Coordination Chemistry Reviews, 56 (1984) 269–389
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Chapter 5

ELEMENTS OF GROUP 5

M.F.A.Dove and D.B.Sowerby

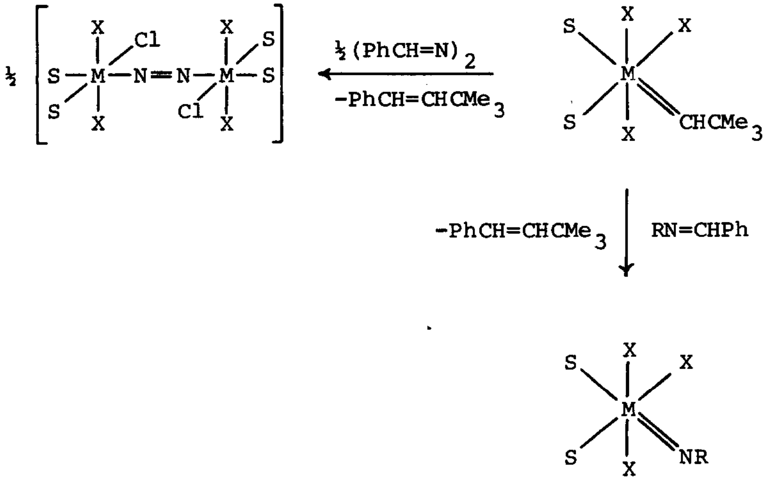
0010-8545/84/$36.30

5.1 NITROGEN

5.1.1 Nitrogen and Nitrides

The reactions of active nitrogen with the four fluoroethenes, C_2H_3F , 1,1-$C_2H_2F_2$, C_2HF_3 and C_2F_4, have been investigated in a conventional flow system:[1] reaction intermediates and products were detected mass spectrometrically. Both H and F atoms were shown to play significant roles in the reactions.

The photolysis of $Ni(CO)_4$ at 114K in liquid Kr containing N_2 yields $Ni(CO)_3N_2$, which then appears to decompose to $Ni(CO)_4$ by two concurrent processes.[2] One route with an activation enthalpy of 10 kcal mol^{-1} is dissociative and this may be taken as a measure of the Ni-N_2 bond energy. Comparative calculations on $Co_2(CO)_6(\mu\text{-}X_2)$, $X_2 = N_2$, P_2, S_2^{2+} or C_2H_2, and also on the known $Ni_2Ph_2(\mu\text{-}N_2)^{4-}$ indicate that there is nothing wrong with a side-on or π-bonded dinitrogen ligand in the $M_2L_6(\mu\text{-}N_2)$ system.[3] Hoffmann et al. conclude by saying that "the absence of this structure is most conspicuous. We eagerly await its synthesis." Organoimido and μ-dinitrogen complexes of Nb and Ta have been prepared by an interesting series of reactions, Scheme 1.[4] The organoimido

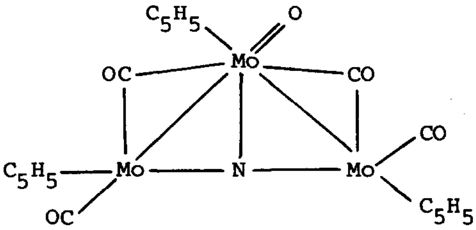


M = Nb,Ta; X = Cl,Br; R = Ph,CMe_3,Me; S = THF.

Scheme 1

complexes react with PhCHO to give RN=CHPh in high yield: the μ-N_2 complexes are readily converted by acetone to Me_2C=N-N=CMe_2 and by HCl to $N_2H_4.2HCl$.

The i.r. spectra of the family of trigonal prismatic cluster anions $[M_6(CO)_{15}N]^-$ have been investigated.[5] Using ^{14}N- and ^{15}N-labelled compounds Creighton et al. have identified the a_2'' and e' motions of the interstitial atom for M = Co or Rh. Interestingly the force constants for the isoelectronic nitrogen and carbon species, $[M_6(CO)_{15}C]^{2-}$, differ but slightly. A new nitrido metal cluster has been identified in which the coordination of nitrogen is 3-fold (T-shaped).[6] The reaction of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with ethyldiazoacetate produces green, air-stable crystals of $[Mo_3(N)(O)(CO)_4(\eta\text{-}C_5H_5)]$, (1), in 5% yield.



(1)

5.1.2 Bonds to Hydrogen

Further studies of the reactions of NH singlet radicals, obtained by the photolysis of HN_3 in the liquid phase, have confirmed the view that they insert readily into C-H bonds.[7] Polycrystalline rhenium is said to show an initial catalytic activity in the ammonia synthesis reaction which is nearly an order of magnitude greater than that of Fe(111) at 20atm and 603-713K.[8] However rhenium appears to suffer reversible poisoning at NH_3 pressures of 1-2 torr.

The phase digram and transition properties of condensed ammonia have been measured to 10 kbar and over the range 200-305K.[9] The results show that the melting curve has distinct branches. The differences in the electric dipole moments and polarizabilities of NH_3 and ND_3 have been determined; a correction for the thermal population of vibrationally excited levels was shown to be essential.[10]

Reaction of metallic copper with NH_4Cl takes place over the temperature range 100 to 300°C and is accompanied by the loss of NH_3, equation (1).[11] The reaction is still incomplete at 400°C

$$Cu + NH_4Cl \rightarrow CuCl + NH_3 + \tfrac{1}{2}H_2 \qquad ...(1)$$

when 75 to 80% of the copper is present as CuCl. The electrical properties of solutions of metals in liquid ammonia has been reviewed by Edwards.[12] The first reduction process of O_2 in liquid NH_3 at a Pt electrode is a one electron process forming O_2^-, which is a stable species in this solvent.[13] The voltammetric behaviour of NH_3 in the $(Na,K)NO_3$ melt at 518K has been investigated.[14] Mechanistic models for the oxidation and reduction of NH_3 were suggested.

The co-deposition of Ar/NH_3 and Ar/HF samples at 12K has produced 5 additional bands in the i.r. spectrum.[15] One band was shown to coincide with the known 1:2 adduct, NH_4HF_2; the other 4 bands have been assigned to the 1:1 H-bonded complex. The assignments were confirmed by isotopic substitution. The data provide evidence that the complex has a substantial polar character. The 1:1 complex between H_2O and NH_3 has also been studied in Ar and N_2 matrices.[16] Water is H-bonded to NH_3 exclusively through deuterium.

Rapid determination of mixtures of hydrazine and hydroxylamine, in the concentration range 0.01-0.5 mmol dm^{-3}, has been achieved by potentiometric titration using an iodine-sensitive electrode.[17] Trueblood and coworkers[18] have reported three crystal structures of the 1:1 complexes of 18-crown-6 with the perchlorates of $N_2H_5^+$, NH_3OH^+ and $MeNH_3^+$. Despite arguments in the literature that NH_4^+ and substituted ammonium ions are (like Rb^+) too large to fit into an 18-crown-6 ring the new data show that the $-NH_3^+$ group can readily move almost to the centre of the ring. This is typified by the hydrazinium complex where the stability of the complex is enhanced, albeit only modestly, by other interactions. Thus the atoms attached to $-NH_3^+$ in each of these structures undergo considerable thermal motion in directions predictable from the pattern of H-bonding. The purification has been described of diammonium imidobissulphonate, $HN(SO_3NH_4)_2$, triammonium imidosulphonate, $NH_4[NSO_3NH_4]_2$, and ammonium nitrilotrissulphonate,

$N(SO_3NH_4)_3$, from commercial ammonium imidosulphonate, the intermediate in the preparation of sulphamic acid from SO_3 and NH_3.[19]

5.1.3 Bonds to Boron

The base strength of amines NRR'R" has a marked effect on the rate of halogen redistribution in the boron halide adducts.[20] It was also pointed out that the chiral adducts formed between BF_2X and unsymmetrical amines contain diastereotopic and, therefore, magnetically non-equivalent fluorines. The molecular structure of boranediamine, $BH(NH_2)_2$, has been determined from the microwave spectra of the isotopic species.[21] The C_{2v} molecule has B-N distance and N-B-N angle equal to 1.418Å and 122.0° and a dipole moment of 1.24_5D. The double bond character of the B-N bond, as indicated by ab initio calculations, is confirmed by the planarity at boron, the short B-N bond length (cf. in BH_2NH_2 and $H_3B{\cdot}NH_3$ 1.391 and 1.672Å respectively), and the high torsional barrier about the B-N bond. The reaction of $Ph_4As[ReNCl_4]$ with excess BBr_3 yields $[Br_4Re{\equiv}N{\cdot}BBr_3]^-$ as the tetraphenylarsonium salt.[22] The new anion, which apparently contains a triple bond Re≡N, undergoes thermal decomposition at 210°C to $ReNBr_4^-$ and BBr_3.

5.1.4 Bonds to Carbon or Silicon

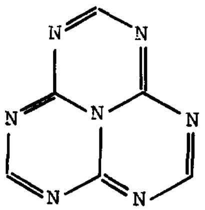
The products of photolysis of cyanogen azide, NCN_3, in solid argon or nitrogen matrices have been studied by i.r. absorption and UV-visible emission spectroscopy.[23] Among the photolysis products identified were CN, NCN, $N(^2D)$ as well as C atoms. The photolysis of pentafluorophenylazide or isocyanate in low temperature matrices gives pentafluorophenylnitrene:[24] this was shown to react with CO photochemically, but not thermally, to give the isocyanate.

Doubt has been cast on the interpretation of the e.s.r. spectra assigned to aminyl radicals: thus Brand and coworkers[25] have detected no e.s.r. signals from $(R_3Si)_2N{\cdot}$, R = Me or Et. Moreover they showed that $(Et_3Si)_2N{\cdot}$ reacts with propene even at 130K according to equation (2). On the other hand they detected

$$(Et_3Si)_2\dot{N} + MeCH{=}CH_2 \rightarrow (Et_3Si)_2NH + \dot{C}H_2{\cdot}CH{=}CH_2 \qquad ...(2)$$

assignable e.s.r. spectra for $(t\text{-}Bu)\dot{N}OSiMe_3$, $(t\text{-}Bu)\dot{N}SiMe_3$, (t-Bu)$Me_2$SiN(t-Bu) and (t-Bu)N=CN$(SiEt_3)_2$; hence they infer that disilylaminyl radicals are much more reactive than their dialkylaminyl counterparts.

The alkylation of sulphur difluoride imides, R_fNSF_2 (R_f = CF_3, C_2F_5, i-C_3F_7, C_6F_5, FSO_2, SF_5) by $ROSO^+MF_6^-$ occurs at nitrogen yielding $R_fRNSF_2^+MF_6^-$.[26] The aminosulphinyl derivatives $R_fRNSO^+MF_6^-$ are made analogously or by fluoride abstraction from R_fRNSOF. The synthesis of tri-s-triazine, (2), has been reported and some physical and spectroscopic properties investigated.[27] The structure determination reveals that there is only a slight departure from planarity and the peripheral C-N bonds (1.33Å average) are only slightly shorter than the central ones (1.39Å average). A further example of N-C bond formation is to be found in equation (3). The tungsten hydrazide(2-) complex (3) reaction



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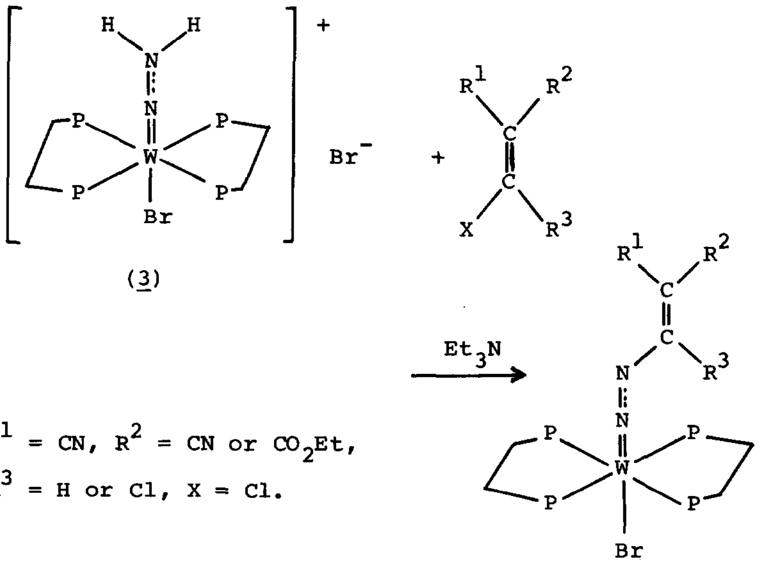


(3)

R^1 = CN, R^2 = CN or CO_2Et,
R^3 = H or Cl, X = Cl.

...(3)

with cyanoalkenes produces a series of cyanovinyldiazenido complexes.[28]

Following the report that the W≡W bond in $W_2(OCMe_3)_6$ is cleaved by alkynes to give mononuclear alkylidyne complexes, it has been shown that the analogous reaction occurs with nitriles, RCN, to form an alkylidyne complex as well as the nitrido complex $WN(OCMe_3)_3$, as a white sublimable product.[29] Catalytic reductions of MeNC by the electrochemically reduced species derived from $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ have been reported by Tanaka et al.[30] Thus $[Fe_4S_4(SPh)_4]^{4-}$ produced principally CH_4 and a large amount of H_2; the other reduction product $MeNH_2$ reacts with HCHO, one of the products of oxidation of MeOH, to form Me_2NH and $MeNHCH_2OH$. Acetonitrile was similarly reduced to C_2H_6 and NH_3.

Goddard[31] has carried out ab initio calculations on a series of aminoalkyl radicals (H_2NCH_2, $HMeNCH_2$, Me_2NCH_2, H_2NCMeH and H_2NCMe_2) and the parent amines. The first vertical ionisation potentials for each were reported. It was shown that the aminomethyl radical is 8 to 10 kcal mol^{-1} stabilised relative to the methyl radical: the calculations indicate that methyl substitution at N has a small destabilising effect on this radical, an observation which conflicts with recent experimental work. The photoelectron spectra of a series of N-aryl cyclic amines indicate that the conformation of the aryl group, with respect to the amine lone pair, varies as the ring size and as ortho methyl substituents are placed on the aryl group. Values of ionisation potentials and line shapes were both indicative of conformation. The gas phase basicities of these compounds were predicted from ionisation potentials using Aue's correlations.

Waterfeld and Mews[33] have reported that the reaction mixture Cl_2-HgF_2 brings about the addition of ClF to C≡N in CF_3CN and in cyanogen; similarly N-bromo-amines and -imines were isolated from R_fCN-Br_2-HgF_2 systems. The recently reported,[34] improved preparation of perfluoromethanimine, CF_2=NF, has been followed by a detailed spectroscopic and structural study of this compound.[35] The results were compared with those of methanimine CH_2=NH and related isoelectronic species. On the basis of electron diffraction and microwave studies of CF_2=NH the C-F bonds were shown to be short, 1.300(3)Å, and the N-F bond long, 1.389(2)Å. Ab initio calculations on both CF_2=NF and CH_2=NH were also presented and discussed.

Tetraalkylammonium graphite lamellar compounds are known and can be formed efficiently by electrochemical means. A preliminary report describes their use as reducing agents in organic chemistry.[36] A precursor to fluoride silicalite, which is a new microporous silica polymorph, has been obtained from a hydrothermal system containing silica, tetrapropylammonium and fluoride ions.[37] The ideal chemical composition of the precursor is $n\text{-}Pr_4NF.(SiO_2)_{24}$. Because of the suggestion that quaternary ammonium cations can act as templates around which tetrahedral frameworks assemble during crystallisation, the crystal structure has been determined. It was concluded that the tetra(n-butyl)ammonium ion would not have sufficient room in this structure.

5.1.5 Bonds to Nitrogen

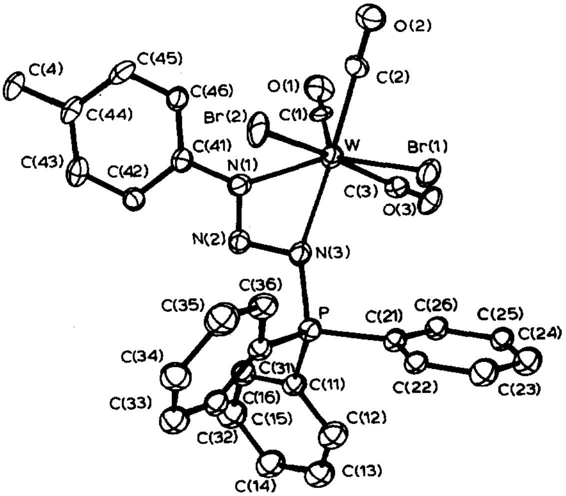
A theoretical study of metal dinitrogen complexes and the effect of protonation on them implies a remarkable degree of electron redistribution within the ligand;[38] the results are consistent with the experimental observation that the M-N bond is strengthened on protonation and the N-N bond is weakened. Activation of N_2 on supported Ru catalysts, with respect to isotopic equilibration and reduction by H_2 to NH_3, has been reported by Bossi et al.[39] The reactivity scale for NH_3 synthesis was found to be $MgO >> SiO_2 > Al_2O_3$ with an apparent activation energy of ca. 100kJ mol^{-1} for Ru on all three supports. The formation of nitrogen (probably N_2)/ alkali metal species on Al_2O_3, MgO or CaO surfaces at 350°C has been proposed by Aika et al.[40] Their evidence comes from i.r. absorptions in the range 1900-2200 cm^{-1}, irrespective of whether NH_3 or N_2 was used as the source of nitrogen. Although Ru serves as a catalyst for the formation of these species it has no significant effect on the position of the absorption band, however, the oxide surface does have a marked effect.

New observations on the reduction of N_2 in the $V(OH)_2/Mg(OH)_2$ and $V(OH)_2/ZrO_2.H_2O$ systems have been published by Schrauzer and coworkers.[41] They infer that the reduction of N_2 can be directed, to yield predominantly either N_2H_4 or NH_3, by an appropriate choice of conditions. Thus high dilution, N_2 pressure, NaOH concentration and a low V/Mg ratio all favour the formation of hydrazine. The conversion of dinitrogen bound terminally at a mononuclear Mo site into an imido ligand and a secondary amine has been achieved by the reactions shown in Scheme 2 (dppe = diphos).[42]

$$\begin{tikzcd}
{\underset{(\underline{4})}{[Mo(N_2)_2(dppe)_2]}} \arrow[r, "RBr"] & {[MoBr(N_2R_2)(dppe)_2]^+} \arrow[d, "2e^-"] \\
{[MoBr(NH)(dppe)_2]^+ + R_2NH} & {[Mo(N_2R_2)(dppe)_2]} \arrow[l] \arrow[d, "N_2; H^+; 2e^-"] \\
 & {(\underline{4}) + R_2NNH_2}
\end{tikzcd}$$

<u>Scheme 2</u>

Hillhouse et al.[43] have reported that the reaction of aryl azides, ArN_3, with $MBr_2(CO)_3(PPh_3)_2$, M = Mo or W, yields remarkably stable compounds of the type $MBr_2(CO)_3(ArN_3PPh_3)$. The mode of binding of the phosphazide ligand was elucidated by a low temperature structure determination of the complex with M = W and Ar = p-tolyl, Figure 1.



<u>Figure 1</u>. Drawing of a molecule of $WBr_2(CO)_3(p\text{-}CH_3C_6H_4N_3PPh_3)$. The hydrogen atoms have been omitted. Vibrational ellipsoids are drawn at the 50% probability level (reproduced by permission from Inorg. Chem., 21(1982)2064).

The N_3W metallacycle was found to be nearly planar. Dillworth et al.[44] have described a molybdenum complex ion, $[Mo_2O_2(\mu\text{-}N_3)(SCH_2CH_2CH_2S)_3]^-$, in which the bridging azide ligand is bent, NNN angle 153°. This non-linearity was attributed to an intermolecular effect with a methylene hydrogen, which interaction they considered to be not electronic in origin.

