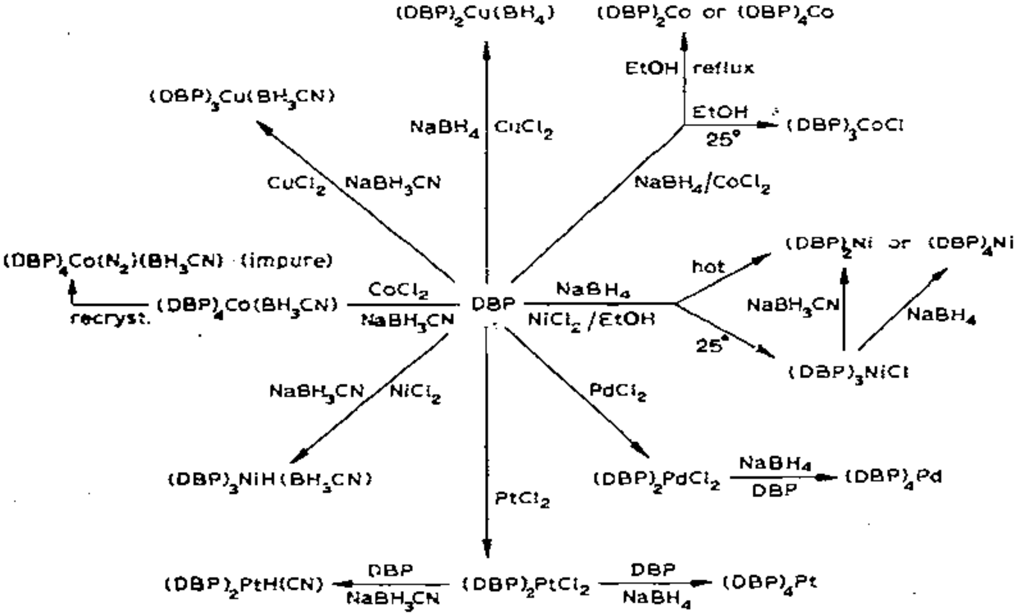
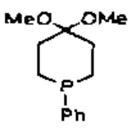


Fig. 2. Reactions of DBP with transition metal chlorides in the presence of BH_4^- or BH_3CN^-.

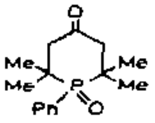
bonded isomer of $(DBP)_3Cu(BH_3CN)$ may be prepared regardless of the conditions employed. This too has been attributed [69] to the geometrical rather than the donor character differences between Ph_3P and DBP.

D. COMPLEXES OF SIX- AND SEVEN-MEMBERED CYCLIC PHOSPHINE DERIVATIVES

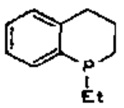
In comparison with the studies of metal complexes of five-membered cyclic phosphine derivatives discussed in the previous section, relatively few such studies of six- and seven-membered cyclic phosphines have been made although the results of some of these investigations are of considerable interest. Systems which have received attention are the phosphorinane (LII), the phosphorinanone oxide (LIII), the related fused ring compounds (LIV) and (LV), the particularly interesting λ^3-phosphorin (LVI), the tricyclic system (LVII) and the dihydrodibenzophosphepin (LVIII).



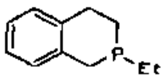
LII



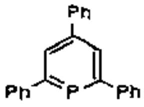
LIII



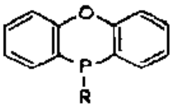
LIV



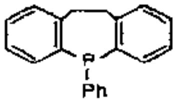
LV



LVI



LVII



LVIII

McPhail et al. have shown in two studies [70] that 1-phenyl-phosphorinanes of type (LII) and the corresponding 1-phenyl-4-phosphorinanones adopt a flattened chair conformation in the solid state with the *P*-phenyl group in the axial position. NMR studies indicate that this conformational arrangement also predominates in solution. In extending these conformational studies to metal complexes of phosphorinane derivatives in order to determine the conformational effects of complexation, McPhail et al. [71,72] have prepared and determined the crystal and molecular structure of dichlorobis-(4,4-dimethoxy-1-phenylphosphorinane) nickel(II) ($(phos)_2NiCl_2$ where phos = the phosphorinane ligand LII).