Several electron-poor dipolarophiles (alkynes, alkenes and nitriles) have been shown to react with azidocobalt chelate complexes of the type $LCo(chelate)(N_3)$ under mild conditions to form initially co-ordinated 5-membered heterocycles.[45] Non-terminal alkynes yield tetrazoles, alkenes yield triazolines and nitriles yield tetrazoles. Carbon monoxide reacts with such cobalt complexes to form isocyanato complexes, LCo(chelate)(NCO). Salts containing the hexaazidocobaltate(III) anion, $Co(N_3)_6^{3-}$, have been prepared for the first time:[46] suitable precipitants for this anion are $M(NH_3)_6^{3+}$, M = Co, Cr or Rh.

A new electron diffraction study of gaseous hydrazine has been published;[47] by means of a combined analysis with the rotational constants, and without information from N_2D_4, a new set of parameters were generated which differ significantly from the earlier study by Morino et al. in the NNH angles for the two types of hydrogen (inner, essentially eclipsed) - $\widehat{NNH}$(outer) = 106±2° and $\widehat{NNH}$(inner) = 112±2°. The kinetics of formation of monomethylhydrazine from $MeNH_2$ and NH_2Cl have been investigated over the pH range 11.5 to 15.[48] The reaction is first order in both reagents but also has a pH independent and a pH dependent term. The catalytic decomposition of aqueous hydrazine over Pt black proceeds according to equation (4);[49] however, irradiation (300-420nm) of such solutions in a presence of a $Pt\text{-}TiO_2$ catalyst

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \qquad \ldots(4)$$

$$2N_2H_4 \rightarrow 2NH_3 + H_2 + N_2 \qquad \ldots(5)$$

causes reaction (5) to take place.

Mass spectrometric analysis of the N_2 and N_2O evolved from the reaction between $^{15}N_2H_5^+$ and excess HNO_2 is consistent with scrambling occurring between all three nitrogens.[50] A cyclic form of hydrazoic acid was postulated as a reaction intermediate. At lower acidities (pH 3.7) substantial yields of NH_3 and N_2O were detected. In another laboratory isotopic tracer experiments on the $H^{15}NO_2$-$N_2H_5^+$ reaction have corroborated the existence of separate high- and low-acidity pathways.[51] The isotopic composition of a mixture of N_2O and N_2 generated from a solution with initial $[HNO_2]/[N_2H_5^+]$ = 2.0 and 0.6M in H^+ was consistent with N-scrambling via a cyclic azide intermediate: these and other results can also be interpreted as mixtures of reaction products resulting from double nitrosation and linear azide pathways. No evidence could be obtained for photochemical cyclisation of azide in solution.

The crystal structure of trans-tetrazene-(2), H_2N-N=N-NH_2, has been determined at -90°C.[52] Four different molecules are present in the unit cell; Figure 2 gives the average bond lengths (Å) and bond angles. The intermolecular contacts form a 3-dimensional network involving H-bonds with N-H--N distances ranging from 3.03 to 3.42Å. Thermolysis of tetrazene was shown to yield hydrazinium azide, $N_2H_5^+N_3^-$, or ammonium azide depending on the conditions. A series of complexes containing the σ,σ-N,N'-bonded tetraazabutadiene ligand has been prepared by the addition of aryl azides on $Ni(COD)_2$,[53] $Nicp_2$,[54] or $Pt(COD)_2$.[55]

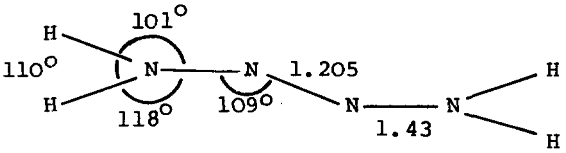
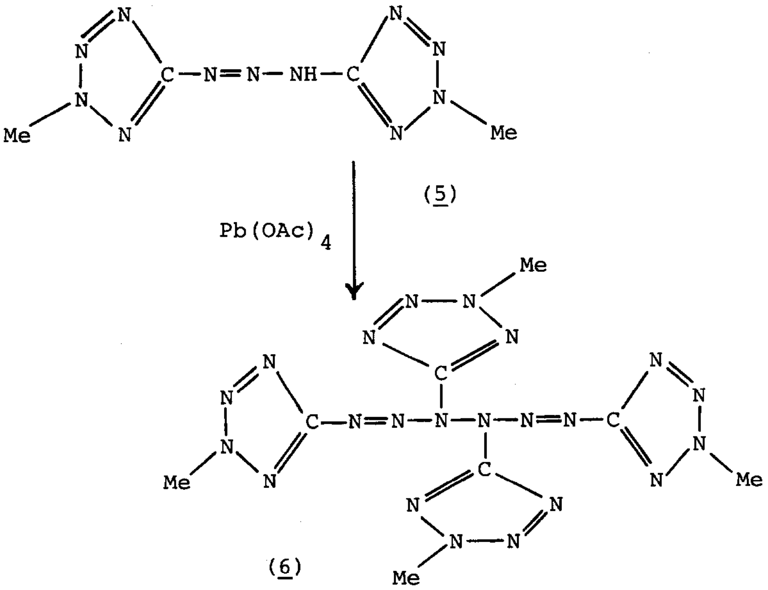


Figure 2. The molecular structure of trans-tetrazene-(2).

Huber has briefly reviewed the evidence for the existence of N_6, cyclohexatriene, in the light of recent suggestions that it might exist at low temperatures.[56] He has also provided the results of additional calculations on this problem; he concluded that in the gas phase cyclo-N_6 is ca. 10^3 kJ mol^{-1} less stable than $3N_2$ and moreover, that the activation energy for this decomposition is zero. Linear hexaazane compounds are rare however Butler and Garvin[57] have synthesised 1,3,4,6-tetrakis-(2-methyltetrazol-5-yl)-hexaaza-1,5-diene (6) by the reaction of the triazane (5) with lead tetraacetate in acetic acid, Scheme 3. The new compound (6) is a white, crystalline, shock-sensitive material which was characterised in solution by spectroscopic methods and by mass



(5)

(6)

Scheme 3

spectrometry.

The equilibrium geometry of a new, planar, symmetrical (possibly high pressure) cis-ONNO isomer has been calculated.[58a] It has N-N and N-O distances of 1.26 and 1.50Å respectively and the NNO angle is 96°; moreover it is estimated to be 44 kcal mol^{-1} less stable than the isomer with the longer (1.79Å) N-N bond. However, the structure of the NO dimer, cis-planar in the gas phase, has been determined from measurements of the rotational transition frequencies for ^{14}N- and ^{15}N-labelled species.[58b] This has permitted an unambiguous determination of the N-N and N-O bond lengths, 2.237(2) and 1.161(6)Å, and the NNO angle, 99.6(4)°. These do not match any of the calculated data sets. The triplet-sensitised decomposition of organic hyponitrites, trans-RON=NOR, produces alkoxy radicals in good yields and is a viable alternative to the use of peroxides.[59] The molecular structure of trans-di-tertiarybutyl hyponitrite has been determined from a single crystal, low temperature, X-ray study.[60] The reported bond lengths for N=N, N-O and O-C are respectively 1.252(5), 1.380(6), and 1.471(7)Å; the NNO angle is 106.5(3)°. Infrared and Raman assignments were made with the aid of ^{15}N substitution, thus the

Raman active $\nu(N{=}N)$ was located at 1509 cm^{-1}. Using an ab initio approach Casewit and Goddard[61] have solved for the geometries and energies of nine isomers of N_2H_2O, including NH=NOH, $H_2N{\cdot}NO$ and HN=N(O)H. The heats of formation were used to examine several chemical processes such as deoxygenation of N-nitroso compounds, nitrosation of amines, and reaction (6), the postulated key step in

$$H_2N + NO \rightarrow NO + H_2O \qquad \ldots(6)$$

the $DeNO_x$ process for reducing NO to N_2 in stationary power plants.

5.1.6 Bonds to Oxygen

The ^{14}N quadrupole coupling components for both atoms in the weakly bound $^1\Sigma$ $ON\text{-}NO_2$ molecule have been redetermined more accurately:[62] there is a substantial effect on the electric field gradients at both N atoms as compared with the component molecules. The secondary ion mass spectra of N_2O, NO, N_2O_3 and N_2O_4 as undiluted solids have been measured.[63] The nature and energy of the primary (noble gas +1) ions were found to be important. All the solids produced a rich variety of positive and negative secondary ions with a strikingly high abundance of cluster ions, especially when Xe^+ was the primary ion.

Nitric acid is an important reservoir for both HO_x and NO_x species in the stratosphere: it is removed by solar photolysis as well as by reaction with OH radicals. A kinetic study of this reaction has shown that the yield of NO_3 is close to unity at both 251 and 298K.[64] Methyl peroxynitrate, MeO_2NO_2, has been shown to be capable of playing a role in the NO_x budget of the lower stratosphere: this conclusion is based on a study of the kinetics of thermal decomposition over a range of temperature and pressure.[65] The kinetics of reaction (7), in both directions,

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \qquad \ldots(7)$$

where M = N_2, as well as its equilibrium constant have been investigated by Wayne et al.[66] The UV absorption cross sections for N_2O_5 have been measured for wavelengths between 200 and 380nm and at temperatures between 223 and 300K.[67] The spectrum above 290nm shows a pronounced temperature dependence.

The $NO\text{-}H_2$ reaction on $Pt\text{-}V_2O_5/Al_2O_3$ catalysts has been shown to be composed of three main stages:[68] the formation of NH_3 on Pt; the NO-NH_3 reaction on Pt to form N_2 or N_2O; the reduction of V_2O_5 by H_2. The mechanism of the NO-NH_3 over vanadium oxide catalysts has also been studied separately from 100° to 500°C.[69] The same reagents produce N_2 and N_2O in the homogeneous reaction involving dinitro(alkyldiamine)cobalt(III) complexes in DMF.[70] The N_2/N_2O ratio can be controlled by changing the nature of the alkyldiamine ligand.

The action of gaseous NO_2 in a carrier gas with alkenes and other unsaturated compounds leads to addition products at high NO_2 concentrations, up to 50%, whereas below 1% hydrogen abstraction predominates.[71] The reactions of NO_2 with $CH_3CO\cdot$ and $CF_2Cl\cdot$, equations (8) and (9), have been investigated.[72] A new flow

$$CH_3CO + NO_2 \rightarrow CH_3CO_2 + NO \qquad \ldots(8)$$

$$CF_2Cl + NO_2 \rightarrow CF_2ClO + NO \qquad \ldots(9)$$

method for the syntheses of $EtNO_2$, EtONO and $EtONO_2$ starts from ethane, NO_2, and H_2O_2 and takes place on a boric acid-coated surface.[73] The synthesis of acetyl nitrite has been reported:[74] it is green below -78°C and a pale brown liquid at room temperature. Experiments showed it to be a useful nitrosating agent.

Nazarov et al.[75] have prepared a graphite-N_2O_4 compound by the action of N_2O_4 on $C_4F.0.46ClF_3$ or $C_4F_{1.92}.0.46ClF$. The i.r., ^{19}F n.m.r. and UV spectra of the new compound $C_4F_xCl_y.zN_2O_4$ were described.

A study of the nitrating behaviour of NO_2BF_4-crown ether complexes in CH_2Cl_2 towards benzene and toluene has shown that the crown ether moderates the reactivity of NO_2^+.[76] Moreover the concentration ratio of ether to salt as well as the nature of the crown ether affect the substrate and positional selectivity of the nitrating agent. The argument concerning the active nitrosating agent in dilute aqueous solutions of nitrous acid, $H_2NO_2^+$ vs NO^+, has been reconsidered by Dix and Williams.[77] They have shown that in the nitrosation of alcohols in THF there is no sign of a rate-limiting NO^+ formation process, presumably because any medium effect has been minimised. Consequently they favour $H_2NO_2^+$ as the effective species.

Two organic sensitizers, S, N-methylphenothiazine and N,N,N',N'-tetramethylbenzidine, have been found to reduce nitrate ion irreversibly.[78] The proposed sequence of reactions, equations (10)-(12), assume that photolytic excitation to the triplet state (S^T) takes place.

$$S^T + NO_3^- \rightarrow S^+ + NO_3^{2-} \qquad ...(10)$$

$$NO_3^{2-} + H_2O \rightarrow NO_2 + 2OH^- \qquad ...(11)$$

$$NO_2 + S \rightarrow S^+ + NO_2^- \qquad ...(12)$$

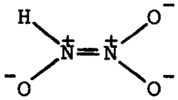
The kinetics of the reactions of NH_2OH with HNO_2 and HNO_3 have been reinvestigated and some modifications of the previously proposed mechanisms offered.[79] In weakly alkaline medium the oxidation of NH_2OH by iodine proceeds according to equation (13).[80]

$$2NH_2OH + 2I_2 \rightarrow N_2O + 4I^- + H_2O + 4H^+ \qquad ...(13)$$

However, in acidic media the process is not only slower but also the stoichiometry depends on the pH and the ratio of NH_2OH to I_2.

15-Nitrogen n.m.r. spectra of hyponitrite ion, $N_2O_2^{2-}$, as a function of pH have been interpreted as signifying O-protonation. This contrasts with the N-protonation of $N_2O_3^{2-}$. This difference as well as new chemical evidence from the thermal decomposition of both anions is consistent with different reaction pathways, equations (14) and (15), in spite of the closely similar rate constants and activation enthalpies.[81] Alkali metal

$$HO{-}N{=}N{=}O^- \rightarrow OH^- + O{=}N{=}N \qquad ...(14)$$



$$\rightarrow HNO + NO_2^- \qquad ...(15)$$

hyponitrates, $M_2N_2O_3$, M = Li-Cs, have been obtained by the reaction of free NH_2OH with $EtONO_2$ in the presence of MOEt or MOH in absolute EtOH.[82] For M' = K-Cs the salts can be prepared from the lithium salt on addition of M'F in aqueous solution. I.r. spectra correspond to vibrations of planar $ONNO_2^{2-}$ with C_s symmetry. Thermal decomposition occurs over the temperature range 290-370°C to form $M_2N_2O_2$.

The extraction of HNO_2 from aqueous solution by dihexylsulphoxide in octane has been investigated:[83] the distribution coefficient is more favourable than for nitric acid. The electron diffraction patterns of $RbNO_2$ and $CsNO_2$ in the gas phase at ca. 560°C indicate that the structure of the monomers is essentially planar with C_{2v} symmetry.[84a] The ONO angle, 117°, and the N-O distance, 1.256(5)Å, are significantly smaller than those reported previously by Tuseev et al.[84b] Structural studies by Jansen[85] of Na_3NO_3, from -140° to +20°C, have indicated two phase transitions: the main structural features of the antiperovskite $NO_2(ONa_3)$ type of structure remain unchanged, however the dynamically disordered NO_2^- ion in the high temperature (>-53°C) form become ordered and yield an antiferroelectric arrangement in another phase, below -122°C. Possible structures of the intermediate temperature phase were proposed. The tetrahedral orthonitrate ion, NO_4^{3-}, has been identified in the structure of Na_3NO_4.[86] The mean value for the N-O distances, 1.39Å, and some spectroscopic data were also reported.

The crystal structure of a novel nickel(II) dimeric cation in $[Nien_2NO_2]_2(BPh_4)_2$ has been obtained[87] and reveals the presence of one monodentate and one tridentate, i.e. chelating and bridging, nitrito ligand per dimer unit. 17-Oxygen n.m.r. spectroscopy of labelled $[Co(NH_3)_5(ONO)]^{2+}$ has shown that spontaneous intramolecular O to O exchange in the nitrito ligand occurs as a rate comparable with that of the spontaneous O to N isomerisation.[88]

Bonner and Pearsall[89] have established the stability limits for $Fe(NO)^{2+}$ against reduction to N_2O and beyond to N_2. They reported evidence that HNO (or NO^-) is the primary product of reduction of NO by aqueous Fe(II). They have also determined the formation constant for $Fe(NO)^{2+}$ and shown that it is pH independent, over the range pH 0.5 to 3.3, in aqueous sulphate solution but is enhanced by acetate ion.[90] Above pH 4 they found clear evidence for the formation of $Fe(NO)_2^{2+}$, which probably has one OH^- in the coordination sphere, and they discussed the mechanism of reduction in this system.

Meyer et al.[91] have reported that the reduction of coordinated nitrosyl to ammonia occurs for a variety of polypyridyl complexes of both Ru and Os, equations (16) to (18); they proposed that the mechanism involves a series of one electron transfer steps. They also describe the catalytic reduction of nitrite to NH_3 based on

$$\text{cis-}[Ru(bpy)_2(NO)Cl]^{2+} \xrightarrow[+5H^+]{+6e^-} \text{cis-}[Ru(bpy)_2(NH_3)(H_2O)]^{2+} \quad ...(16)$$

$$\text{cis-}[Ru(bpy)_2(NO)(NO_2)]^{2+} \xrightarrow[+12H^+]{12e^-} \text{cis-}[Ru(bpy)_2(NH_3)_2]^{2+} \quad ...(17)$$

$$[Os(trpy)(bpy)(NO)]^{3+} \xrightarrow[+5H^+]{6e^-} [Os(trpy)(bpy)(NH_3)]^{2+} \quad ...(18)$$

the water-soluble metalloporphyrin Fe(II)-TPPS; a current efficiency of 50% was claimed assuming a six-electron reduction.

Studies of the reactions of $[Ru_3(CO)_{10}(NO)]^-$ with strong protonic acids and methylating agents have shown that O-protonation and -methylation, respectively, of the nitrosyl ligand takes place.[92] This contrasts with the behaviour of

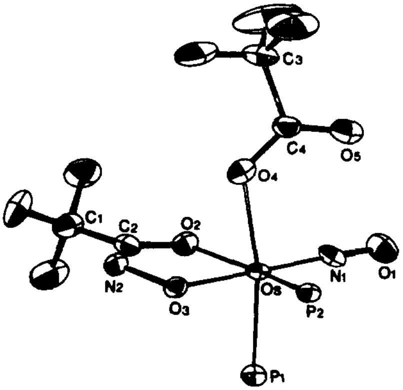


Figure 3. A perspective drawing of $Os\{\overline{ON{:}C(O})CF_3\}(O_2CCF_3)(NO)(PPh_3)_2$ showing the atom labelling scheme. The solvent molecule and six phenyl groups have been omitted for clarity. Some important bond distances (Å) and angles (deg.) are: $Os-P_1$ = 2.378(2), $Os-P_2$ = 2.397(2), $Os-N_1$ = 1.739(7), $Os-N_2$ = 2.069(6), $Os-O_3$ = 1.973(6), $Os-O_4$ = 2.116(6), N_1-O_1 = 1.207(10), C_2-O_2 = 1.310(10), C_2-N_2 = 1.277(11), N_2-O_3 = 1.421(9), C_1-C_2 = 1.511(13), P_1-Os-P_2 = 106.51(8), O_2-Os-O_3 = 78.2(2), $N_2-C_2-O_2$ = 127.0(8), $Os-O_3-N_3$ = 115.7(5), $Os-O_2-C_2$ = 109.0(5), $O_3-N_2-C_2$ = 109.3(7) (reproduced by permission from Inorg. Chim. Acta, 65(1982)L231).

mononuclear nitrosyls which are converted to N-protonated complexes. The attack of CF_3CO_2H on $[Os(NO)_2(PPh_3)_2]$ converts one nitrosyl ligand into a trifluoroacetatohydroxamate(2-) ligand, $CF_3C(O){=}NO$.[93] The structure of the compound isolated in this novel reaction is shown in Figure 3. The reaction of NO^+ with hydridocarbonylate anions of Os and Ru has yielded nitrogen bridged clusters, $Os_4(\mu\text{-}NO)$[94] and $COs_{10}(\mu\text{-}NO)$,[95] and the nitrido cluster group Ru_4N.[94] A series of metal nitride clusters of formula $[M_3(N)(O)(CO)_4(\eta\text{-}C_5H_5)_3]$ have been obtained by heating $[M(CO)_2(NO)(\eta\text{-}C_5H_5)]$ together with $[M_2(CO)_6(\eta\text{-}C_5H_5)_2]$, M = Mo or W, at 200°C.[96] The reaction evidently involves N-O bond cleavage and the oxygen appears as CO_2.

5.1.7 Bonds to Sulphur

Laser photoelectron spectroscopy has been used to study NS^-. The electron affinity of NS was found to be 1.194±0.011eV and the N-S vibrational frequency in the monoanion was shown to be $880 \pm 70\ cm^{-1}$.[97] Full details of the preparation, i.r., resonance Raman and ^{15}N n.m.r. spectra of the S_3N^- anion, the thioanalogue of peroxynitrite ion, have now been reported.[98] It is formed by the reaction of Ph_3P with $(Ph_3P)_2N^+S_4N^-$ in MeCN, equation (19), and is unstable with respect to S_4N^- in solution and in the solid state

$$Ph_3P + S_4N^- \rightarrow Ph_3PS + S_3N^- \qquad ...(19)$$

above room temperature. Single crystal X-ray data showed that even the Ph_4As^+ salt has disordered anion arrangements: nevertheless SCF calculations were carried out on the anion with assumed parameters for the bond lengths and angles. Solutions of sulphur in liquid NH_3 are said to contain S_4N^- and S_3^-, probably in equilibrium with S_6^{2-}, on the basis of a new Raman study.[99]

A facile and safe preparation of S_2N_2 has been described by Roesky and Anhaus.[100] It involves the displacement of the more volatile base S_2N_2 by S_4N_4 at 80°C in high vacuum, equation (20). The S_4N_4 is recycled by means of the reaction in equation (21). A

$$2S_4N_4 + S_2N_2.2AlCl_3 \xrightarrow{80^\circ} S_2N_2 + 2(S_4N_4.AlCl_3) \qquad ...(20)$$

$$S_4N_4.AlCl_3 + 3AlCl_3 \xrightarrow{20^\circ} 2(S_2N_2.2AlCl_3) \qquad ...(21)$$

$$\tfrac{1}{2}S_8 + S_4N_4 + 6AsF_5 \xrightarrow[\text{trace } Br_2]{SO_2} \underset{(77\%)}{4NS_2AsF_6} + 2AsF_3 \qquad \ldots(22)$$

convenient synthesis of dithionitronium hexafluoroarsenate (77% yield) has been reported by Passmore et al.[101] Reactions of $S_3N_3Cl_3$ with $SbCl_5$ in a 1:2 ratio have yielded $(S_4N_4)(SbCl_6)_2$ as the major product in SO_2, CH_2Cl_2 or $SOCl_2$;[102] with a 1:1 ratio and CH_2Cl_2 as solvent both $(S_5N_5)SbCl_6$ and $S_4N_4SbCl_5$ were formed and have been characterised by X-ray crystallography. The planar pentathiazyl cation is intermediate between the "azulene-like" and heart-shaped conformations previously reported for this cation. The reactions of $S_3N_3F_3$ with AsF_5,SbF_5 and SO_3 yielded $(SN)AsF_6$, $(SN)Sb_2F_{11}$ and $SN(SO_3F)$ respectively. Poly(sulphur nitride) has been prepared in ca. 65% yield by the reaction of excess Me_3SiN_3 with $S_3N_3Cl_3$, $S_3N_2Cl_2$ or S_3N_2Cl at -15°C in MeCN solution.[103] Other routes to the polymer shown to be effective were $S_3N_3Cl_3$ + NaN_3 or NS_2AsF_6 + CsN_3 in SO_2 at -20°C.

Alkylthioammonium ions, $RSNR_3^+$, are highly effective azasulphenylating agents. Thus the alkylation of N,N-dimethylmethanesulphenamide with alkyl iodides resulted in S-N cleavage and the reaction sequence (23):[104] the products of this

$$MeSNMe_2 + RI \xrightarrow{CHCl_3} [MeSN(R)Me_2{}^+I^-] \xrightarrow{RI} Me_2NR_2{}^+ + \tfrac{1}{2}Me_2S_2 + I_2 \qquad \ldots(23)$$

reaction are those expected from thioammonium ions and iodide. Structural work on sulphonate derivatives of ammonia and hydroxylamine has now been extended to include some methyl substituted derivatives of ammonia. In $K_2[MeN(SO_3)_2]$ the bonds angles at N are close to 119° whereas in $K[MeNH(SO_3)]$, $HMe_3N^+SO_3^-$ and $K[Me_2N(SO_3)].0.66H_2O$ the average values are close to 112°.[105,106]

Organosulphurdiimides, $S(NR)_2$, are attacked by KO(t-Bu) in boiling dimethoxyethane to give dipotassium sulphur diimide, K_2SN_2, in ca. 90% yield.[107] Potassium sulphinylamide, KNSO, can be prepared analogously. Agarwala et al.[108] have reported the first isolation of a coordinated N-thionitro group in the complex $Co(NSO)Cl_2(P(OPh)_3)_2$ by the addition of $(NSCl)_3$ to $CoH(P(OPh)_3)_4$. I.r. absorptions at 1540 and 990 cm^{-1} were assigned to N=O and N=S stretching modes, respectively.

The molecular structure of $MeN=SF_4$ has been determined by a combined analysis of electron diffraction and microwave spectroscopic data.[109] The methyl group is in the axial plane of the SF_4 unit, Figure 4, so that the two axial fluorines are non-equivalent. The S-N bond length is significantly shorter than in

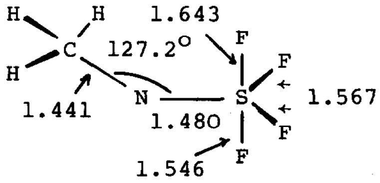
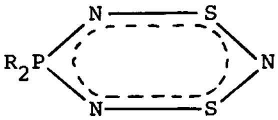


Figure 4. The molecular geometry of $MeN=SF_4$. Lengths (Å) and angles of selected bonds.

$FN=SF_4$ which also shows a rigid S=N bond.[129] The reaction of N-(pentafluoro-λ^6-sulphanyl)iminosulphurtetrafluoride, $F_5S-N=SF_4$, with anhydrous HF has been shown to generate $(SF_5)_2NH$ quantitatively.[110] The new secondary amine is a weak acid and its salts can be converted by F_2 or ClF to $(SF_5)_2NX$, X = F or Cl. The structures of the compounds with X = H and F have been determined by electron diffraction.[111] Both have planar S_2NX frameworks with similar SNS angles, 135° and 138° respectively. Clifford et al[112] have synthesised several new compounds containing the SF_5N group by the action of certain acyl halides on SF_5NH_2. The reaction mixture Cl_2-HgF_2 has been shown to effect the addition of ClF to $N{\equiv}SF_3$;[33] similarly the reaction of $N{\equiv}SF_3$ with CF_3SCl and HgF_2 has been reported to produce $SF_5N(SCF_3)_2$ in high yield.

5.1.8 Bonds to Phosphorus

The 1:1 adduct of NH_3 and PF_5 has been prepared in low yield (8%) from NH_3 and PF_5 and also in 41% yield by the action of HF on $P_3N_3F_6$.[113] The molecular structure as determined by X-ray methods shows the expected octahedral geometry with a N-P bond length of 1.842Å. The reaction of R_2PPR_2, R = Me or Ph, or $P(OPh)_3$ with S_4N_4 produces compound (7).[114] The product was characterised by ^{15}N n.m.r. spectroscopy and, for R = Ph, X-ray crystallography. Anhydrous HF cleaves the P-N bond in $Fe(\eta$-$C_5H_5)(CO)I(PPh_2NMeCHMePh)$ to give quantitatively $Fe(\eta$-$C_5H_5)(CO)I(PPh_2F)$.[115] Extensive



(7)

racemisation with respect to the chiral Fe atoms during the cleavage reaction could be excluded. Palmesen has discussed the evidence for micellar-like behaviour in aqueous solutions of bis(triphenylphosphine)iminium, $(Ph_3P{=}N{=}PPh_3)^+$, salts:[116] whereas the Cl^- and SO_4^{2-} salts appear to show a Krafft-type transition between 40° and 50°C the nitrate does not. He concluded that the phenomena have a similar origin to that of associated compounds.

5.1.9 Bonds to Xenon

The publication of the crystal structure of fluoro(imidobis-(sulphurylfluoride))xenon(II), $FXeN(SO_2F)_2$, has provided definitive proof that this compound contains a Xe-N bond.[117] A new system containing Xe(II) bonded to two nitrogen atoms has been reported;[118] these xenon compounds are discussed more fully in Chapter 8.

5.1.10 Bonds to Metallic Elements

Hydroxamic acid complexes have been shown to coordinate to transition metals through the oxygen of the -NH(OH) group. However glycinohydroxamic acid $NH_2CH_2CONH(OH)$, ghaH, has now been shown to form a $Ni(gha)_2$ complex in which all four nitrogens of both monoanions are coordinated to Ni(II) in a square planar arrangement.[119] The reaction of $Ph_4As[ReNCl_4]$ with excess BBr_3 yields $[Br_4Re{\equiv}N{-}BBr_3]^-$ as the arsonium salt.[120] The new anion, which apparently contains a triple bond to Re, undergoes thermal decomposition at 210°C to BBr_3 and $ReNBr_4^-$, in which the Re≡N bond was shown to be 1.62Å. The structure of $[Cd_2(NCS)_4(butrz)_3]_\infty$, butrz = 4-t-butyl-1,2,4-triazole, consists of a zig-zag chain with alternate bridges of 3 butrz groups and 2 N-bonded isothiocyanate ligands.[121]

5.1.11 Bonds to Halogens

More perfluoroammonium salts have been generated by Christe and Wilson; in one study[122] the anions were WF_7^- and UF_7^- and the solid products were vacuum stable at 125°C. Both salts decompose at higher temperatures according to equation (24) with no evidence for the formation of higher oxidation states of W and U. The yellow salt $NF_4^+XeF_7^-$ has been prepared from XeF_6 and NF_4HF_2;[123] it could be converted in small amounts to white $(NF_4)_2XeF_8$ by selective

$$NF_4MF_7 \xrightarrow{\Delta} NF_3 + F_2 + MF_6 \qquad ...(24)$$

$$2NF_4XeF_7 \xrightarrow{488nm} (NF_4)_2XeF_8 + XeF_6 \qquad ...(25)$$

laser photolysis, equation (25). Such a photolysis was rationalised in terms of the different colours of the compounds. There was evidence also that NF_4XeF_7 is solvolysed in BrF_5. A range of NF_4^+ salts with other anions has been examined by differential scanning calorimetry.[124] The enthalpies of reaction in water were also measured and used to obtain an alternative set of formation enthalpies for the compounds NF_4BF_4, NF_4PF_6, NF_4AsF_6, NF_4SbF_6, NF_4GeF_5 and $(NF_4)_2GeF_6$. These formation enthalpies were used to estimate the F^+ ion affinity of NF_3(g), -845 kJ mol^{-1}, and the enthalpy of formation of NF_4^+(gaseous). The reaction enthalpy of reaction (26) was estimated to be +36(±40)kJ mol^{-1},

$$NF_3(g) + F_2(g) \longrightarrow NF_4^+F^-(s) \qquad ...(26)$$

and, since the free energy change must be even less favourable, this rationalises previously unsuccessful attempts to synthesise $NF_4^+F^-$ at temperatures down to 77K by UV photolysis.

The enthalpy change for the $N_2F_4 \rightleftharpoons 2NF_2$ equilibrium has been determined, over the temperature range 50° to 200°C and pressures between 5 and 26 torr, using an i.r. diode laser to measure relative NF_2 concentrations.[125] The value obtained, 78±6 kJ mol^{-1}, is in good agreement with previous data. The n.m.r. (^1H and ^{19}F), i.r. and Raman spectra of several salts of NH_3F^+, including two new ones, $NH_3F^+SO_3X^-$, X = F or Cl, have been reported.[126]

The N-F bond in CF_2=NF has been shown to be long, 1.389(2)Å, from an electron diffraction and microwave study of the compound.[35] There is evidence for the formation of the perfluoromethanamine anion, CF_3NF^-, from CF_2=NF in the presence of F^-:[127] this species is proposed as an intermediate in reactions with CF_3COF and in dimerisation reactions. The nitride fluoride, F_4ReN, isolated from the action of Me_3SiN_3 on ReF_6, is converted by ClF_3 to the nitrenes $F_5Re(NF)$ and $F_5Re(NCl)$.[128] The molecular geometry of these two new compounds was estimated by X-ray structure determinations. The Re-N-X, X = Cl or F, arrangement is essentially linear, the Re-N bond lengths are similar, and the N-Cl and N-F bonds 1.56(2) and 1.257(13)Å respectively. This N-F bond is markedly shorter than that recently found in $F_4S{=}NF$, 1.357(8)Å which has a non-linear S-N-F unit (118(1)°).[129] The latter compound has been prepared by the dehydrofluorination of SF_5NHF by KF. DesMarteau and coworkers[129] also prepared the previously unknown SF_5-NClF from $F_3S{\equiv}N$ by the low temperature reaction with ClF and then F_2: reduction of the product with Hg in CF_3CO_2H yielded SF_5-NHF.

The equilibria and kinetics of chlorine transfer in aqueous solution from chloramine to form N-chloro derivatives of methylamine, aminoacids and peptides have been reported.[130] The rates are independent of pH from 4 to 7. They imply that NH_3Cl^+ is a very active agent; the rate constants increase with amine basicity up to a maximum rate of 2.4×10^8 $M^{-1}s^{-1}$ (25°C, 0.5M $NaClO_4$). Triethylhydrazinium and triphenylaminophosphonium chlorides appear to act as in situ sources for NH_2Cl and act as aminating agents towards Ph_2PCl.[131] The i.r. spectrum of NCl_2 in an Ar matrix has been studied;[132] the bond angle was calculated to be 111±4° from the isotope shift data. This value is close to that predicted from SCF-MO calculations (109.8°). The NBr_2 radical was also investigated experimentally and the bond angle shown to be less than 99.6°.

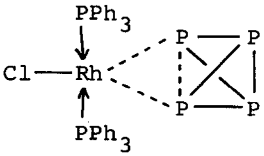
The decomposition of polymeric $NI_3.NH_3$ in liquid NH_3 has been re-investigated.[133] The net reaction produces NH_4I and N_2. On the basis of UV spectroscopic studies there is now support for Jander's proposal that NH_2I is an intermediate in the decomposition reaction. The decomposition rates are also consistent with the formation of $N_2H_5^+$ in the rate determining step.[134]

5.2 PHOSPHORUS

5.2.1 Phosphorus, Polyphosphines and Phosphides

The solubility of water in purified white phosphorus at temperatures greater than 390°C is less than 0.1mg/gP according to a recent reinvestigation;[135] this figure is substantially lower than that previously reported. When white phosphorus reacts in the presence of cyclohexene, oxygen and cyclohexene hydroperoxide in benzene solution, the product is a complex network of organophosphorus oxide units.[136] After hydrolysis or alcoholysis, n.m.r. spectroscopy shows the presence of a mixture of anhydrides and esterified phosphonous, phosphonic, phosphorous and phosphoric acid anhydrides. The major organo-phosphorus species are the anhydrides of cis-cyclohexene-1,2-diphosphonic acid and benzene phosphonic acid, the latter results from solvent participation.

The coordination behaviour of P_3 and P_4 units towards transition metals has been reviewed.[137] The presence of a P_4 unit behaving as an η^2-ligand has been established by ^{31}P n.m.r. spectroscopy in the rhodium complex (8),[138] and a coordinated cyclic P_2S unit is present in (9) which results when $Co(BF_4)_2.6H_2O$ reacts with P_4S_3 in the presence of 1,1,1-tris(diphenylphosphino)methyl-ethane (triphos).[139] An X-ray structure shows that P_2S behaves as an



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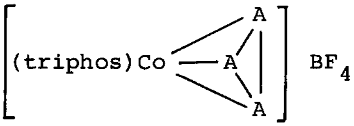


(9, A = 0.67P and 0.33S occupancy).

η^3-ligand in which each site has $^2/3$ phosphorus and $^1/3$ sulphur occupancy.

Although the diphosphene, PhP=PPh, cannot be isolated as a stable entity, it can be stabilised by coordination to a transition metal. This has been demonstrated by the isolation of $Pd(PhP{=}PPh)(Ph_2PCH_2CH_2PPh_2)$ from the reaction of $Li_2(PhPPPh)$ and $PdCl_2(Ph_2PCH_2CH_2PPh_2)$ in THF.[140] The diphosphene is sideways bonded as a η^2-ligand with Pd-P distances of 2.304 and 2.366Å, the P-P distance is 2.121Å.

Recent experiments have confirmed that the monosubstituted phosphorus(III) chloride $ArPCl_2$ is the product from a reaction between PCl_3 and $(t\text{-}Bu)_3C_6H_2Li$ (ArLi), but when two mols of the lithium aryl are used the product is the diphosphene, ArP=PAr, in 55% yield.[141] Photolysis of solutions of this compound in the presence of di(t-butyl)peroxide leads to a range of new phosphorus centred radicals and among those identified by e.s.r. spectroscopy are $\dot{P}_2Ar_2(Ot\text{-}Bu)$ and $\dot{P}Ar(Ot\text{-}Bu)$.[142]

Alkyl-substituted diphosphenes have been isolated during the course of 1982 by the reactions outlined in equations (27),[143] (28)[143] and (29).[144] In the absence of trapping agents, such as 2,3-dimethylbutadiene which yields the heterocycle (10), the products from equation (29) are polyphosphines.

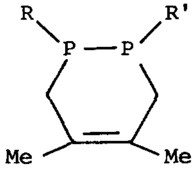
$$(Me_3Si)_3CPCl_2 \xrightarrow[\text{THF}]{\text{Na naphthenide}} (Me_3Si)_3CP{=}PC(SiMe_3)_3 \qquad ...(27)$$

$$(Me_3Si)_3CPCl_2 + (Me_3Si)_3CLi \rightarrow (Me_3Si)_3CP{=}PC(SiMe_3)_3 \qquad ...(28)$$

$$RPCl_2 + (Me_3Si)_2PR' \rightarrow RP{=}PR' + 2Me_3SiCl \qquad ...(29)$$

R = R' = t-Bu
R = t-Bu, R' = mesityl.

Reactions designed to give P(I) halides invariably lead to orange-red amorphous solids but the reduction of phosphorus trichloride with tin(II) chloride in the presence of the chelating diphosphine, $Ph_2PCH_2CH_2PPh_2$, leads to colourless crystals of (11).[145] The cation, in which the P-P distances are 2.122 and and 2.128Å and the P-P-P angle 88.9°, can be considered as a phosphorus(I) complex of the diphosphine chelate.