A preliminary X-ray crystallographic analysis [71] of the dark red complex established that, as would be expected, there is a square planar arrangement about the nickel atom with the two 4,4-dimethoxy-1-phenylphosphorinane (LII) ligands in the chair conformation and mutually *trans*. However, rather surprisingly, it was also established that in one of the phosphorinane ligands, the *P*-phenyl group occupies an axial position while in the other it occupies an equatorial position. Moreover, it was found that the ring puckering at the phosphorus atom in the ligand with the equatorial phenyl group is considerably greater than in the other ligand where the axial phenyl group causes flattening of the ring through 1,3-diaxial interactions.

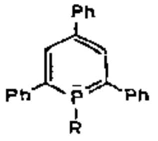
In a more detailed report [72], it was also shown that for $(phos)_2NiCl_2$, whereas the Cl—Ni—Cl grouping is virtually linear (179.4°), the P—Ni—P grouping departs significantly from linearity (175.0°) as a result of non-bonded intramolecular repulsions. Examination of molecular models of the complex showed no additional significant non-bonding phosphorinane—phosphorinane interactions when the *P*-phenyl substituents in the two ligands are similarly arranged (i.e. both axial or both equatorial). It was therefore concluded [72] that neither conformation (axial or equatorial) is particularly favoured in the complex and that the two different arrangements observed in the crystalline complex are due to crystal packing forces.

In passing, it is worth noting that the behaviour of 4,4-dimethoxy-1-phenylphosphorinane (LII) towards nickel(II) chloride is entirely different from that of the similar five-membered ring ligand 1-benzyl-3-phospholene where the complex *cis* L_2NiCl_2 is formed [12] in which (as already discussed) there are major departures from linearity in the Cl—Ni—P unit.

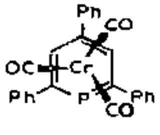
With respect to 4-phosphorinanone derivatives, there are apparently no reports of metal complexes in which coordination is through the phosphorus atom. However, there is one very brief mention [73] of a metal complex of a 4-phosphorinanone-1-oxide in a paper devoted mainly to organic reactions of the phosphorinanone corresponding to the oxide (LIII). Thus, the oxide (LIII) reacts smoothly in absolute ethanol with anhydrous cobalt(II) chloride to give L_2CoCl_2 in which the ligand is bound to the cobalt through the oxygen atom in a tetrahedral arrangement. No further details were given.

Likewise, complexes of 1-ethyl-1,2,3,4-tetrahydrophosphinoline (LIV) and 2-ethyl-1,2,3,4-tetrahydroisophosphinoline (LV) have received only passing mention [74] in a paper primarily concerned with the synthesis of these two phosphorus heterocycles. It was found that both of these cyclic phosphines with potassium tetrabromopalladate(II) give adducts of the type L_2PdBr_2. Again, no further details were given.

Undoubtedly by far the most interesting of the six-membered cyclic phosphines for which coordination studies have been undertaken is the λ^3-phosphorin system of which 2,4,6-triphenyl-λ^3-phosphorin (LVI) is an example. Although a detailed discussion is outside the scope of this review, the reasons why this system is of particular interest are briefly as follows. Unlike other tertiary phosphines, the phosphorus atom of λ^3-phosphorins appears to have virtually no nucleophilic character in organic reactions even though the phosphorus lone pair (like the nucleophilic lone pair of the nitrogen atom in the apparently analogous pyridine system) is not required for the aromatic sextet. Thus, 2,4,6-triphenyl-λ^3-phosphorin (LVI) will not react with alkylating agents [75] to form quaternary phosphorinium salts neither will it react [76] with the strongly electrophilic dimethyl acetylenedicarboxylate even though tertiary phosphines such as triphenylphosphine react [77] virtually instantaneously with this electrophile at −50°. Clearly, there is something unusual about the electronic structure of the λ^3-phosphorin system and this is emphasized by the observation that although (LVI) does not have the nucleophilic character which superficially might be expected by analogy with other tertiary phosphines and with pyridine, it does in fact have quite good electrophilic character and will undergo addition reactions at the phosphorus atom with organolithium compounds to give anions of type (LIX).



LIX



LX

Schweig and co-workers [4,78] have carried out several investigations of the electronic structure of λ^3-phosphorins by CNDO/2 calculations and by photoelectron spectroscopic studies on suitable λ^3-phosphorin derivatives. The more important conclusions arrived at from these studies are that there is an important $3p_z$ contribution to the P—C π-bonding which also has a significant $3d$ component, the phosphorus lone-pair orbital is the second highest occupied molecular orbital (unlike the analogous pyridine system where the nitrogen lone pair is in the highest occupied orbital) and the highest occupied M.O. is a π-orbital. Furthermore, the phosphorus lone-pair orbital is more diffuse, less directional and has greater s character than the corresponding orbital in pyridine and the energy sequence of the three ground state π-orbitals is different from that in pyridine. Finally, CNDO/2 estimates of the basicity of the phosphorus atom in λ^3-phosphorins give the extraordinarily low value of $\mathrm{p}K_a = -10$ (c.f. triphenylphosphine, $\mathrm{p}K_a = 2.73$; trialkylphosphines, $\mathrm{p}K_a =$ ca. 8).