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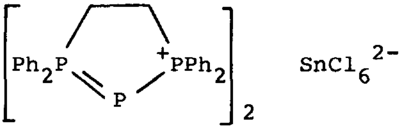

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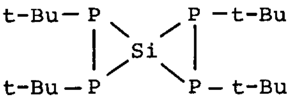
The versatile intermediate, K_2(t-BuPP t-Bu), reacts with $SiCl_4$,[146] Me_2SiCl_2[147] and 1,1-dichloroethane[148] to give the cyclic compounds (12), (13) and (14) respectively. Compound (12) is formed as a mixture of two diastereoisomers, which can be separated by fractional crystallisation. As shown in Figure 5, they differ in the relative arrangements of the trans orientated t-Bu groups. The P_4Si_2 ring in compound (13) is in an almost



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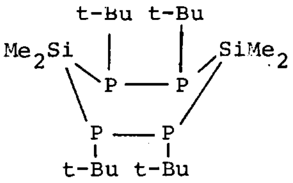

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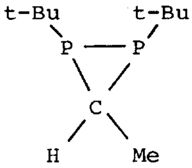

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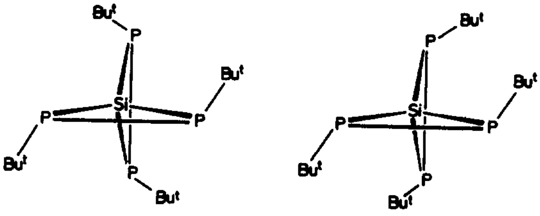
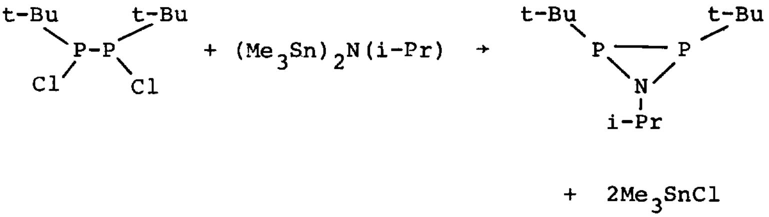


Figure 5. Structures of the isomeric forms of $(t\text{-}Bu_2P_2)_2Si$ (reproduced by permission from Z. Anorg. Allg. Chem., 491(1982)27).

ideal boat conformation which is unusual as repulsions between the all trans oriented t-butyl groups and the phosphorus lone pairs usually lead to either chair or twisted boat arrangements. Hydrolysis of the dipotassium salt, $K_2(t\text{-}BuPP\,t\text{-}Bu)$, leads to the new diphosphine t-BuPHPHt-Bu, a compound which also results from methanolysis of the silyldiphosphine, $[(Me_3Si)t\text{-}BuP)]_2$.[149] The product is a 7:3 mixture of the dl- and meso- forms.

Reaction of PBr_3 with tris(t-butyl)cyclotriphosphine is considered to proceed via the linear tetraphosphine Br(t-Bu)P.P(t-Bu).P(Br).P(t-Bu)Br, which rearranges intermolecularly to give the observed product, tris(bromo-t-butylphosphino)-phosphine, $P[P(t\text{-}Bu)Br]_3$, a derivative of iso-P_4H_6.[150] With PCl_5 in a 2:1 ratio, the cyclotriphosphine yields a stable diphosphine, Cl(t-Bu)P.P(t-Bu)Cl, together with PCl_3 and $t\text{-}BuPCl_2$ as by-products.[151] At room temperature, n.m.r. spectroscopy indicates a 1:4 mixture of the dl- and meso- forms, and the compound undergoes ring closure, as shown in equation (30), to give a new azadiphosphirane.[152] The ^{31}P n.m.r. spectrum of the



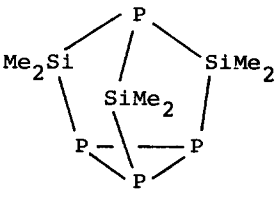
...(30)

compound is independent of temperature, pointing to planar geometry at nitrogen with N→P dative π-bonding.

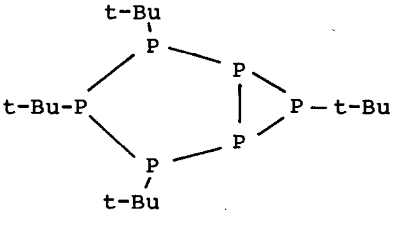
A structure determination for $(t\text{-}BuP)_3$ shows that the presence of two t-butyl groups in cis-positions leads to large P-P-C angles (ca. 123°) through steric hindrance.[153] In contrast the angle with the trans group is ca. 105°. Detailed n.m.r. data have been correlated with this structure and it is now possible to deduce bond angles in other cyclotriphosphines from ^{31}P data.

The silyldiphosphine, $(Me_3Si)_2P.P(SiMe_3)_2$, reacts in ether solution with t-BuLi to give $(Me_3Si)_2P.P(Li)SiMe_3$, which decomposes even at low temperatures into $(Me_3Si)_3P$, $(Me_3Si)_2PLi$ and Li_3P_7.[154] With the triphosphine $[(Me_3Si)_2P]_2PH$, t-BuLi gives $[(Me_3Si)_2P]_2PLi$ which in turn can be converted to $[(Me_3Si)_2P]_2PR$, where R = Me or Me_3Si, on reaction with respectively methyl chloride or Me_3SiCl.

The trisilatetraphospha-nortricyclene(<u>15</u>) can displace either benzene or cycloheptatriene(≡R) from $RCr(CO)_3$ to give red crystals of $[P_4(SiMe_2)_3]_3[Cr(CO)_3]_2$.[155] The product occurs in both orthorhombic and hexagonal forms, but in each the chromium atoms are attached to one phosphorus atom of the P_3 ring of all three molecules of (<u>15</u>). The disilylated tetraphosphine,



(<u>15</u>)

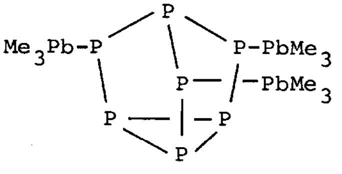


(<u>16</u>)

$Me_3Si(t\text{-}BuP)_4SiMe_3$, contains slightly different P-P bond lengths, i.e. those involving atoms attached to silicon are 2.188Å while the central P-P bond is longer (2.214Å).[156]

The bicyclic structure, shown in (16), in which three membered and five membered phosphorus rings share a common edge, has been observed in the structure of t-Bu_4P_6.[157] The rings are almost perpendicular with, unusually, the five membered system being close to planarity; the t-butyl groups occupy all trans positions.

A stable phosphorus-lead compound (17) has been prepared by displacing the $SiMe_3$ groups in $P_7(SiMe_3)_3$ with Me_3PbCl in monoglyme at -50°C.[158] The mean P-Pb distance is 2.611Å. The tin analogue can be obtained similarly while the germanium compound results from the Na_3P_7-Me_3GeCl reaction. The bicyclic structure (18, M = P) with ca. C_{2h} symmetry has been determined for t-Bu_6P_8;[159] the P-P bridge bond is 2.218Å, almost equal to the mean P-P distance (2.21Å), and again the substituents occupy all trans positions. An arsenic analogue (18, M = As) has also been isolated from a dehalogenation reaction of a 3:1 mixture of t-$BuPCl_2$ and $AsCl_3$ with magnesium in THF solution.[160] As with the phosphorus analogue, its structure consists of two slightly folded, σ-bonded, four membered rings with trans oriented substituents. Important bond distances are As-As 2.441, As-P 2.356 and P-P 2.226Å.



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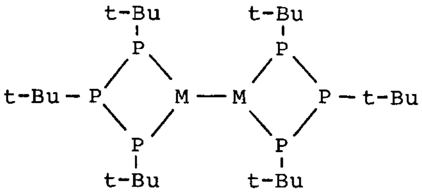
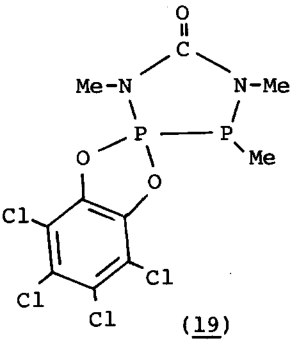


(18)

Crystalline complexes containing the bis(phosphinoyl)phosphido group can be obtained from reactions between molybdenum or tungsten hexacarbonyls and the piperidinium salt, $C_5H_{10}NH_2^+[(EtO)_2P(O).P.P(O)(OEt)_2]^-$.[161] Structures have been determined for two such compounds, the first containing a $W(CO)_5$ group attached to the central phosphorus atom and the second in which the central phosphorus carries two $Mo(CO)_5$ groups.

2,2-Dimethylpropylmagnesium chloride and t-$BuPCl_2$ reactions probably lead to the diphosphine, t-$BuCH_2$(t-Bu)P.P(t-Bu)CH_2t-Bu, which with hydrogen peroxide yields the corresponding dioxide t-BuCH$_2$(t-Bu)P(O).P(O)(t-Bu)CH$_2$t-Bu.[162] Its structure shows an eclipsed conformation with the P=O and P'-t-Bu groups almost diametrically opposed. The related diphosphine dioxide, Ph$_2$P(O).P(O)Ph$_2$, is isostructural with the corresponding sulphide from X-ray powder diffraction,[163] and the diphosphine itself reacts with potassium selenocyanate in acetonitrile giving the unstable Ph$_2$P(Se)SeP(Se)Ph$_2$ by both oxidation and selenium insertion.

The novel λ^5P-λ^3P compound (19) reacts with Fe$_2$(CO)$_9$ to give a product in which the phosphorus(III) atom is coordinated to an Fe(CO)$_5$ group;[164] the phosphorus(V) atom is in basically square pyramidal coordination. Data are also available for two compounds containing bonds between two phosphorus(V) atoms. In the first case (20) the atoms show respectively four- and five-fold coordination,[165] but in the latter (21), which results from the oxidation of the diphosphabicyclooctane (22) with tetrachloro-o-benzoquinone, the coordination number for each phosphorus atom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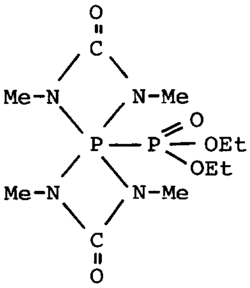
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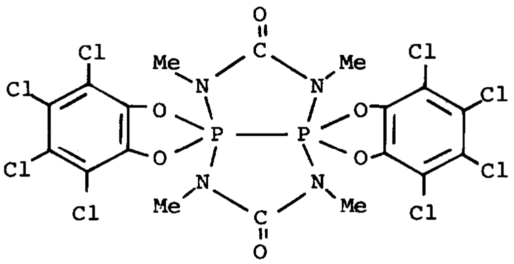
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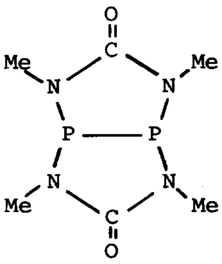

(22)

is five.[166]

The molar volume of phosphorus in a range of metal phosphides has been investigated showing significant trends.[167] In the salt-like species, for example, the volume increment increases with increased negative charge of the phosphide and decreases with increased cation charge. In some cases a correlation between molar volume and bonding type is possible.

N.m.r. parameters for, mainly, THF solutions of alkali metal phosphides have been measured in the presence of cryptands,[168] and among the new binary phosphides prepared and investigated are BaP_{10}[169] and Cu_2P_7.[170] The former, obtained from BaP_3 and red phosphorus at 1050K, is resistant to both acids and bases, decomposing on heating to Ba_3P_{14} and finally BaP_3. Its structure, shown in Figure 6, contains a two dimensional anionic structure, based on interconnection of the pentagonal phosphorus tubes found in Hittorf's phosphorus. Equilibrium pressures for the decomposition of CdP_2, Cd_3P_2 and CdP_4, etc. have been determined and analysed to give the heats and entropies of formation.[171]

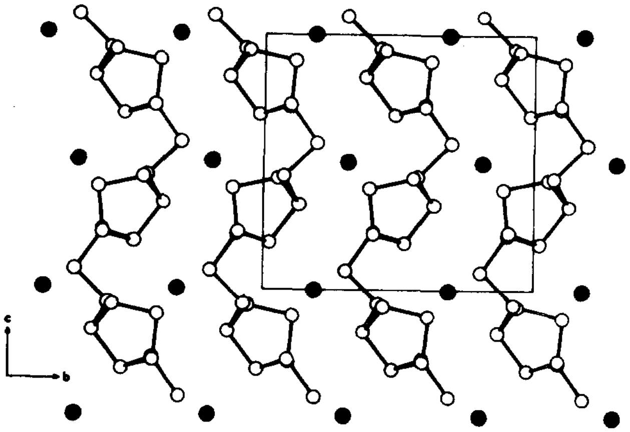


Figure 6. Projection of the BaP_{10} structure on to the (100) plane (reproduced by permission from Z. Anorg. Allg. Chem., 491(1982)286).

New ternary germanium phosphides and arsenides have been isolated from high temperature reactions with stoichiometric mixtures of the elements.[171,172] For Ba_2GeP_2 and the arsenide, the structures show the presence of isolated $Ge_2P_4{}^{8-}$ and $Ge_2As_4{}^{8-}$ ions where the mean Ge-P distance is 2.28Å (Ge-As, ca. 2.40Å). The Ge-Ge-P angles are 111.1 and 112.6° and the P-Ge-P angles have a mean value of 128.0°.[172] Polymeric Ge_2P_6 chains, on the other hand, are present in $Ca_3Ge_2P_4$ and $Sr_3Ge_2P_4$, while in $Ba_3Si_2As_4$ the same type of unit, i.e. Si_2As_6 chains, is present but they are linked differently.[173]

Structures for Ti_7P_4 and $Ti_{14-x}Cu_xP_9$ for x = 0.14 are isotypic with Nb_7P_4 and $Zr_{14}P_9$ respectively,[174] while reactions between the stoichiometric amounts of rhenium and phosphorus in metallic tin yield the new species ReP_3[175] and Re_2P_5.[176] The former is isostructural with the newly prepared TcP_3, in which the metal atom is in distorted octahedral coordination by phosphorus and the phosphorus atoms are tetrahedrally coordinated by technetium and phosphorus.[175] Tetrahedral coordination of phosphorus is also found in Re_2P_5 but if ionicity is considered the structure contains homoatomic P_2 and P_4 zig-zag chain anions.[176]

Compounds with the stoichiometry Ca_3PI_3 and Ca_2PI can be isolated from high temperature solid state reactions between Ca_3P_2 and CaI_2 in 1:3 and 1:1 ratios.[177] The arsenic analogues have also been obtained.

5.2.2 Bonds to Carbon or Silicon

The +3 Oxidation State. This section and the one following on the +5 oxidation state begin with a discussion of species containing multiple bonds between phosphorus and carbon. Photoelectron spectroscopy has been used to optimise the conditions for the gas phase pyrolysis of chloro(trimethylsilylmethylene)phosphines, $R(Me_3Si)C{=}PCl$, to yield the phosphaalkynes $PhC{\equiv}P$ and $Me_3SiC{\equiv}P$.[178] A recent X-ray structure on the metal carbonyl complex, $Co_2(CO)_6(t\text{-}BuCP)W(CO)_5$, shows behaviour of the phospha-alkyne as a six electron donor (see Figure 7).[179] The compound is prepared as shown in Scheme 4.

$$\begin{tikzcd}
t\text{-}BuC{\equiv}P + Co_2(CO)_8 \arrow[r] & Co_2(CO)_6(P{\equiv}C\text{-}t\text{-}Bu) \arrow[d, "W(CO)_5THF"] \\
 & Co_2(CO)_6(P{\equiv}C\text{-}t\text{-}Bu)W(CO)_5
\end{tikzcd}$$

Scheme 4

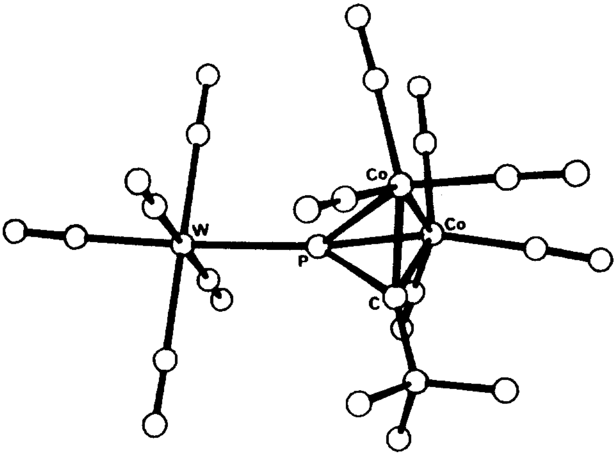
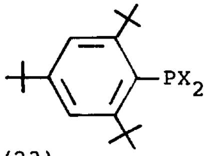


Figure 7. Crystal structure of $Co_2(CO)_6$(t-BuCP)$W(CO)_5$ (reproduced by permission from J. Organomet. Chem., 238(1982)C82).

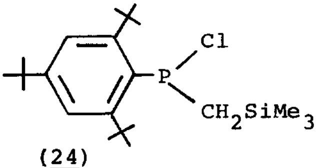
Microwave spectroscopic data for six isotopically substituted 1-chlorophosphaethenes, CH_2=PCl, obtained by pyrolysis of the appropriately substituted methyl dichlorophosphite indicate a planar structure with C=P and P-Cl bond distances of 1.655 and 2.060Å respectively and a Cl-P-C angle of 103.3°.[180] A reinvestigation of the methyldichlorophosphite pyrolysis shows the presence of CH_2=PCl, HC≡P, CH_3Cl and HCHO together with an unknown symmetric top molecule considered to be P_4O_7 from a microwave study.[181]

Platinum complexes, i.e. cis- and trans-[$PtCl_2(PEt_3)L$] and cis-[PtX_2L_2] where X = Cl, I or Me, have been isolated where L = (mesityl)P=CPh_2.[182] The ligand is bonded to platinum via the phosphorus lone pair at a distance of 2.199Å from a full structure determination on cis-[$PtCl_2(PEt_3)L$].$CHCl_3$.

The lithium derivative of tris(t-butyl)benzene reacts with either PCl_3 or the substituted compound $Me_3SiCH_2PCl_2$ to give (<u>23</u>, X = Cl) and (<u>24</u>) respectively.[183] Compound (<u>23</u>, X = Cl) can be reduced



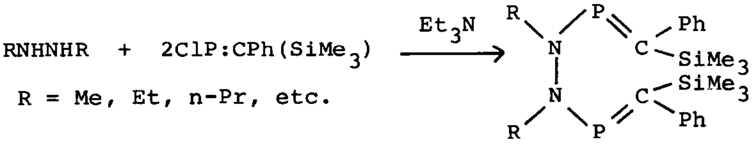
(<u>23</u>)



(<u>24</u>)

with $LiAlH_4$ to the corresponding phosphine (23, X = H) while on heating, compound (24) can lose either hydrogen chloride or trimethylchlorosilane yielding respectively $(t\text{-}Bu)_3C_6H_2P{:}CH(SiMe_3)$ or $(t\text{-}Bu)_3C_6H_2P{:}CH_2$.

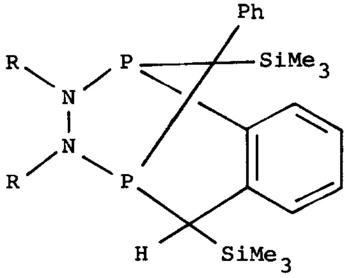
Disubstituted hydrazines and chlorophosphaalkenes react to give diazadiphosphahexadienes (25) as shown in equation (31) as unstable



...(31)

(25)

intermediates,[184] but the isolated products are tricyclic compounds (26), resulting from intramolecular Diels-Alder reactions. If the hydrazine in equation (31) carries an α-carbon



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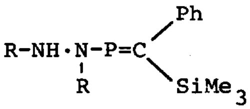
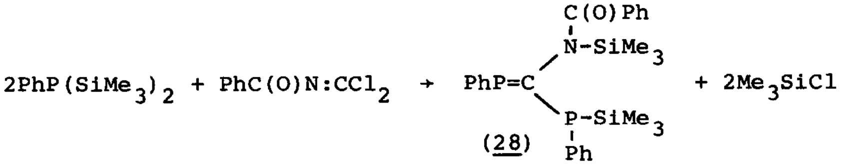


(27)

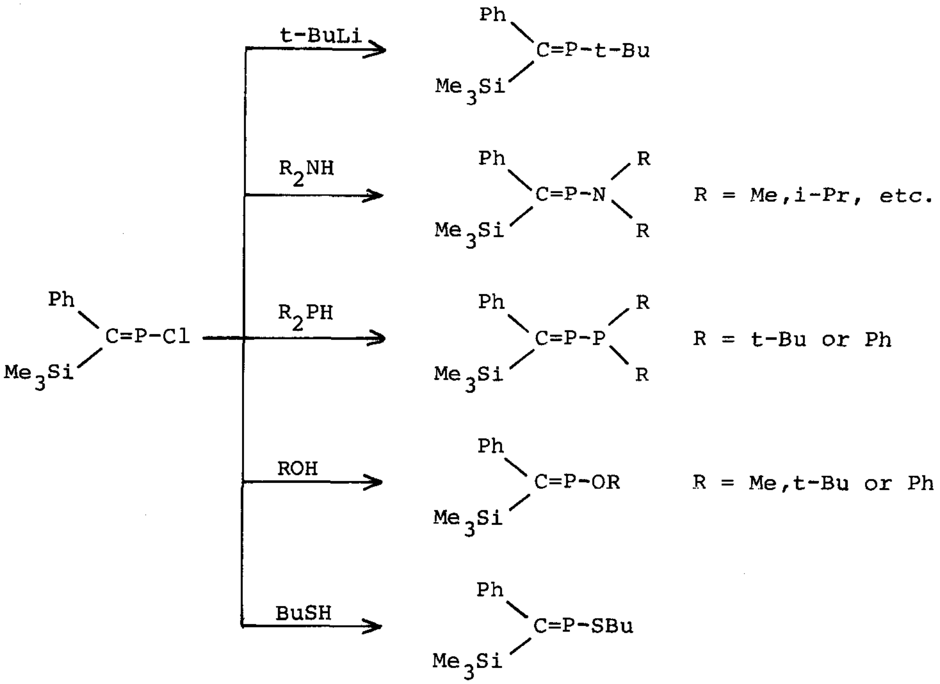
branched substituent however, the products are substituted phosphaalkenes (27).

A series of novel phosphaalkenes have been synthesised from the parent P-chloro-derivative as shown in Scheme 5.[185] The initial product (28) from the reaction in equation (32) contains a phosphaalkene bond, but the compound isomerises to give the



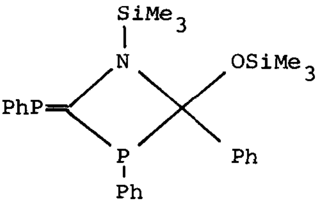
$$2PhP(SiMe_3)_2 + PhC(O)N{:}CCl_2 \rightarrow PhP{=}C[N(C(O)Ph)SiMe_3][P(Ph)SiMe_3] + 2Me_3SiCl \quad \ldots(32)$$

(28)



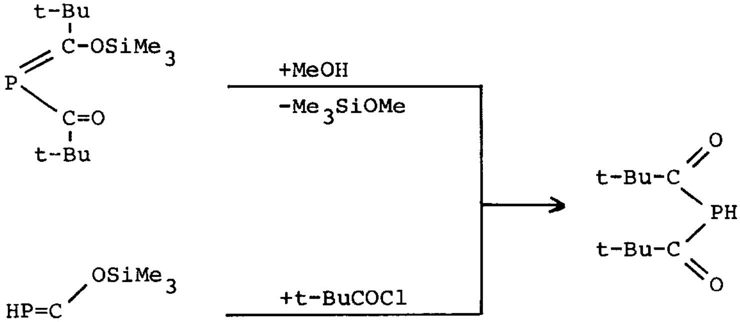
Scheme 5

azaphosphetidine (29) for which a full X-ray structure is available (P=C, 1.70Å).[186]

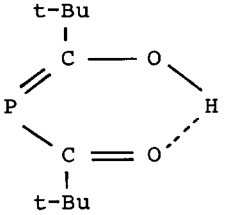


(29)

Bis(2,2-dimethylpropionyl)phosphine (30), which can be synthesised as shown in equation (33), is present in solution as a mixture of the keto (30) and enol (31) forms, the equilibrium depending on the solvent dielectric constant.[187] Treatment of (30) with $NaN(SiMe_3)_2$ in dimethoxyethane gives the sodium salt (32) (≡LNa), which with $CrCl_3.3THF$ and $NiBr_2.DME$ is converted into CrL_3 and $NiL_2.DME$, respectively.



(30) ...(33)



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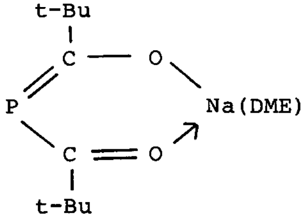
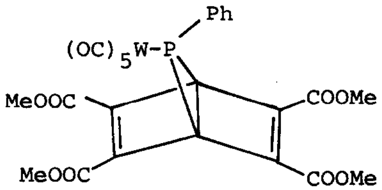


(32)

Trapping experiments have recently shown that on heating the phosphinidine complex (33) generates a previously unknown species, $PhP{=}W(CO)_5$, containing a terminal phosphinidine unit.[188] This observation has been used in the synthesis of a series of phosphirene complexes (34, M = Cr or W, R = Me or Ph, R^1 = Et or Ph) by reaction with, particularly, electron rich alkynes. An X-ray structure for (34, M = W, R = R^1 = Ph) shows that discrete molecules are present in which the C-P-C ring angle (42.8°) is the smallest yet observed; the phosphirene ring is probably stabilised by both the bulkiness and electron withdrawing power of the



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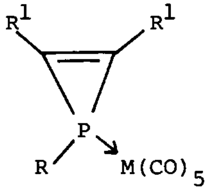
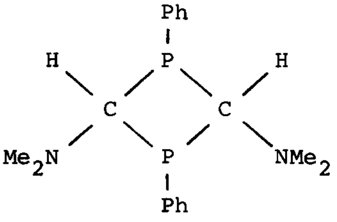


(34)

$W(CO)_5$ group.

Stabilised phosphinyl radicals, i.e. species intermediate between two-coordinate phosphenium cations and phosphide anions, are good ligands as shown by the isolation of $[(Me_3Si)_2CH]_2PFe(CO)_4$ and $[(Me_3Si)_2CH]_2PCo_2(CO)_6$ from reactions of $[(Me_3Si)_2CH]_2P$ with respectively $Fe_2(CO)_9$ and $Co_2(CO)_8$.[189]

The structure of the diphosphetane (35), which is a byproduct in the synthesis of $PhP{=}CH(NMe_2)$, contains a folded P_2C_2 ring with phenyl groups above and amine groups below the ring; the mean P-C



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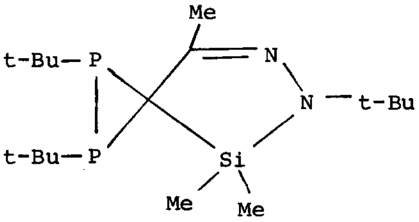

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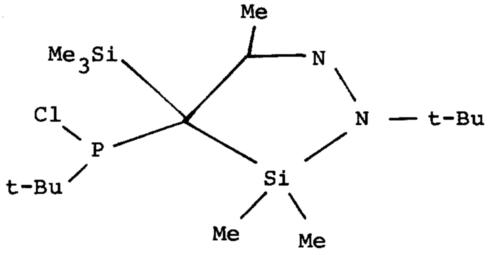
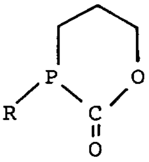


(37)

distance is 1.89Å, with C-P-C and P-C-P angles of 84 and 93° respectively.[190] The diphosphirane (36) can be synthesised by a novel route involving loss of Me_3SiCl from (37).[191]

^{13}C and ^{1}H n.m.r. data for, inter alia, $PhMH_2$, Ph_2MH and Ph_2MNa where M = P or As, have been used to assess the extent of pπ-pπ interaction between the phenyl ring and the substituent.[192]

Primary phosphine reactions with chloroformic esters in benzene solution in the presence of potassium carbonate lead to the mono- and di-substituted compounds $RPHCOOR^1$ and $RP(COOR^1)_2$ where R = Ph, cyclohexyl or $NC(CH_2)_2$ and R^1 = Et, Bu or $CH_2{=}CHCH_2$.[193] The former can be converted, when R^1 contains an unsaturated group, to the ring compound (38). Photochemical addition reactions



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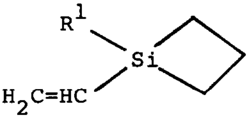

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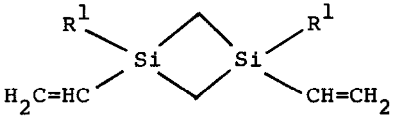
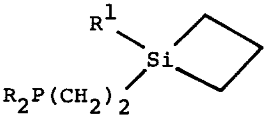
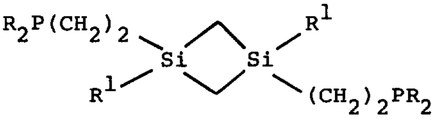


(40)

between secondary phosphines, R_2PH where R = Me or CF_3, and the substituted vinyl silanes (39) and (40) do not follow the Markownikoff rule, but give respectively the phosphanoethyl compounds (41) and (42).[194] The latter form complexes of the



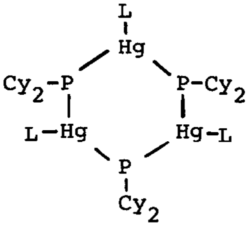
(41)



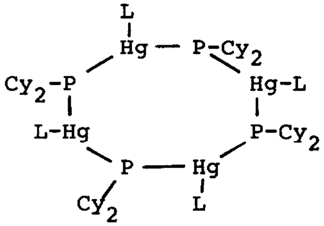
(42)

type $Fe(CO)_4L$ but there is no evidence for species containing stabilised phosphanoethylsilaethenes.[195]

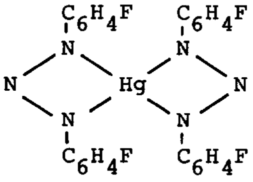
The new compounds, (43) and (44), containing respectively six- and eight-membered Hg-P ring systems, have been observed in the



(43, Cy = cyclohexyl,
L = $N_3(C_6H_4F)_2$



(44)



(45)

product from a reaction between Cy_2PH (Cy = cyclohexyl) and the mercury complex (45) ($\equiv HgL_2$);[196] an analogue of compound (43) can be isolated when di(t-butyl)phosphine is used .

The unstable (chloromethyl)dimethylphosphine, which has been synthesised by the reaction in equation (34), reacts with oxygen,

$$\mathrm{MeClP(CH_2Cl) + LiMe \rightarrow Me_2P(CH_2Cl) + LiCl} \qquad \ldots(34)$$

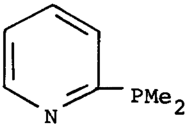
methyl bromide and $LiPMe_2$ to give as expected $Me_2P(O)CH_2Cl$, $Me_3P(CH_2Cl)Br$ and $Me_2PCH_2PMe_2$, respectively.[197]

The basicities of a range of 4-substituted triphenylphosphines, together with the tri-t-butyl and tricyclohexyl derivatives have been measured by titration with perchloric acid in nitromethane solution.[198] In the substituted aryl series, pK_a values vary from 8.65 for the 4-dimethylamino compound to 1.03 with 4-chloro substituents; the most basic compound is the t-butyl derivative with a pK_a of 11.4. In general, n.m.r. parameters for the free and protonated bases do not show a good correlation with the measured pK_a values.

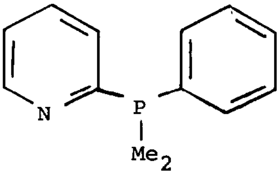
Tris[2,6-bis(difluoromethyl)phenyl]phosphine, together with the corresponding arsine and the two oxides have been synthesised for detailed n.m.r. study.[199] Complexation of cadmium salts by tri-butyl- and tri-cyclohexyl-phosphines in dichloromethane solution has been investigated by n.m.r. spectroscopy showing that the coordination number of cadmium depends on the nature of both the phosphine and the anion.[200]

Among the products isolated from reactions between triphenylphosphine and TcO_4^- in hydrochloric acid solution are $TcCl_4(PPh_3)_2$, $TcCl_5(PPh_3)^-$ and $TcCl_6^{2-}$.[201] The second compound has been investigated by single crystal X-ray diffraction, and a crystal structure determination on bis(trimesitylphosphine)silver(I) hexafluorophosphate shows an essentially linear (179.4°) P-Ag-P system.[202]

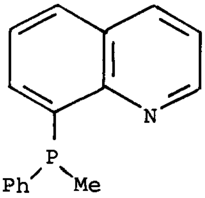
The pyridyl phosphines (<u>46</u>) and (<u>47</u>) have been synthesised, converted to the methylphosphonium salts and by proton abstraction converted to the phosphonium methylides.[203] The



(<u>46</u>)



(<u>47</u>)

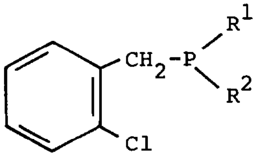


(<u>48</u>)

related diphenyl(2-pyridyl)phosphine (≡L) forms the gold and silver complexes AuCl.L and $Ag_2Cl_2L_3$.[204] In the former the ligand is bonded via the phosphorus lone pair but in the latter, while one silver atom is bonded to two ligands through phosphorus atoms, the second silver atom in addition to attaching the third ligand also forms a weak Ag---N contact. Two new asymmetric ligands, (<u>48</u>) and the related arsenic compound, have been synthesised from 8-chloroquinoline and the absolute configuration of a palladium complex of (<u>48</u>) has been determined after separation by fractional crystallisation.[205]

The donor powers of a group of phenyl substituted phosphines carrying up to two 2- or 3-furyl, 2- or 3-thienyl or 1-methylpyrrol-2-yl groups towards both selenium and Pt(II) has been assessed by ^{31}P n.m.r. spectroscopy.[206] The ^1J(Se-P) and ^1J(Pt-P) coupling constants increase as the heteroaryl group becomes more electron withdrawing indicating an increase in the s character of the phosphorus lone pair. Tri(ferrocenyl)-phosphine (Fe_3P) on reaction with iodine gives both 1:1 and 1:2 complexes formulated as $(Fe_3PI)I$ and $(Fe_3PI)I_3$ respectively.[207]

Metallation of o-chlorobenzyldiorganophosphines (<u>49</u>) with n-BuLi gives α-metallation and/or nucleophilic substitution at phosphorus depending on substituent size and the acidity of the methylene protons.[208] This is in contrast to the behaviour of the related o-bromo-compound which gives only α-metallation products.



(<u>49</u>)

A reinvestigation of the methylenebis(dichlorophosphine) preparation from phosphorus trichloride, dichloromethane and aluminium chloride shows that in addition to $CH_2(PCl_2)_2$ there is simultaneous preparation of the triphosphapentane, $Cl_2PCH_2PClCH_2PCl_2$, and the chloromethyl substituted methylene diphosphine $Cl_2P.CH_2.PCl.CH_2Cl$.[209]

Silver hexafluorophosphate and bis(dimethylphosphino)methane give the complex $Ag_2(Me_2PCH_2PMe_2)_2(PF_6)_2$ with a structure containing a centrosymmetric eight membered ring structure in which ligands bridge between the two silver atoms.[210] The related diphenylphosphine ligand, $Ph_2PCH_2PPh_2$ (≡L), also generally behaves as a bridging group but from an X-ray structure it is monodentate in the complex $[(t\text{-}BuNC)_2PdL_2](BPh_4)_2$.[211]

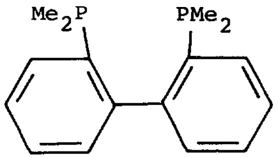
^{31}P and ^{7}Li n.m.r. data point to monomeric covalent structures for both $LiCH(PPh_2)_2$ and $LiCH(PPh_2)[P(S)Ph_2]$ but to a dimeric structure for the related $LiPPh_2$ in ether at low temperatures.[212] Detailed n.m.r. parameters have been obtained for compounds of the type $Ph_2(Y)XP(Z)Ph_2$ where X = CH_2, $(CH_2)_2$, $(CH_2)_3$, etc. and Y/Z = lone pair or Se.[213]

The 1:1 adduct of $Hg(CN)_2$ with 1,2-bis(diphenylphosphino)ethane contains infinite chains in which the mercury atoms are approximately tetrahedrally coordinated to two cyanide groups and two PPh_2 groups;[214] the Hg-P distances, 2.534 and 2.606Å are significantly different. The related perfluorophenyl substituted ligand, $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$, is an air stable solid obtainable by treating 1,2-bis(dichlorophosphino)ethane with either LiC_6F_5 or a Grignard reagent.[215]

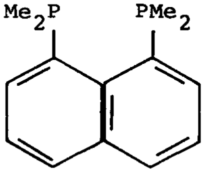
The tetraphenyldiphosphoxane group, Ph_2POPPh_2, behaves as a chelating group in the chromium and molybdenum complexes, $(OC)_4M(Ph_2POPPh_2)$.[216] Important structural parameters for the molybdenum complex are Mo-P 2.458, 2.476Å, P-O-P 103.3° and P-Mo-P 63.8°. With the isomeric ligand, $Ph_2P(O)PPh_2$, reactions with chromium, molybdenum and tungsten hexacarbonyls lead to $(OC)_5M[PPh_2(O)PPh_2]$, in which the metal is coordinated to the phosphorus(III) atom.[217] On heating in diglyme however, there is further loss of CO and the ligand rearranges to give the diphosphoxane complexes mentioned above.

Synthesis of the new chelating ligands, $Ph_2MCH_2CMe_2CH_2MPh_2$ for M = P or As, from 2,2-dimethyl-1,3-dibromopropane together with the formation of $Mo(CO)_4L$ and $W(CO)_4L$ has been announced.[218] With the bifunctional aminophosphine $Ph(Et_2N)P(CH_2)_4P(NEt_2)Ph$, similar $M(CO)_4L$ products are obtained with chromium, molybdenum and tungsten carbonyls in which coordination occurs via the phosphorus atoms.[219] N.m.r. data point to the presence of both dl- and meso- forms of the ligand with the racemic form appearing to predominate in the molybdenum complex.

Bis(dimethylphosphine)-derivatives of both biphenyl (<u>50</u>)[220] and naphthalene (<u>51</u>)[221] have been isolated. The former gives a rhodium(I) chloride complex and can be converted to the diquaternary salt (52) by dibromomethane. Deprotonation leads



(50)



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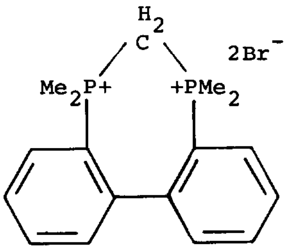
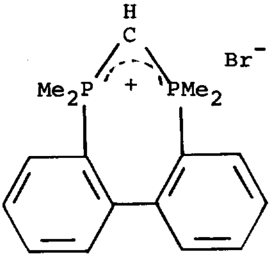


(52)



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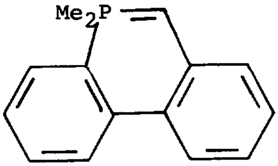


(54)

initially to the semiylide salt (53) but with KH in THF, an $MePCH_2$ fragment is lost giving the phosphaphenanthrene (54).[220] In contrast the naphthalene compound (51) gives only a monoquaternary salt with methyl iodide and a complex mixture of salts with a dihalomethane.[221]

Reaction of the sodium salt, Ph_2PNa, with 1,8-dibromo-3,6-dioxaoctane gives the new ligand $Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$, which readily forms complexes with nickel(II) salts.[222] The thiocyanate complex is a monomer, $Ni(NCS)_2L$, according to an X-ray structure, with coordination via the phosphorus atoms. Rather surprisingly the P-Ni-P angle is 175.9°, showing that the ligand spans trans-positions in the coordination sphere. Five coordinate complexes, e.g. $[NiClL]PF_6$ and $[CoClL]BF_4$, have been prepared and characterised by crystallography when L is the linear tetradentate diphosphinediamine, $CH_2(CH_2.PPh.CH_2CH_2CH_2NH_2)_2$.[223] In each case there is square pyramidal geometry about the metal atom with the chlorine atom occupying the apical position.