In view of the unusual nature of the λ^3-phosphorin system, there have been several studies of metal complex formation. In the first of these [79], chromium(0) hexacarbonyl was treated with the phosphorin (LVI) in boiling dibutyl ether to give the red-brown complex tricarbonyl(2,4,6-triphenyl-λ^3-phosphorin)chromium(0) in moderate yield. The IR, NMR and mass spectra of this complex were interpreted in terms of π-bonding of the phosphorin ring to the $Cr(CO)_3$ grouping and this was confirmed in a later X-ray crystallographic study [80] which shows the structure to be as shown in (LX) with the chromium atom centrally located above the plane of the phosphorin ring. The geometry of the arrangement together with the rather long P—Cr distance (2.48 Å) was taken to indicate [80] that the adduct is an example of a true aromatic complex.

These results are not unexpected since other studies [4,78] have shown the λ^3-phosphorin system to be a fully delocalized six π-electron aromatic system and it is well known that Cr^0 species are particularly suited to π-complex formation with such systems.

In a later study, Fraser et al. [81] investigated the reactions of 2,4,6-triphenyl-λ^3-phosphorin (LVI) with halides of transition metals in various oxidation states where π-complex formation would not normally be expected to occur. It was found that under certain conditions, the λ^3-phosphorin can in fact have quite strong σ donor character through the phosphorus atom although this would not be expected in view of the extremely low basicity calculated for the phosphorus atom and the virtually non-existent nucleophilic character of the λ^3-phosphorin system in organic reactions already discussed. For example, the phosphorin (LVI) readily reacts with MCl_5 (M=Nb or Ta) to give $LMCl_5$ (L=2,4,6-triphenyl-λ^3-phosphorin), with $PdCl_2$ to give $LPdCl_2$ or L_2PdCl_2 depending upon the reactant proportions, and with $(C_2H_4)_4$-Rh_2Cl_2 to give the Rh^I complex $L_4Rh_2Cl_2$. Furthermore, not only does the phosphorin (LVI) have apparently fairly normal tertiary phosphine donor character under these conditions, it will also reduce certain transition metal species to lower oxidation states in the manner of a typical tertiary aryl phosphine. Examples of this behaviour are the treatment of phosphorin with copper(II) chloride to give LCuCl (L = the phosphorin LVI), with rhodium(III) chloride to give L_3RhCl (analogous to Wilkinson's catalyst [46]) and with ruthenium(III) chloride to give L_2RuCl_2. No reactions were observed to occur with nickel(II) chloride or rhenium(III) chloride.

This behaviour has been interpreted [81] as being due to perturbation by the transition metal species of the orbital sequence in the free phosphorin ligand which then behaves like a normal tertiary phosphine and enters into σ complex formation.

Very recently, Nöth and co-workers have extended their original studies [79,80] (already discussed) on the reactions of the phosphorin (LVI) with chromium(0) hexacarbonyl and have made three further reports [82—84] on similar reactions involving Cr^0, Mo^0 and W^0 carbonyls under a variety of conditions. These studies have shown that σ-bonding as well as π-bonding of the phosphorin ligand may occur with various metal carbonyl species depending upon the conditions used. Thus, 2,4,6-triphenyl-λ^3-phosphorin (LVI) has been found to react [82] with the hexacarbonyls of Cr^0, Mo^0 and W^0 in tetrahydrofuran under photochemical excitation with a high pressure mercury lamp to give the corresponding 2,4,6-triphenyl-λ^3-phosphorin-metal(0) pentacarbonyl in moderate yield (40—55%) according to the following scheme.

$$C_{23}H_{17}P + M(CO)_6 \xrightarrow[THF]{h\nu} (C_{23}H_{17}P)M(CO)_5$$

Somewhat better yields and purer products are obtained, however, if preliminary irradiation of the $M(CO)_6$ in dry tetrahydrofuran is carried out for 1—3 h and then followed by addition of the phosphorin and heating under reflux of the resulting mixture. In this method, the ligand displacement reaction shown below occurs. This second method is particularly useful in the case of tungsten(0) hexacarbonyl where use of the first procedure also gives

$$C_{23}H_{17}P + (THF)M(CO)_5 \xrightarrow[THF]{} (C_{23}H_{17}P)M(CO)_5$$

rise to significant quantities of the bis(2,4,6-triphenyl-λ^3-phosphorin)-tungsten(0) tetracarbonyl complex $(C_{23}H_{17}P)_2W(CO)_4$.

These bis(2,4,6-triphenyl-λ^3-phosphorin)-metal(0) tetracarbonyl complexes $[(C_{23}H_{17}P)_2M(CO)_4]$ are also readily prepared [82] for all three metals by treatment of the corresponding norbornadienyl-metal(0) tetracarbonyl with the phosphorin and also, in the case of tungsten, by similar treatment of bis-(acetonitrile)tungsten(0) tetracarbonyl. Yields are high (ca. 60%) in this reaction and the products are easily isolated.

Deberitz and Nöth [82] have carried out a detailed analysis of the IR, electronic, ^1H and ^{31}P NMR and mass spectra for both $(C_{23}H_{17}P)M(CO)_5$ and $(C_{23}H_{17}P)_2M(CO)_4$ and have concluded that all of the evidence is consistent with σ-bonding of the ligand to the metal atom through the lone pair of the phosphorus. They also stated that, under these conditions, the phosphorin acts as a weakly basic ligand.

That the phosphorin ligand in $(C_{23}H_{17}P)Cr(CO)_5$ is indeed bonded through the lone pair has been confirmed very recently [83] by an X-ray crystallographic analysis. This study has shown that the P—Cr bond is relatively short at 2.37 Å (slightly shorter than in the corresponding triphenylphosphine complex), the heterocyclic ring remains planar in the complex with the ring dimensions very similar to those of uncomplexed λ^3-phosphorins and, rather unexpectedly, the P—Cr bond is inclined at an angle of 8° to the plane of the phosphorin ring.

Finally, Deberitz and Nöth have reported [84] that the π-complex tricarbonyl(2,4,6-triphenyl-λ^3-phosphorin)molybdenum(0), analogous to $(C_{23}H_{17}P)$-$Cr(CO)_3$ already discussed, cannot be prepared in the same manner as the chromium complex by treatment of $Mo(CO)_6$ with the phosphorin in boiling dibutyl ether since decomposition and precipitation of the metal occurs. However, this molybdenum(0) π-complex may be prepared [84] by two other methods. The first of these involves a ligand displacement reaction in which tricarbonyl(mesitylene)molybdenum(0) in dry THF is treated with the phosphorin at room temperature to give the desired adduct. The second procedure is an intramolecular process in which the σ-adduct $(C_{23}H_{17}P)Mo(CO)_5$ is heated in dibutyl ether to give $(C_{23}H_{17}P)Mo(CO)_3$. The yield in the first reaction is moderate (45%) while that in the second reaction is excellent (90%). Again, spectroscopic data strongly indicate π-bonding of the phosphorin ligand to the molybdenum atom.

In conclusion, turning to other phosphorus heterocyclic systems, there have been only brief reports of metal complexes of the six-membered cyclic phosphine (LVII) and the seven-membered ligand (LVIII). Both of these systems are discussed in the same paper [59] in relation to the five-coordinate Ni^{II}, Pd^{II} and Pt^{II} complexes formed by 5-alkyl-5*H*-dibenzophospholes (L, R=alkyl) and the related four-coordinate complexes formed by 5-phenyl-5*H*-dibenzophosphole (L, R=Ph) already discussed in the previous section. In this connection, it was found that 10-methyl-10-phenoxaphosphine (LVII), (R=Me) also readily forms five-coordinate complexes of the type L_3MX_2 (L=the phenoxaphosphine ligand) with Ni^{II} chloride, Pd^{II} bromide and Pt^{II} chloride in ethanol. These adducts are extensively dissociated in dichloromethane solution. These complexes closely resemble the corresponding 5-alkyl-5*H*-dibenzophosphole complexes and it would appear that the increase in ring size therefore has little effect upon the type of complex formed.