A bis(phosphinomethyl)phosphine has been prepared following equation (35).[224] Reaction with oxygen gives a mixture of $[Me_2P(O)CH_2]_2PMe$ and $[Me_2P(O)CH_2]_2P(O)Me$ while with methyl iodide the product is $[(Me_3PCH_2)_2PMe]I_2$. Rather than producing

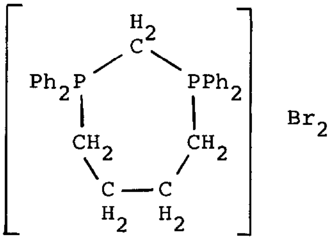
$$\mathrm{MePX_2} + \mathrm{2LiCH_2PMe_2} \xrightarrow[-45^{o}C]{Et_2O} \mathrm{2LiX} + \mathrm{(Me_2PCH_2)_2PMe} \qquad ...(35)$$

X = Cl or OPh

$C(PMe_2)_4$, reaction between Me_2PCl and the lithium salt $Li[C(PMe_2)_3]$ leads to the isomer $Me_2P\text{-}PMe_2{=}C(PMe_2)_2$;[225] the simplest member of this new class of phosphorus ylids, i.e. $Me_3P{=}C(PMe_2)_3$ has also been isolated and its behaviour as a bidentate ligand investigated.

A crystal structure determination on the ligand, 1,1,1-tris-[(diphenylphosphino)methyl]ethane $MeC(CH_2PPh_2)_3$ used extensively in complex compounds containing P_3 units, shows neither crystallographic nor pseudo- three fold symmetry as the conformation of one of the chains is markedly different.[226] On coordination only minor conformational changes occur. Complex compounds between nickel(II) bromide and the chelating chiral tetraphosphaalkanes, $MeRP(CH_2)_3PMe(CH_2)_mPMe(CH_2)_3PRMe$ ($\equiv$L) where R = H or Me and m = 2 or 3, have been isolated and the structure of [NiLBr]Br (R = H; m = 2) determined.[227]

A seven membered cyclic bis(phosphonium) salt, (55) has been isolated together with the linear compound, butane-1,4-bis-[diphenyl(diphenylphosphinomethyl)phosphonium]bromide, $[Ph_2PCH_2PPh_2(CH_2)_4PPh_2CH_2PPh_2]^{2+}2Br^-$, from a reaction between bis(diphenylphosphino)methane, $CH_2(PPh_2)_2$ and 1,4-dibromobutane.[228]



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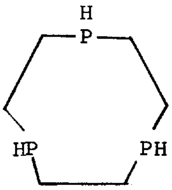


(56)

Further reactions of the linear product are summarised in Scheme 6.

Synthesis of a metal complex of the macrocyclic triphosphine (56) from (mesitylene)$Mo(CO)_3$ and alkylphosphine depends on a kinetic template effect and proceeds via the P-bonded intermediate, $(OC)_3Mo(PH_2CH_2CH{=}CH_2)_3$.[229] Heating in benzene solution yields

$$[Ph_2P\text{-}CH_2\text{-}PPh_2\text{-}(CH_2)_4\text{-}PPh_2\text{-}CH_2\text{-}PPh_2]\,Br_2$$

$$\Big\downarrow 2Me_3P{=}CH_2$$

$$Ph_2P\text{-}CH{=}PPh_2\text{-}(CH_2)_4\text{-}PPh_2{=}CH\text{-}PPh_2$$

$$\Big\downarrow 2MeI$$

$$[MePh_2P\overset{\cdots}{—}CH\overset{\cdots}{—}PPh_2\text{-}(CH_2)_4\text{-}PPh_2\overset{\cdots}{—}CH\overset{\cdots}{—}PPh_2Me]I_2$$

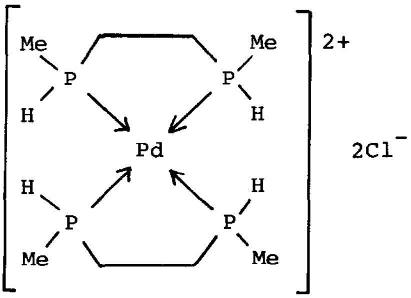
$$\Big\downarrow Me_3P{=}CH_2$$

$$MePPh_2P{=}C{=}PPh_2\text{-}(CH_2)_4\text{-}PPh_2{=}C{=}PPh_2Me$$

Scheme 6

the final product by an anti-Markownikov addition of PH across the double bond of a neighbouring allyl group. The ligand coordinates in fac-positions with Mo-P distances of 2.507, 2.455 and 2.465Å.

Two further phosphorus macrocyclic species, which are analogues of the well known crown ethers, have also been reported. In the first example, a tetraphosphine is produced by exploiting a template effect with the Pd(II) complex (57) in a reaction with acetylacetone.[230] The product (58) occurs in two forms for which structural data are available. The second compound (59) is a tetraphosphacyclo-octadecane obtained in a one step process from



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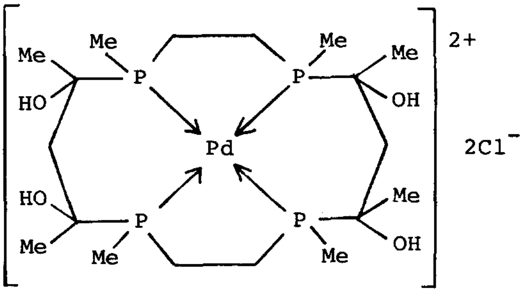

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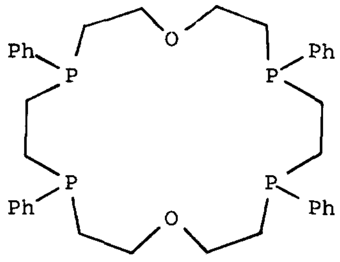


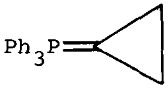
(59)

1,2-bis(phenylphosphino)ethane, phenyl lithium and 2,2'-dichloroethyl ether.[231] Five diastereoisomers have been isolated and characterised and nickel(II) and cobalt(II) complexes produced from the two more readily available forms.

A number of complexes containing the coordinated $Et_3P.CS_2$ group have been produced. For example, reactions with $Co(H_2O)_6^{2+}$ in the presence of 1,1,1-tris[(diphenylphosphine)methyl]ethane (≡L) can lead to either $[LCo(S_2CPEt_3)](BPh_4)_4$, $[LCo(S_2CHPEt_3)](BPh_4)_2$ or $[LCo(\mu\text{-}CS_2)CoL](BF_4)_2$ depending on the detailed preparative route.[232] If the diethyl analogue of L is used, the product is the related complex $[L^1Co(S_2CHPEt_3](BPh_4)_2$, which shows cobalt in distorted square pyramidal coordination to three phosphorus atoms from L^1 and two sulphur atoms of the $S_2C(H)PEt_3$ group. High electrophilicity for the carbon atom of the S_2CPEt_3 group in $[LCo(S_2CPEt_3)](BPh_4)_2$ is shown by its reaction with BH_4^- to give $[LCo(S_2CHPEt_3)](BPh_4)_2$;[233] in the presence of OEt^-, the complex reacts with oxygen and sulphur to give respectively $[LCo(S_2CO)]$ and $[LCo(S_2CS)]$. A full structure determination for the former, containing the coordinated dithiocarbonate group, shows the cobalt again in distorted square pyramidal coordination to three phosphorus and two sulphur atoms. Related compounds can be obtained from similar reactions with $Fe(H_2O)_6^{2+}$; isolation of $[L_2Fe(S_2CPEt_3)](BPh_4)_2$ is reported, which can be converted to the dithioformate complex $[L_2Fe(S_2CH)](BPh_4)$ by hydride ion attack.[234]

The +5 Oxidation State. Reactions between $M(CO)_6$, where M = Cr, Mo or W, and $Me_3P{=}CH_2$ lead to phosphonium acyl metal phosphorus ylides of the type $Me_4P[(OC)_5M{=}C(O).CH{=}PMe_3]$.[235] Such compounds react further with $Me_3SiOSO_2CF_3$ to give siloxy substituted compounds $(OC)_5M{=}C(OSiMe_3).CH{=}PMe_3$; the structure of the latter compound where M = W has been determined. The related $Ph_3P{=}CHR$ ylids, where R = H, Me or i-Pr, react with Group 4 organometallic halides leading to species of the type $[Ph_3PCHR\text{-}MPh_3]^+Cl^-$ for M = Ge, Sn or Pb and $[Ph_3PCHR]_n^+(MCl_n)^-$ for M = Ge or Pb.[236]

Pure samples of triphenylphosphonium cyclopropylide (60) have been obtained for the first time by treating (3-bromopropyl)-triphenylphosphonium bromide with potassium hydride in THF.[237]



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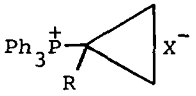
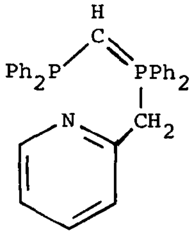


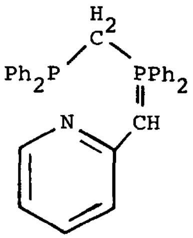
(61, X = Br or I)

The geometry in the solid state has been confirmed by an X-ray structure which shows the ylidic P=C distance of 1.696Å. The compound reacts with hydrogen bromide and methyl iodide to give (61), R = H or Me respectively, and forms 1:1 adducts with Me_3Al and Et_3Ga.[238]

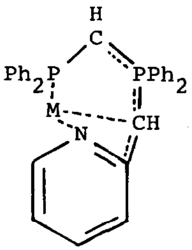
Deprotonation of the mixture of ylids (62) and (63) with either potassium hydride or sodium amide leads to metal derivatives of the unusual anion (64);[239] a structure has been determined for the potassium salt with two mols of THF of solvation. A similar



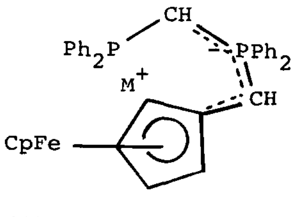
(62)



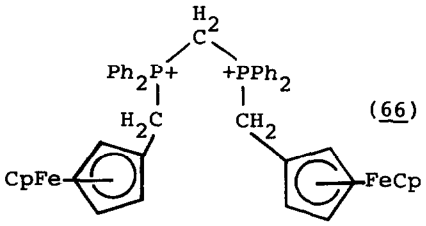
(63)



(64, M = Na or K)

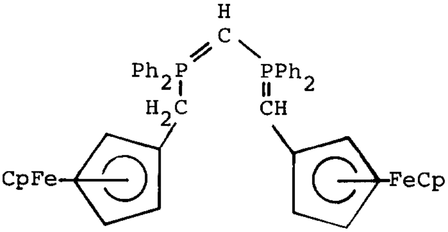


(65, M = Na or K)



(66)

species (65) is the deprotonation product from the new ferrocenyl ylid, and here there is n.m.r. evidence for interaction between the alkali metal cation of the ferrocenyl rings.[240] The diquaternary salt (66), which can be isolated from ferrocenylmethyl chloride and bis(diphenylphosphino)methane, can be converted into a mixture of the double ylids (67) and (68) on treatment with base.



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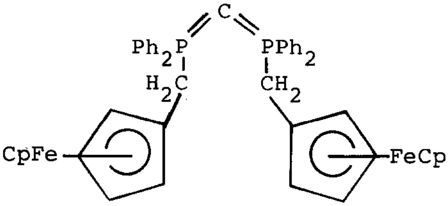
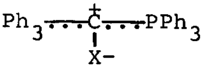


(68)

The double ylid, $Ph_3P{=}C{=}PPh_3$, when treated with sulphur or selenium under mild conditions, gives the red intermediate,  $Ph_3 \cdots \overset{+}{\underset{X^-}{C}} \cdots PPh_3$ where X = S or Se.[241] The selenium compound is sufficiently stable for an X-ray investigation which shows little change in the P=C=P framework on incorporation of selenium; the C-Se distance (1.99Å) also indicates only loose addition of the selenium.

Compounds containing a three coordinate phosphorus(V) atom with two double bonds to carbon, i.e. $R{-}P[{=}C(SiMe_3)_2]_2$ where R = C_6H_{11}, Ph or Me_2N, have been synthesised from reactions of organodichlorophosphines and the lithiated chlorobis(silyl)methane $LiCCl(SiMe_3)_2$.[242]

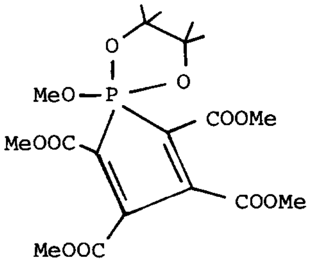
Conformations of more than 1000 structures containing the Ph_3PX unit have been analysed in terms of the torsion angles of the phenyl groups, and using the structure correlation method it has been possible to chart the low energy stereoisomerisation paths for Ph_3PO and related molecules.[243]

Further investigations into the behaviour of phosphorus compounds in strongly acidic media have been carried out for $Ph_2P(O)OH$, $Ph_2P(O)Cl$, Ph_3PO, Ph_3PS and $MeP(O)Cl_2$ in 100% H_2SO_4, $HSClO_3$ and 25% oleum.[244] In all cases there is an initial protonation but sulphonation and solvolysis of the chlorides can also take place. For example, there is ^{31}P n.m.r. evidence for the formation of $(HO_3SC_6H_4)PhP(OH)_2^+$ and $(HO_3SC_6H_4)_2P(OH)_2^+$ when

$Ph_2P(O)OH$ reacts with 25% oleum, and with $MeP(O)Cl_2$ in the same medium, the evidence suggests successive formation of $MeP(OH)Cl_2^+$, $MeP(OH)_2Cl^+$ and $MeP(OH)_3^+$.

Evidence is now available showing that the synthesis of the methane diphosphonic ester, $CH_2[P(O)(OPh_2)_2]_2$ from ethyl diphenylphosphite and diiodomethane proceeds via the intermediate $ICH_2P(O)(OPh_2)_2$.[245] Salts of the tris(diphenylthiophosphinoyl)-methanide ion $C[P(S)Ph_2]_3^-$[246] and the related methyl substituted anion, $C[P(S)Me_2]_3^-$[247] have been reported and such species, which behave as uninegative tridentate ligands, are likely to be useful in the preparation of metal cage compounds.

An unusual pentacoordinated phosphole structure is found in the spirophosphorane (69) obtained when the dioxaphospholane (70) is treated with dimethylacetylenedicarboxylate.[248] The phosphorus is in basically trigonal bipyramidal coordination with oxygen (1.659Å) and carbon (1.885Å) atoms in axial positions, equatorial positions are filled by the methoxy group (1.604Å), oxygen (1.617Å) and the second carbon atom (1.837Å). A cis-trans mixture of the disulphide (71) is produced when sulphur reacts with 2,6-dimethyl-1,3-dioxa-2,6-diphosphacyclo-octane.[249] The pure trans form, which shows an asymmetric boat-chair ring conformation, can be isolated by fractional crystallisation from benzene. The structure also shows equal bond lengths in the two P-C-C-O-P fragments but there are differences in the two O-C-C angles (108.4 and 113.9°).



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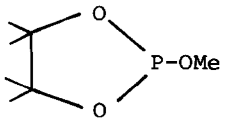

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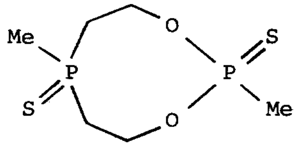
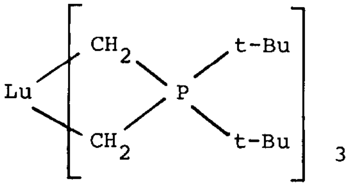


(71)

Coordination by carbamylmethylenephosphonates, $(RO)_2P(O)CH_2C(O)NEt_2$ where R = Et, i-Pr, n-Bu and n-C_6H_{13}, has been investigated and the structure of the mercury complex determined.[250] The free ligands lose a proton in the presence of sodium or sodium hydride with formation of the anionic bases $(RO)_2P(O)CHC(O)NEt_2^-$.

Reactions of the dimethylide salt, $Li[(H_2C)_2P(t\text{-}Bu)_2]$, with $LuCl_3$ and Cp_2LuCl lead to the complexes (72) and (73) respectively.[251]



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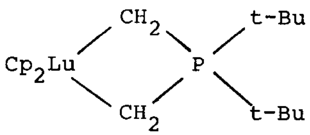
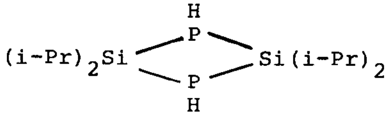


(73)

Silicon Derivatives. Treatment of the silylphosphine, Me_3SiPPh_2, with acyl chlorides leads to compounds of the type $RC(O)PPh_2$, where R = F_2CCl, H_2CCl, $HCCl_2$, CCl_3,[252,253] $MeCHClCH_2$ and $ClCH_2(CH_2)_2$.[254] The structure of the dichloromethyl derivative $HCCl_2C(O)PPh_2$ has been determined.[252] In general, acyl phosphines containing single carbon R groups are stable at room temperature, but on heating to ca. 80°C they decompose to Ph_2PCl and a ketene.[252] The propionyl and butyryl derivatives, on the other hand, are stable only at low temperature and on decomposition lose hydrogen chloride and polymerise.[254] They can however be stabilised as complexes with $BrMn(CO)_5$. Acylphosphines are oxidised in ether solution by oxygen gas to the corresponding phosphine oxide, $RC(O)P(O)Ph_2$;[255] hydrolysis leads to complete decomposition but in the presence of diphenylphosphinic acid they yield diphosphorylated alcohols, $Ph_2P(O)CR(OH)P(O)Ph_2$.

When lithium phosphide reacts with $i\text{-}Pr_2SiF_2$ the product is a surprisingly stable silylphosphine, $i\text{-}Pr_2SiF(PH_2)$, which eliminates lithium fluoride on treatment with n-BuLi to produce the diphosphadisilacyclobutane (74).[256] Compounds in the silyl-



(74)

phosphine series $(Ph_3Si)_nP(SiMe_3)_{3-n}$ for n = 1-3 are the products of reactions between a potassium phosphide-sodium phosphide mixture and stoichiometric mixtures of Ph_3SiCl and Me_3SiCl.[257]

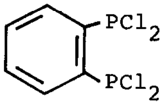
5.2.3 Bonds to Halogens

The +3 Oxidation State. U.v. photolysis of a mixture of MF_3, for M = P or As, and ozone in a noble gas matrix leads to oxygen atom transfer with formation of $M(O)F_3$.[258] The arsenic compound has not previously been prepared and its vibrational spectra are consistent with C_{3v} symmetry. Interaction between BH_3 and a series of substituted phosphines, e.g. PF_nH_{3-n} and PMe_nH_{3-n}, has been investigated by u.v. photoelectron spectroscopy, showing that the high basicity of PF_2H and the high stability of the adduct $HF_2P.BH_3$ can be correlated with a lower first ionisation energy for PF_2H than would be expected on interpolation between the values for PH_3 and PF_3.[259]

The first example of a halogen isotope shift in ^{31}P n.m.r. spectroscopy has been observed for PCl_3 and PBr_3 at 200K and very high field (9.4T).[260] The shifts for the former are separated by 3.1Hz (no signal observed for $P^{37}Cl_3$) while the expected four peaks for PBr_3 are equally spaced by 0.95Hz. In both cases, the lower frequency resonances are associated with the heavier isotopomers. ^{31}P n.m.r. has been used to follow the oxygen-chlorine exchange processes between As_2O_3 and a series of phosphorus chlorides including PCl_3, $POCl_3$, Et_2POCl, $(PhO)_2POCl$ and $(Me_2N)_2POCl$.[261] In all cases there is evidence for the formation of P-O-P bonds with, for example, PCl_3 being converted to P_4O_6 and Et_2POCl to $Et_2P(O)OP(O)Et_2$.

Structures have been determined for the PCl_4^- and $P(CN)_3Cl^-$ anions, recently isolated from reactions between PCl_3 or $P(CN)_3$ and quaternary ammonium or phosphonium salts or crown ether-alkali metal salts.[262] The PCl_4^- ion has an unsymmetrical pseudo-trigonal bipyramidal structure with equatorial P-Cl distances of 2.044 and 2.049Å; the axial distances are 2.118 and 2.850Å. In $P(CN)_3Cl^-$ the axial bonds to Cl and CN are again asymmetric, the distances being longer than the corresponding bonds in the parent PX_3 molecules.