Similar complexes are formed by 10-ethyl-10-phenoxaphosphine with Ni^{II} bromide and iodide but with Ni^{II} chloride and thiocyanate, Pd^{II} bromide and Pt^{II} chloride, only four-coordinate square-planar complexes are formed. It is interesting to note here that the four-coordinate complex L_2NiI_2, which is also easily prepared, is tetrahedral and paramagnetic whereas the complex L_2NiCl_2 is square-planar and diamagnetic. With 10-phenyl-10-phenoxaphosphine (LVII, R=Ph), only four-coordinate complexes are formed. Thus, the tendency of the system (LVII) to form five-coordinate complexes is somewhat less than that of the 5-alkyl-5*H*-dibenzophospholes (L, R=alkyl).

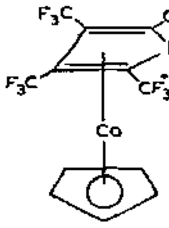
In similar studies [59] on 10,11-dihydro-5-phenyl-5*H*-dibenzo[*b*,*f*]-phosphepin (LVIII), it was found that only four-coordinate complexes are formed with Ni^{II} halides. This is not unexpected in view of the *P*-phenyl substituent which blocks formation of five-coordinate complexes when 5-phenyl-5*H*-dibenzophosphole (L, R=Ph) is used. However, the four-coordinate complexes formed between NiX_2 and the phosphepin (LVIII) are square planar and diamagnetic whereas the analogous complexes formed with the *P*-phenyl ligands triphenylphosphine, 5-phenyl-5*H*-dibenzophosphole and 10-phenyl-10-phenoxaphosphine are all tetrahedral and paramagnetic. Indeed, it was claimed [59] that these NiX_2 complexes of (LVIII) were the first examples of square-planar Ni^{II} complexes formed by a triarylphosphine.

E. ADDENDUM

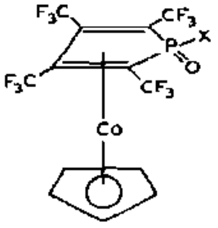
Since the major portion of this review was prepared, several other reports on various aspects of complexes of transition metal with cyclic phosphine derivatives have appeared. For example, in a recent report from the patent literature regarding 3-phospholene (IX) derivatives, it has been shown [85] that 3-phospholene—Pd^0 complexes (such as tetrakis(1-ethyl-3-methyl-3-phospholene)palladium(0)) catalyze the reaction between methyl acetocetate and isoprene to give methyl α-prenylacetoacetate.

There are also two reports [86,87] on the use of 1-alkoxy-2-phospholene-1-oxides (derivatives of VIII) and 1-alkoxy-3-phospolene-1-oxides (derivatives of IX) in the extraction of gold and silver by complexation from solutions of their salts. The degree of extraction apparently increases with increasing length of the alkoxy chain and, in general, appears to be more efficient with the 2-phospholene-1-oxides. The process is particularly useful for the recovery of gold from commercial cyanide solutions and the gold is re-extracted from the phospholene oxide complexes by treatment with $Na_2S_2O_3$ followed by acidification [87].

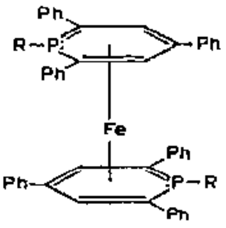
Regarding other cyclic phosphine systems, π-phosphole and phosphole oxide complexes of cobalt have been synthesized [88] by an unusual method in which the phosphole ring is constructed by addition of hexafluoro-2-butyne to the phosphorus trifluoride—cobalt cyclopentadienyl complex (π-C_5H_5)Co(PF_3)$_2$. This gives the complex (LXI) which, on hydrolysis, gives (LXII; X = F or OH). Similar thiophene complexes may be prepared by treatment of suitable manganese carbonyl—sulfur ligand complexes with hexafluoro-2-butyne. The complex (LXI) is unusual not only in the method of formation but also in that it is the only known simple phosphole derivative containing 5-coordinate phosphorus. This phosph(V)ole type of structure has been postulated for several other phosphorus compounds synthesized by various methods but all such structures have since been revised [25,89].



LXI



LXII



LXIII

Finally, two further papers have recently appeared on complexes of the phosphorin derivatives (LVI) and (LIX). Thus, 2,4,6-triphenylphosphorin (LVI) will coordinate [90] to gold(I) chloride and iodide through the phosphorus non-bonding electron pair in a manner similar to that previously observed for a variety of metal halides [81] and carbonyls [82]. In a development of this work, Märkl and Martin [91] have treated iron(II) chloride with the anion (LIX) and the corresponding *P*-methyl derivative (under conditions similar to those used in the formation of ferrocene) to give π-complexes of the type (LXIII (R = Ph or Me). Strong evidence for the π-bonded structure is provided by the ^{31}P and ^{1}H NMR spectra of both complexes which appear to be inconsistent with possible σ-bonded structures. Similar reactions were carried out between (LIX) and its corresponding *P*-methyl derivative with silver nitrate and mercury(II) acetate. In both cases, (LVI) is regenerated and it is thought possible that σ-complexes containing P—Ag or P—Hg bonds may play a part in these reactions.

ACKNOWLEDGEMENTS

We thank the National Research Council of Canada for their generous financial support of this work, and one of us (A.N.H.) gratefully acknowledges sabbatical leave facilities provided by the Faculty of Science, Mahidol University, Bangkok 4, Thailand.

REFERENCES

1 See, for example, L.D. Quin, J.G. Bryson and C.G. Moreland, J. Amer. Chem. Soc., 91 (1969) 3308.
2 W. Egan, R. Tang, G. Zon and K. Mislow, J. Amer. Chem. Soc., 92 (1970) 1442; 93 (1971) 6205.
3 W. Schäfer, A. Schweig, G. Märkl, H. Hauptmann and F. Mathey, Angew. Chem. Int. Ed., 12 (1973) 145.
4 A. Schweig, W. Schäfer and K. Dimroth, Angew. Chem. Int. Ed., 11 (1972) 631.
5 R. Bausch, E.A.V. Ebsworth and D.W.H. Rankin, Angew. Chem. Int. Ed., 10 (1971) 125.
6 R.I. Wagner, L.V.D. Freeman, H. Goldwhite and D.G. Rowsell, J. Amer. Chem. Soc., 89 (1967) 1102.
7 T.H. Siddall, R.L. McDonald and W.E. Stewart, J. Mol. Spectrosc., 28 (1968) 243.
8 G. Grüttner and E. Krause, Chem. Ber., 49 (1916) 437.
9 F.G. Mann, The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony and Bismuth, 2nd Ed., Wiley—Interscience, New York, 1970 p. 51.
10 Shell Internationale Research Maatschappij, N.V., Netherlands Patent Application 6,516,164 (1966); Chem. Abstr., 66 (1967) 28392r.
11 L.D. Quin, J.H. Somers and R.H. Prince, J. Org. Chem., 34 (1969) 3700.
12 A.T. McPhail, R.C. Komson, J.F. Engel and L.D. Quin, J. Chem. Soc., Dalton, (1972) 874.
13 L.D. Quin, J.G. Bryson and J.F. Engel, Phosphorus, 2 (1973) 205.
14 J.P. Fackler, J.A. Fetchin, J. Mayhew, W.C. Seidel, T.J. Swift and M. Weeks, J. Amer. Chem. Soc., 91 (1969) 1941.
15 F.G. Mann and I.T. Millar, J. Chem. Soc., (1951) 2205.
16 J.W. Collier, F.G. Mann, D.G. Watson and H.R. Watson, J. Chem. Soc., (1964) 1803.
17 F.G. Mann, I.T. Millar and F.H.C. Stewart, J. Chem. Soc., (1954) 2832.
18 F.G. Mann and H.R. Watson, Chem. Ind., (1958) 1264.
19 J.W. Collier and F.G. Mann. J. Chem. Soc., (1964) 1815.
20 J.W. Collier, A.R. Fox, I.G. Hinton and F.G. Mann, J. Chem. Soc., (1964) 1819.
21 F.G. Mann, D. Purdie and A.F. Wells, J. Chem. Soc., (1936) 1503.
22 F.G. Mann, A.F. Wells and D. Purdie, J. Chem. Soc., (1937) 1828.
23 M.F. Perutz and O. Weisz, J. Chem. Soc., (1946) 438.
24 For a brief discussion regarding the aromatic character of pyrroles and related heterocyclopentadienes see L.A. Paquette, Modern Heterocyclic Chemistry, W.A. Benjamin, New York, 1968 Chap. 4.
25 A.N. Hughes and C. Srivanavit, J. Heterocycl. Chem., 7 (1970) 1.
26 W.B. Farnham and K. Mislow, Chem. Commun., (1972) 469.
27 G. Märkl and R. Potthast, Tetrahedron Lett, (1968) 1755.
28 F. Mathey and R. Mankowski-Favelier, Org. Magn. Resonance, 4 (1972) 171.
29 T. Bundgaard and H.J. Jakobsen, Tetrahedron Lett, (1972) 3353.
30 P. Coggon, J.F. Engel, A.T. McPhail and L.D. Quin, J. Amer. Chem. Soc., 92 (1970) 5779.
31 E.H. Braye and W. Hübel, Chem. Ind., (1959) 1250; E.H. Braye, W. Hübel and I. Caplier, J. Amer. Chem. Soc., 83 (1961) 4406.
32 B.J. Hallam and P.L. Pauson, J. Chem. Soc., (1958) 642; T.A. Manuel and F.G. Stone, Proc. Chem. Soc., (1959) 90; R. Pettit, J. Amer. Chem. Soc., 81 (1959) 1266; E. Weiss and W. Hübel, J. Inorg. Nucl. Chem., 11 (1959) 42.
33 R.C. Cookson, G.W.A. Fowles and D.K. Jenkins, J. Chem. Soc., (1965) 6406.
34 R.A. Walton, J. Chem. Soc. A, (1966) 365.
35 M.A. Bennett and P.A. Longstaff, Chem. Ind., (1965) 846.
36 I.G.M. Campbell, R.C. Cookson, M.B. Hocking and A.N. Hughes, J. Chem. Soc., (1965) 2184.