The phenylenebis(dichlorophosphines), (75) and (76),[263] have been prepared and data are available on the preparation, reactivity and spectra of a series of bifunctional bromophosphines,



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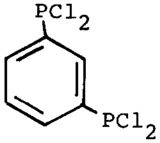


(76)

$Br_2P-(CH_2)_n-PBr_2$ where n = 1 to 10.[264] Phosphorus tribromide and $(OC)_5M.THF$, where M = Cr or W, react to give a series of products, including $(OC)_5M.PBr_3$, the diphosphine complex $(OC)_5MBr_2PPBr_2M(CO)_5$, and a product, $(OC)_5MPO(CH_2)_4Br$, resulting from ring cleavage of THF.[265] The chromium and molybdenum compounds containing stabilised P_2Br_4 can also be obtained by treating $(OC)_5M.PBr_3$ with magnesium in THF solution.

The +5 Oxidation State. Treatment of a bromotrialkylphosphonium bromide with sodium fluoride in acetonitrile solution is a relatively simple method for producing R_3PF_2 where R = Et, i-Pr and n-Bu,[266] and phosphorus-fluorine bonds are also formed when sulphuryl chloride fluoride reacts as shown in equations (36) and (37).[267]

$$R^1R^2P(S)OR^3 + SO_2ClF \rightarrow R^1R^2P(O)F + SO_2 + R^3Cl + S \qquad ...(36)$$

$$R_3PS + 2SO_2FCl \rightarrow R_3PF_2 + 2SO_2 + SCl_2 \qquad ...(37)$$

Gas phase electron diffraction data for the mixed trifluoromethylfluorophosphoranes, $(CF_3)_nPF_{5-n}$ for n = 1-3,[268] show that the mono-trifluoromethyl derivative is a 60:40 mixture of conformers with the CF_3 group in respectively equatorial and axial positions. In the bis compound the CF_3 groups occupy axial positions while in $(CF_3)_3PF_2$, the trifluoromethyl groups move to the equatorial sites. Rationalisation of these structures depends on bond energy considerations and steric interactions between the CF_3 groups and the rest of the molecule.

Redistribution of the fluoro- and alkoxy- groups in $PhPF_{4-n}(OR)_n$, where R = CH_2CF_3 or CH_2CCl_3, favours the mixed species according to n.m.r. spectroscopy as shown, for example, by the non-detection of the disproportionation products of $PhPF_2(OR)_2$.[269] In addition there was no evidence for either the exchange of phenyl groups nor for the conversion to ionic forms.

Gauche-gauche and gauche-anti conformers in equal amounts are present in gaseous $CH_2(PF_2S)_2$ according to recent electron diffraction measurements, which also gave the following molecular parameters: r(P=S) 1.879, r(P-F) 1.548, r(P-C) 1.807Å and P-C-P 122.6°.[270] In the related compound $O(PF_2S)_2$, although the PF_2S groups have gauche conformations, the overall symmetry could be either C_s or C_2. In this compound, molecular parameters are: r(P-O) 1.610, r(P=S) 1.865, r(P-F) 1.526Å and P-O-P 130.9°.

Lattice energies calculations for the three ionic forms of PCl_5, i.e. $PCl_4^+\ PCl_6^-$, $2PCl_4^+\ PCl_6^-Cl^-$ and $PCl_4^+Cl^-$, give the values 462.4 and -880.4 kJ mol^{-1} for the standard heats of formation of PCl_4^+ and PCl_6^- respectively.[271] The chloride ion affinities of PCl_5 and PCl_4^+ (equations (38) and (39)) can then be

$$PCl_5(g) + Cl^-(g) \rightarrow PCl_6^-(g) \qquad \Delta H = -259.5\ kJ\ mol^{-1} \qquad ...(38)$$

$$PCl_4^+(g) + Cl^-(g) \rightarrow PCl_5(g) \qquad \Delta H = -591.3\ kJ\ mol^{-1} \qquad ...(39)$$

calculated, showing that $KPCl_6$ or $CsPCl_6$ will have only borderline stability but that there is no thermodynamic barrier to the formation of PCl_5 in the $PCl_4^+\ Cl^-$ form.

Chlorination of phosphites and phosphinites using PCl_5 in dichloromethane solution follows the reactions in equations (40)-(42),[272] and catechyl phosphorus trichloride can be used to

$$PCl_5 + (EtO)_3P \rightarrow (EtO)_2P(O)Cl + PCl_3 \qquad ...(40)$$

$$PCl_5 + (PhO)_3P \rightarrow (PhO)_4PCl \qquad ...(41)$$

$$PCl_5 + (C_6H_4O_2)POPh \rightarrow C_6H_4O_2P(OPh)Cl_2 \qquad ...(42)$$

$(C_6H_4O_2$ = catechyl)

exchange chlorine atoms[273] and as a dehydrating agent.[274]

A number of new phosphorus(V) cyanides and thiocyanates have been prepared and identified.[275] The former, $PCl_{6-n}(CN)_n^-$ where n = 1 to 3, result when PCl_6^- and silver cyanide react in dichloromethane solution; the tricyanide is a mixture of the fac- and mer- isomers, the latter being obtained pure. Corresponding reactions with either silver, lithium or ammonium thiocyanates are rapid and with excess reagent fully substituted $P(NCS)_6^-$ salts are produced. These are however unstable and readily lose CS_2. With smaller quantities of MNCS the formation of mixed chlorothiocyanato species has been observed by ^{31}P n.m.r. spectroscopy.

Reaction of the dichlorophosphate salt, $Ph_4AsPO_2Cl_2$, in dichloromethane solution with $SnCl_4$, $TiCl_4$ and $MoCl_5$ gives respectively $(Ph_4As)_2[SnCl_4(PO_2Cl_2)]_2$, $(Ph_4As)_2[TiCl_4(PO_2Cl_2)]_2$ and $(Ph_4As)_2[MoOCl_3(PO_2Cl_2)]_2$.[276] The presence of bridging dichlorophosphate groups, suggested by i.r. spectroscopy, has been confirmed in the case of the molybdenum compound by a full structure determination. As shown in Figure 8, the anion consists of a centrosymmetric, non-planar, eight membered ring system; important structural parameters are: P-O 1.487, 1.477, P-Cl 1.996, 2.005Å, O-P-O 121.1, Cl-P-Cl 101.2 and P-O-Mo 137.5, 141.4°. Bridging dichlorophosphates are also present in the complex compounds $(Ph_4As)_2[MNCl_3(PO_2Cl_2)]_2$ obtained using $MNCl_3$, where M = Mo or W.[277] Vibrational spectra for $Ph_4AsPO_2Cl_2$, which is prepared by treating Ph_4AsCl with $P_2O_3Cl_4$ in dichloromethane solution, yield values of 9.08 and 2.16 N cm^{-1} respectively for the P-O and P-Cl stretching force constants.

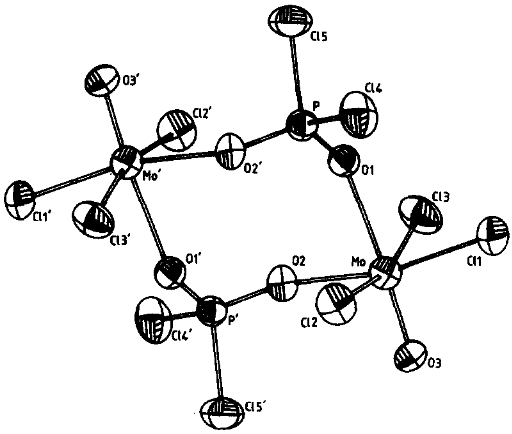


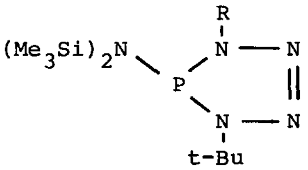
Figure 8. Structure of the $[MoOCl_3(PO_2Cl_2)]_2^{2-}$ ion (reproduced by permission from Z. Anorg. Allg. Chem., 486(1982)136).

5.2.4 Bonds to Nitrogen

The +3 Oxidation State. Ab initio calculations using double zeta basis sets for the singlet and triplet isomers of the composition

H_2PN give the following order of stability: HP=NH $^1A'$(trans) ~ H_2NP $^3A''$ ~ HP=NH $^1A'$(cis) < H_2N-P $^1A_1$ << HP-NH ^3A < H_2P-N $^1A_1$ < H_2P-N $^3A''$.[278] The reactivity of π-bonded P(III) systems, i.e. RP=X where X = CH_2, NR or O, has also been investigated by ab initio methods.[279] In such compounds, both π and σ orbitals, associated respectively with the P=X double bond and the lone pair on phosphorus, are closely spaced as HOMO's; the LUMO in each case is the π^* orbital. If the HOMO-LUMO sequence is π-π^*, reaction will lead to a [2+2] cycloaddition while the alternative σ-π^* sequence results in [2+1] or [4+1] cycloaddition products. It is found that when the electronegativity of the π-donating ligand X is increased, the σ and π orbitals cross and the latter reaction paths are favoured.

Reactions of amino-iminophosphines, $(Me_3Si)_2N$-P=NR where R = Me_3Si or t-Bu, with t-butyl azide lead initially to the λ^3-tetraazaphospholenes (77), but on either thermolysis or photolysis



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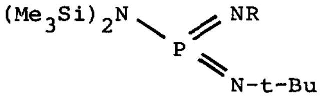
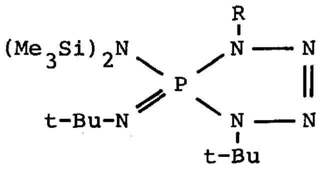


(78)

nitrogen is lost to give diiminophosphoranes (78).[280] Further reaction of (78) with t-butylazide leads to λ^5-tetraazaphospholenes (79) which, in contrast to the λ^3-phospholenes (77), yield λ^5-diazaphosphoridines (80) on photolysis.



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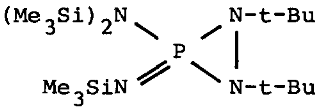

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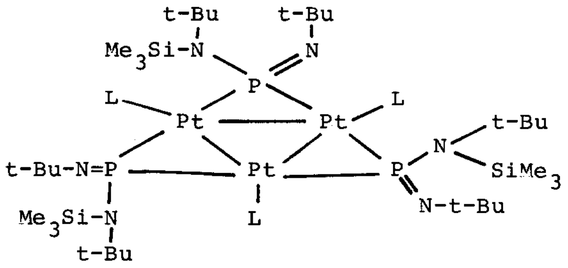
Amino-iminophosphines can also behave as bridging ligands as shown in the platinum(II) complexes (81, a and b);[281] the structure of (81a) has been determined. Reduction of the



($\underline{81}$a, L = CO; b, L = CNt-Bu)

related iminophosphine, $(Me_3Si)_2NP{=}NSiMe_3$, with $LiAlH_4$ leads to the iminophosphoranide anion $[(Me_3Si)_2NP(H){=}NSiMe_3]^-$, rather than a phosphide or an amide, and the reaction product with methyl lithium is the corresponding anion with a P-Me bond.[282]

The first example of a primary aminophosphine, $(Me_3Si)_2NPH_2$, has been isolated as a pyrophoric liquid, stable to at least 100°C, by reducing the corresponding difluoride with $LiAlH_4$.[283] Mixed aminophosphines such as $P(NH_2)X_2$, where X = Cl, Br or I, and $P(NHMe)_2Cl$, which are unknown in the free state can be stabilised in metal complexes as shown in equations (43) and (44).[284]

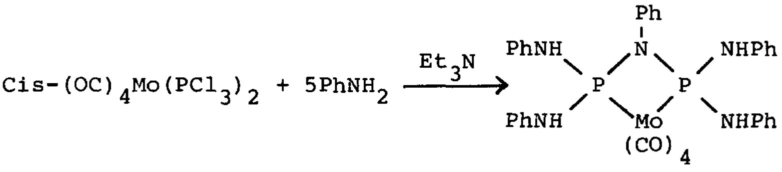
$$(OC)_5MoP(NH_2)_3 + 2HX \rightarrow (OC)_5MoP(NH_2)X_2 + 2NH_3 \qquad ...(43)$$

$$(OC)_5MoP(NHMe)_3 + HCl \rightarrow (OC)_5MoP(NHMe)_2Cl \qquad ...(44)$$

Reaction of the tri(methylamino)phosphine complex with HBr gives a mixture of $(OC)_5MoP(NHMe)Br_2$ and $(OC)_5MoPBr_3$ but with HI only a small quantity of $(OC)_5MoP(NHMe)I_2$ is produced, the major product being an insoluble solid. When $(OC)_5MoP(NHMe)_2Cl$ reacts with triethylamine, there is loss of hydrogen chloride and formation of a complex containing the new diazadiphosphetidine, $MeNHP(NMe)_2PNHMe$, coordinated to two $Mo(CO)_5$ residues.

On transamination with aniline, tris(diethylamino)phosphine, $(Et_2N)_3P$, can be converted to the primary amine derivatives $(PhNH)_3P$ and $[(PhNH)_2P]_2NPh$ and in addition there is ^{31}P n.m.r. evidence for $(Et_2N)_2PNHPh$ and $Et_2NP(NHPh)_2$.[285] The structure of $(PhNH)_3P$ shows C_3 molecular symmetry with P-N distances of 1.697Å and N-P-N angles of 99.5° and although the compound is stable in the solid state, an equilibrium with $PhNH_2$ and $[(PhNH)_2P]_2NPh$ is rapidly established in solution. The bis(phosphino)amine with ca.

C_{2v} symmetry has planar geometry at the phenylimido nitrogen and pyramidal geometry at the phosphorus atoms. Hydrolysis of both $(PhNH)_3P$ and $[(PhNH)_2P]_2NPh$ leads to the phosphine oxide $(PhNH)_2P(O)H$, but there is no evidence in either the solid state or in solution for the isomeric form $(PhNH)_2POH$.[286] Depending on the recrystallisation solvent the phosphine oxide can be isolated in both monoclinic and orthorhombic forms, but from X-ray crystallography the two forms are very similar and differ basically in the hydrogen bonding systems. A complex (<u>82</u>) containing the bis(phosphino)amine has been synthesised as shown in equation (45).[287]



...(45)

(<u>82</u>)

Reduction of the silylaminophosphine, $(Me_3Si)_2NPCl_2$, with $LiAlH_4$ leads to two isomeric forms of each of the diphosphines $(Me_3Si)_2NPH.PClN(SiMe_3)_2$ and $(Me_3Si)_2NPH.PHN(SiMe_3)_2$,[288] and reactions leading to convenient, large scale syntheses of a range of silylaminophosphines are summarised in equations (46) and (47).[289]

$$(Me_3Si)_2NLi + PCl_3 + RMgX \rightarrow (Me_3Si)_2NPR_2 \qquad \text{...(46)}$$

R = Me, Et or CH_2SiMe_3

$$(Me_3Si)_2NLi + PhPCl_2 + RMgX \rightarrow (Me_3Si)_2NPPhR \qquad \text{...(47)}$$

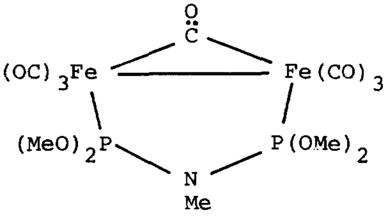
R = Me or Et.

Phosphorus(III) and arsenic(III) tris(pyrrolyl) derivatives, which are formed when the appropriate trichloride reacts with $Li(NC_4H_4)$ in ether solution, are not isostructural, but structures are very similar with N-bonded, monohapto-pyrrolyl ligands.[290] The nitrogen atoms are planar with P-N distances of 1.710, 1.700 and 1.677Å; the mean N-P-N angle is 100.4°. The non-reactivity of the compound towards moisture, ethanol and carbon disulphide is considered to be a consequence of the involvement of the nitrogen lone pairs in the π systems of the ligands.

Methyl iodide and the lithium salt of bis(diphenylphosphino)-amine react as shown in equation (48) to give a diphosphineiminium iodide, rather than a simple methylation product $(Ph_2P)_2NMe$.[291]

$$(Ph_2P)_2NLi + 2MeI \rightarrow (Ph_2MeP{=}N{=}PMePh_2)I + LiI \qquad \ldots(48)$$

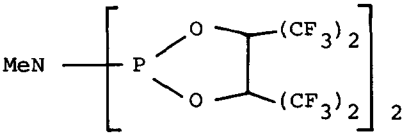
The aminodiphosphines, $MeN[P(OMe)_2]_2$[292] and $RN(PF_2)_2$,[293] where R = Me or Ph, are good ligands and among the compounds isolated is the iron complex (83). In this compound, the Fe_2P_2N system is, unusually, almost planar.[293]



(83)

The bis(difluorophosphine) ligand can behave as either a chelate in the formation of $RN(PF_2)_2.M(CO)_4$ or as a unidentate ligand in $[RN(PF_2)_2]_2M(CO)_4$ where M = Cr, Mo or W. Reaction of $PhN(PF_2)_2$ with $MeN(PF_2)_2.Cr(CO)_4$ leads to trans-$[MeN(PF_2)_2][PhN(PF_2)_2].Cr(CO)_4$; the mer-isomer $[RN(PF_2)_2]_2.$-$Cr(CO)_3$, which contains both uni- and bi-dentate ligands, and the binuclear complex $[PhN(PF_2)_2]_3.Cr_2(CO)_6$ have also been isolated.

The bridged diphosphine $MeN(PCl_2)_2$ on reaction with the dilithium salt of perfluoropinacol gives (84), which can be oxidised by chlorine.[294] The resulting dichloride however



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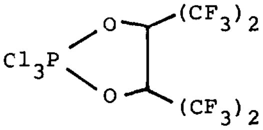

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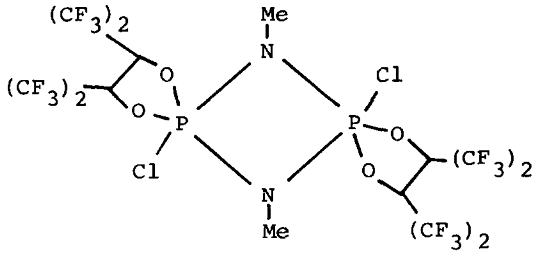
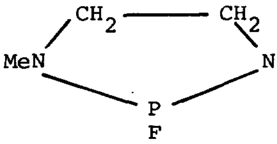


(86)

decomposes with liberation of (85) and formation of the diazadiphosphetidine (86).

Structures for $S_2P_4(NMe)_6$ and $S_3P_4(NMe)_6$ have now been determined completing the $S_nP_4(NMe)_6$ series.[295] P-N distances in the disulphide vary between 1.654 and 1.732Å, showing different values for the four chemically different P-N bonds. The geometry at the nitrogen atoms is planar and shortening of both the P(III)- and P(V)-N bond has been ascribed to N(p)→P(d) π-bonding.