37 D. Budd, R. Chuchman, D.G. Holah, A.N. Hughes and B.C. Hui, Can. J. Chem., 50 (1972) 1008.

38 R. Chuchman, D.G. Holah, A.N. Hughes and B.C. Hui, J. Heterocycl. Chem., 8 (1971) 877.

39 D.G. Holah, A.N. Hughes and B.C. Hui, Can. J. Chem., 50 (1972) 3714.

40 D.G. Holah, A.N. Hughes, B.C. Hui, N. Krupa and K. Wright, Phosphorus, in press.

41 D.G. Holah, A.N. Hughes and K. Wright, Inorg. Nucl. Chem. Lett., 9 (1973) 1265.

42 G. Booth, Adv. Inorg. Radio Chem., 6 (1964) 1.

43 L.D. Quin, S.G. Borleske and J.F. Engel, J. Org. Chem., 38 (1973) 1858.

44 R.S. Nyholm, J. Chem. Soc., (1952) 1257; K. Cohn and R.W. Parry, Inorg. Chem., 7 (1968) 46.

45 Y. Chiang and E.B. Whipple, J. Amer. Chem. Soc., 85 (1963) 2763.

46 F.H. Jardine, J.A. Osborn and G. Wilkinson, J. Chem. Soc. A, (1966) 1711.

47 D. Rose and G. Wilkinson, J. Chem. Soc. A, (1970) 1791.

48 J.D. Gilbert, D. Rose and G. Wilkinson, J. Chem. Soc. A, (1970) 2765.

49 J. Chatt, A.E. Field and B.L. Shaw, J. Chem. Soc., (1964) 3466;
T.A. Stevenson and G. Wilkinson, J. Inorg. Nucl. Chem., 28 (1966) 945.

50 L.M. Venanzi, Chem. Brit., 4 (1968) 162.

51 See, for example, R.A. Walton, Prog. Inorg. Chem., 16 (1972) 1, and references cited therein.

52 D.A. Usher and F. Westheimer, J. Amer. Chem. Soc., 86 (1964) 4732.

53 See, for example, D.B. Copley, F. Fairbrother and A. Thompson, J. Less-Common Metals, 8 (1965) 256.

54 A.F. Bedford, D.M. Heineky, I.T. Millar and C.T. Mortimer, J. Chem. Soc., (1962) 2932.

55 D.G. Holah, A.N. Hughes and B.C. Hui, Can J. Chem., 50 (1972) 2442.

56 D.W. Allen, F.G. Mann and I.T. Millar, Chem. Ind., (1966) 2096.

57 D.W. Allen, I.T. Millar and F.G. Mann, J. Chem. Soc. A, (1969) 1101.

58 D.W. Allen, F.G. Mann, I.T. Millar, H.M. Powell and D. Watkin, Chem. Commun. (1969) 1004.

59 D.W. Allen, F.G. Mann and I.T. Millar, J. Chem. Soc. C, (1971) 3937.

60 H.M. Powell, D.J. Watkin and J.B. Wilford, J. Chem. Soc., A, (1971) 1803.

61 H.M. Powell and K.M. Chui, Chem. Commun., (1971) 1037.

62 a J. Chatt, N.P. Johnson and B.L. Shaw, J. Chem. Soc., (1964) 2508; b R.G. Hayter, Inorg. Chem., 3 (1964) 301; c G.M. Intille, Inorg. Chem., 11 (1972) 695.

63 D.E. Budd, D.G. Holah, A.N. Hughes and B.C. Hui, Can. J. Chem., 52 (1974) 775.

64 D.G Holah, I.M. Hoodless, A.N. Hughes, B.C. Hui and D. Martin, Can. J. Chem., 52 (1974) 3758.

65 L. Vaska, Chem. Ind., (1961) 1402; J.F. Young, J.A. Osborn, F.H. Jardine and G. Wilkinson, Chem. Commun., (1965) 13.

66 C. Masters, B.L. Shaw and R.E. Stainbank, Chem. Commun., (1971) 209.

67 D.G. Holah, A.N. Hughes, B.C. Hui and K. Wright, Inorg. Nucl. Chem. Lett., 10 (1974) 427.

68 D.G. Holah, A.N. Hughes and B.C. Hui, Inorg. Nucl. Chem. Lett., 9 (1973) 1265.

69 D.G. Holah, A.N. Hughes, B.C. Hui and K. Wright, Can. J. Chem., 52 (1974) 2990.

70 A.T. McPhail, J.J. Breen and L.D. Quin, J. Amer. Chem. Soc., 93 (1971) 2574;
A.T. McPhail, J.J. Breen, J.H. Somers, J.C.H. Steele and L.D. Quin, Chem. Commun., (1971) 1020.

71 A.T. McPhail, J.J. Breen, J.C.H. Steele and L.D. Quin, Phosphorus, 1 (1972) 255.

72 A.T. McPhail and J.C.H. Steele, J. Chem. Soc., Dalton, 1972, 2680.

73 F. Asinger, A. Saus and E. Michel, Monatsh., 99 (1968) 1695.

74 M.H. Beeby and F.G. Mann, J. Chem. Soc., (1951) 411.

75 G. Märkl, F. Lieb and A. Merz, Angew. Chem. Int. Ed., 6 (1967) 87.

76 G. Märkl and F. Lieb, Angew. Chem. Int. Ed., 7 (1968) 733.

77 A.W. Johnson and J.C. Tebby, J. Chem. Soc., (1961) 2126.

78 H. Oehling, and A. Schweig, Tetrahedron Lett., (1970) 4941; H. Oehling, W. Schäfer and A. Schweig, Angew. Chem. Int. Ed., 10 (1971) 656; H. Oehling and A. Schweig, Phosphorus, 1 (1972) 203.

79 J. Deberitz and H. Nöth, Chem. Ber., 103 (1970) 2541.

80 H. Vahrenkamp and H. Nöth, Chem. Ber., 105 (1972) 1148.

81 M. Fraser, D.G. Holah, A.N. Hughes and B.C. Hui, J. Heterocycl. Chem., 9 (1972) 1457.

82 J. Deberitz and H. Nöth, J. Organometal. Chem., 49 (1973) 453.

83 H. Vahrenkamp and H. Nöth, Chem. Ber., 106 (1973) 2227.

84 J. Deberitz and H. Nöth, Chem. Ber., 106 (1973) 2222.

85 S. Akutagawa, H. Kumobayashi and A. Komatsu, Ger. Offen. Patent, 2,350,195, 11 Apr. 1974 (Chem. Abstr., 81 (1974) 3379p).

86 A.S. Bobrova, I.K. Shobeev, A.S. Chernyak, B.A. Arbuzov, A.O. Vizel, E.M. Esmont, Yu. F. Tarenko and A.E. Arbuzov, U.S.S.R. Patent, 263,882, 12 Mar. 1973 (Chem. Abstr., 79 (1973) 56381y).

87 A.S. Bobrova, A.O. Vizel, B.A. Arbuzov, I.K. Skobeev, and A.S. Chernyak, Tsvet. Met., (1973) 31 (Chem. Abstr., 79 (1973) 95142r).

88 M.J. Barrow, J.L. Davidson, W. Harrison, D.W.A. Sharp, G.A. Sim and F.B. Wilson, Chem. Commun., (1973) 583.

89 N.E. Waite and J.C. Tebby, J. Chem. Soc. C, (1970) 386.

90 K.C. Dash, J. Eberlein and H. Schmidbauer, Synth. Inorg. Metalorg. Chem., (1973) 375.

91 G. Märkl and C. Martin, Angew. Chem. Int. Ed., 13 (1974) 408.