A metal phosphenium complex formulated as $Co_2(CO)_5(L)_2$ has been isolated from a reaction between $NaCo(CO)_4$ and the cyclic fluorophosphine (87) (≡LF) in THF solution.[296] The structure contains both $Co(CO)_2$ and $Co(CO)_3$ groups bridged by two phosphenium ligands; both phosphorus atoms are displaced toward the $Co(CO)_2$ group (Co-P 2.043, 2.051Å) while Co-P distances to the $Co(CO)_3$ group are 2.393 and 2.426Å. The phosphenium salt $(i\text{-}Pr_2N)_2P^+AlCl_4^-$, reacts with either stannocene and plumbocene by oxidative addition of a C-H bond to the phosphorus atom to give the phosphonium salts (88) rather than heteroatom species containing P-Sn or P-Pb bonds.[297]



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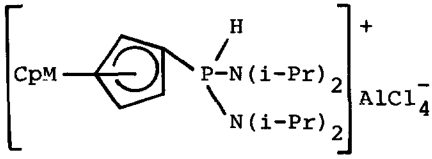
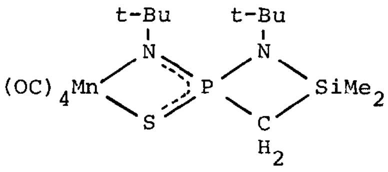


(88, M = Sn or Pb)

The +5 Oxidation State. While the reaction product between $Mn(CO)_5Br$ and the aminobis(imino)phosphorane, $(Me_3Si)_2NP(=NSiMe_3)_2$, is a complex where the phosphorane is "end-on" bonded via an imino-nitrogen atom, the related thiophosphorane, $(Me_3Si)(t\text{-}Bu)NP(=S)(=Nt\text{-}Bu)$ gives a spiro-cyclic product (89), with the phosphorus atom in tetrahedral coordination.[298]



(89)

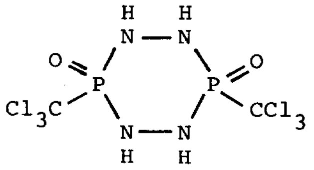
Structures have been determined for tri(morpholino)phosphine oxide[299] and the phenyl substituted phosphine selenides, $Ph_nP(Se)(morpholine)_{3-n}$ for n = 1 and 2,[300] in continuation of studies on the orientation of the nitrogen lone pair. In the phosphine oxide, the mean P-N distance is 1.66Å while the sum of the angles at nitrogen range from 349.1 to 358.6. The lone pair on one of the nitrogen atoms is essentially anti to the P=O bond while the others are approximately orthogonal to the P=O bond and to each other. Structures for two substituted phosphoramidates, $(MeO)_2P(O)NHC_6H_4X$ where X = H or p-NO_2, show the presence of hydrogen bonded dimers when X = H and a discrete monomer structure stabilised by a network of hydrogen bonds for X = p-NO_2.[301]

Two independent molecules are present in the unit cell of $P(O)(NMePCl_2)_3$, with the phosphorus(III) and nitrogen atoms in pyramidal and planar coordination respectively.[302] Oxidation with chlorine in carbon tetrachloride gives $P(O)(NMePCl_4)_3$. The related p-phenyl compound, $P(O)(NMePPhCl)_3$, can be obtained from $PhPCl_2$ and $P(O)(NHMe)_3$ by loss of hydrogen chloride.

The short P-N bond length (1.63Å) in $(PhCH_2)Ph_2(Et_2N)P^+Cl^-$ is indicative of $N(p)\rightarrow P(d)$ π-bonding enhanced by the positive charge on phosphorus.[303] HeI photoelectron spectra have been measured for, inter alia, a series of polycyclic aminophosphines such as $XP(NMeCH_2)_3CMe$ where X = O, S, Se or BH_3.[304]

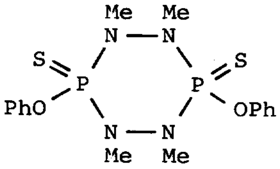
New phosphorus hydrazides, i.e. $PhOP(X)(NRNRR^1)_2$ where X = O or S and R/R^1 = H or Me, have been characterised from reactions between $PhOP(X)Cl_2$ and methyl hydrazine or 1,1- or 1,2-dimethyl hydrazine.[305] The compounds form metal complexes and from the structure of a tetrakis derivative of nickel(II) chloride and diphenylhydrazidothiophosphate, $(PhO)_2P(S)NHNH_2$, the compounds coordinate as unidentate groups via terminal nitrogen atoms.[306] Two new tetraazadiphosphacyclohexanes as a cis-trans isomer mixture can be synthesised following equations (49)[307] and (50).[308]

$Cl_3CP(O)(NHNH_2)_2 + Cl_3CP(O)Cl_2 \rightarrow$



$+ 2HCl$ ...(49)

$PhOP(S)(NMeNHMe)_2 + PhOP(S)Cl_2 \rightarrow$



$+ 2HCl$ ...(50)

The two forms of the thio-derivative can be separated with n.m.r. data pointing to a twist ring conformation in each case.

N-silyliminophosphoranes and N-silyldiphosphazenes react with trifluoroethyldiphenylphosphinite as shown in equations (51) and (52) respectively, to give phosphazeno-phosphines but a related

$R_3P{=}NSiMe_3 + Ph_2POCH_2CF_3 \rightarrow R_3P{=}NPPh_2 + CF_3CH_2OSiMe_3$ ...(51)

R = Me, NMe_2 or Ph.

$(Me_2N)_3P{=}N{-}PR_2{=}NSiMe_3 + Ph_2POCH_2CF_3 \rightarrow (Me_2N)_3P{=}NPR_2{=}NPPh_2$

R = NMe_2 or OCH_2CF_3. $+ CF_3CH_2OSiMe_3$ ...(52)

$(Me_2N)_3P{=}NPPh_2NSiMe_3 + P(OCH_2CF_3)_3 \rightarrow (Me_2N)_3P{=}NPPh_2{=}NP(OCH_2CF_3)_2$

$+ CF_3CH_2OSiMe_3$ ...(53)

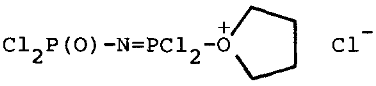
reaction (53) using $P(OCH_2CF_3)_3$ yields a phosphazeno-phosphonous acid ester.[309]

The three independent molecules in the asymmetric unit for $(Me_3P{=}N{=}PMe_3)Br.H_2O$ show a mean P-N bond distance of 1.582Å and P-N-P angles of 140.1, 135.9 and 135.1°, and although the molecules have broadly similar structures different conformations are adopted.[310] The P-N-P bond angle in the related compound $(Ph_3P{=}N{=}PPh_3)^+NCS^-$ is 136.3°.[311]

Unsymmetrically substituted phosphiniminophosphonium salts, $(Bu_3P{-}N{=}PR_3)Br/F$ where R = Me, n-Bu, Me_2N or Et_2N, have been isolated from reactions between $(n{-}Bu_3PF)Br$ and $R_3P{=}NSiMe_3$.[312] The corresponding iodide, perchlorate and hexafluorophosphate can be obtained by metathesis and their use as phase transfer reagents has been investigated.

Crystal structures have been determined for two related compounds, $[Ph_2P(O)]_2NH$ and $[Ph_2P(S)]_2NH$, to investigate possible PNH-POH tautomerism.[313] The latter formula in fact represents the observed structure of the thio-derivative but in the solid state the structure of the former is the tautomer $Ph_2P(O){-}N{=}P(OH)Ph_2$, as suggested previously. In this compound the P-N-P unit is linear in comparison with a P-N-P angle of 132.6° for the thiophosphoryl derivative and the short P-N bond distances (1.535Å) indicate substantial π-bond character. The molecule forms strong, symmetrical hydrogen bonds leading to zig-zag chains along the b axis. A mercury derivative, $[(PhO)_2P(O)]_2NHgPh$, has been isolated and an X-ray study shows a P-N-P angle of 125.8° and P-N bond distances of ca. 1.62Å.[314]

^{31}P n.m.r. data point to the absence of rotational isomers for $Cl_3P{=}N{-}P(O)Cl_2$ in either the neat liquid or in solution at low temperature.[315,316] If the compound is treated with THF at 30°C, in addition to polymeric THF, the product contains an N-substituted imidophosphoryl chloride, $Cl_2P(O).N(CH_2)_4Cl.P(O)Cl_2$.[317] The reaction mechanism probably involves the initial formation of (90), followed by conversion to the O-chlorobutyl isomer, and finally isomerisation to the N-chlorobutyl compound observed.

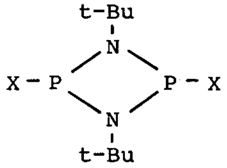


(90)

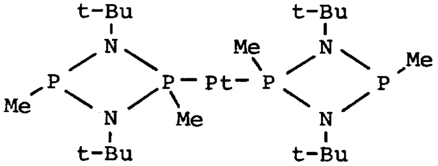
A reinvestigation of the PCl_5-$(PhO)_2P(O)NH_2$ reaction in toluene solution points to the initial formation of the expected Kirsanov product, $(PhO)_2P(O)$-$N=PCl_3$, but that this isomerises to $(PhO)_2PCl=N$-$P(O)Cl_2$ on removal of the solvent.[318]

Transition metal derivatives of the polycyclic cyclam phosphorane have been synthesised and an X-ray structure of the complex with $CpMo(CO)_2$ shows coordination of the ligand via phosphorus and one of the nitrogen atoms.[319] The unusual tetraarylphosphazide group, $Ph_3P=N$-$N=NR$, can be stabilised in compounds of the type $MBr_2(CO)_3(RN_3PPh_3)$, where M = Mo or W, which are obtained when either phenyl or p-tolyl azide is treated with $MBr_2(CO)_3(PPh_3)_2$ in dichloromethane at room temperature.[320] From an X-ray study of the tungsten compound with R = p-tolyl, the phosphazide ligand forms when tolyl azide is inserted into a W-P bond. The group then chelates to the metal atom through the α and γ nitrogen atoms.

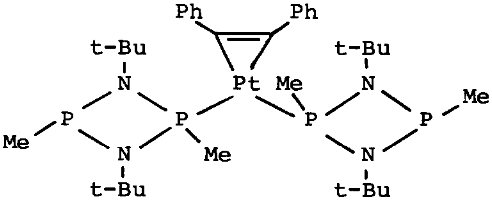
<u>P-N Ring Compounds.</u> A cis-trans isomer mixture (<u>91</u>, X = F), in which the cis form predominates, has been obtained by elimination of Me_3SiNMe_2 from $Me_2NP(F)N(t$-$Bu)SiMe_3$.[321] The related cis-diphosphadiazane (<u>91</u>, X = Me) when treated with Pt(cyclooctadiene)$_2$ gives the new complex (<u>92</u>), and this in turn is converted into (<u>93</u>) and (<u>94</u>) on reaction with diphenylacetylene and fumaric acid dinitrile respectively.[322]



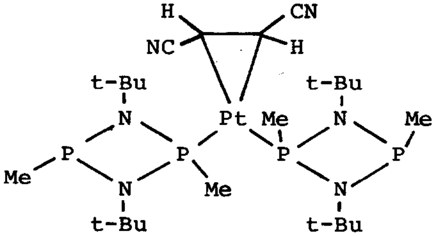
(<u>91</u>)



(<u>92</u>)

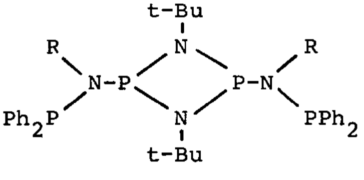


(<u>93</u>)



(<u>94</u>)

Two new diphosphadiazanes, (95)[323] and (96),[324] have been prepared, the former resulting from reactions of (91, X = Cl) with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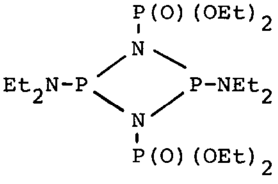
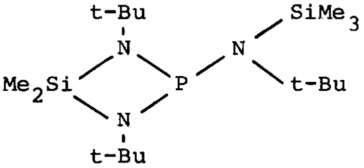

(96)

the appropriate lithiated amine $LiN(PPh_2)R$.[323] Both cis and trans isomers of (95) are produced when R = Me or Et, but with R = i-Pr or t-Bu only the cis form is observed. Variable temperature n.m.r. spectroscopy has been used to probe the preferred conformation of the exocyclic P-N-P skeletons. The structure of compound (96) shows a planar ring with C_i symmetry, the substituents at phosphorus occupying trans positions.[324]

The crystal structure of a new diazaphosphasiletidine (97) has also been determined, and the barrier to rotation about the P-N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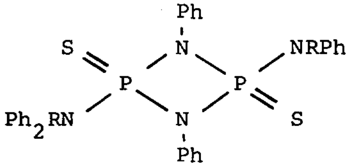
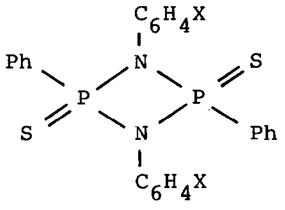

(98)

bond estimated.[325] Oxidation of phosphorus takes place on reaction with sulphur, selenium and methyl iodide.

The trans-form of (98, R = H) can be converted, without isomerisation or significant ring cleavage to (98, R = Me, Et or CH_2Ph) by reaction with n-BuLi followed by either MeI, EtI or $PhCH_2Br$.[326] The structures of the methyl and ethyl derivatives were also determined. Structural studies on two related compounds (99, X = o-Me or o-OMe) show that in both cases the phosphorus substituents occupy trans positions and that steric crowding is relieved in the former by rotation about the C-N bond while in the methoxy compound this bond is bent.[327] The novel chloro-diazadiphosphetidine (100) contains two triazaphosphole rings fused to the P_2N_2 system and phosphorus(V) atoms in both 5- and 4-fold coordina-



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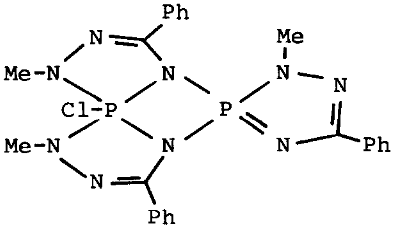
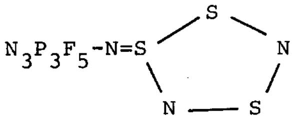


(100)

tion.[328] The geometry at the former is 40% displaced along the coordinate from the ideal trigonal bipyramidal toward the square pyramid, and the triazaphosphole rings occupy a partial meridional partial cis-facial arrangement.

Reaction of $N_3P_3F_6$ with t-BuLi leads to mono-, di- and tri-substituted derivatives with the latter two compounds being exclusively the trans-non-geminal isomers.[329] This is the first example of a regio- and stereo-specific reaction in this area of chemistry. At the trisubstitution stage, cleavage of the ether solvent becomes important and the mixed species $N_3P_3F_3(OEt)(t\text{-}Bu)_2$ can also be isolated. These reactions are in contrast to those involving n-BuLi where only the geminally disubstituted product could be obtained. Enolate anion reactions with $N_3P_3F_6$ have been reinvestigated as the products could be either ketones or vinyl alcohols, depending on whether attack is via the carbon or oxygen end of the ambidentate nucleophile.[330] Most reactions studied involved the acetaldehyde anion with i.r. and n.m.r. data supporting attack by oxygen to give vinyl alcohol products.

One fluorine atom in both $N_3P_3F_6$ and $N_4P_4F_8$ can be substituted with lithioferrocene and the remaining halogens substituted on treatment with CF_3CH_2ONa without cleavage of the skeleton.[331] Similarly, one fluorine in $(NPF_2)_{3-6}$ can be substituted with 2-lithio-1-methyl pyrrole.[332] The structure of the tetrameric product, $N_4P_4F_7(NC_5H_6)$, shows an almost planar eight membered ring with P-N distances ranging between 1.524 and 1.562Å and mean N-P-N and P-N-P angles of 122.9 and 146.4°. There is substantial π-bonding between the bridging nitrogen atom and the attached phosphorus and sulphur atoms (P-N 1.603, S-N 1.555Å, P-N-S 129.9°) according to a structure determination on the (trithiadiazolylidene) amino compound (101).[333]

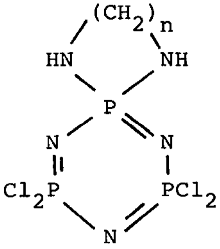


(101)

Recent kinetic investigations of the reactions of t-$BuNH_2$ with both $N_3P_3Cl_6$ and $N_4P_4Cl_8$ show that it is necessary to use rigorously purified materials for reproducibility, and indicate that reaction proceeds via an S_N2 mechanism and formation of a five coordinate phosphorus intermediate.[334] At 20°C, the second order rate constants are 9.7×10^{-3} and 2.28 $dm^3 mol^{-1} s^{-1}$ for the trimer and tetramer respectively; the more rapid reaction with the tetramer can be traced to a lowering of the activation energy.

Ethylglycinate hydrochloride in acetonitrile reacts with $N_3P_3Cl_6$ to give geminally di- and tetra-substituted compounds, which react further with aziridine to give products with potential anticancer activity.[335] β-Halogenoethylamine derivatives, $N_3P_3Cl_{6-n}(NHCH_2CH_2X)_n$ where X = Cl or Br and n = 1, 2 or 4, have also been isolated and moderate biological activity observed for the non-geminal disubstitution product, $N_3P_3Cl_4(NHCH_2CH_2Br)_2$.[336]

The structure of $N_3P_3Cl_5$(NHi-Pr) shows the presence of hydrogen bonded dimers related by a centre of symmetry with P-N distances in the ring ranging between 1.556 and 1.603Å.[337] Overall the ring shows small deviations from planarity in contrast to the prediction of a chair conformation from ^{35}Cl n.q.r. measurements. Spirocyclic products (102) are obtained from reactions between $N_3P_3Cl_6$ and the diamines $H_2N(CH_2)_nNH_2$ where n = 3[338] or 4;[339] and two novel iron carbonyl derivatives (103) and (104) have been



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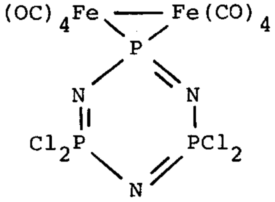

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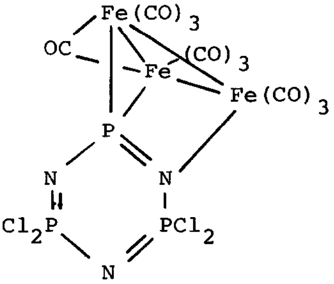


(104)

isolated when the hexachloride reacts with disodium octacarbonyldiferrate.[340] The structures of (103) and (104) follow from n.m.r., i.r. and X-ray studies. The following pyrazolyl (pz), methyl- (Mepz) and dimethyl- (Me_2pz) pyrazolyl substituted phosphazenes have been isolated: $(NPpz_2)_{3-6}$, $(NPMepz_2)_{3-5}$, $(NPMe_2pz_2)_{3,4}$, $N_3P_3Ph_4Mepz_2$, $N_3P_3Ph_4Me_2pz_2$ and $N_3P_3Ph_2Me_2pz_4$; their spectroscopic properties point to electron withdrawing properties for the pyrazolyl groups which thus behave more like halogen than amine substituents.[341] Palladium(II) and platinum(II) complexes can be formed with the pyrazolyl group acting as a donor through its pyridinic ring nitrogen atom.

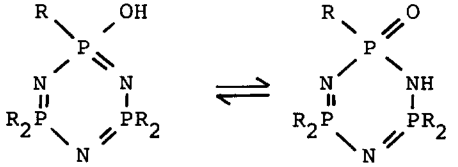
Two different pathways have been identified from a study of the hydrolysis of a series of substituted triphosphazenes, $N_3P_3R_6$ where R = NH_2, NHMe, $NHCH_2COOEt$, imidazolyl, $NHCH_2CF_3$, NHPh, pyrrolyl, piperidino etc.[342] The first involves the removal of one amino group with formation of $N_3P_3R_5OH$ before ring cleavage occurs, while in the second, the ring is cleaved as a fast process following protonation of one of the ring nitrogen atoms.

Anticancer properties are well established for phosphazenes carrying aziridine groups and the preparation of the partially substituted compound, $N_3P_3Cl_2$(aziridinyl)$_4$ has been reinvestigated.[343] This compound on treatment with ammonia in methanol solution is converted mainly to N_3P_3(aziridinyl)$_4$(OMe)NH_2 with N_3P_3(aziridinyl)$_4$(NH_2)$_2$ as byproduct.[344] Phosphazenes already carrying one or two amine substituents react with aziridine in ether solution initially at PCl_2 rather than PCl(amine) sites.[345] Reaction at PCl(amine) sites is in the order PCl(pyrrolidino)>PCl(piperidino)>PCl(morpholino), reflecting not only steric effects but also differences in the electron donating ability of the amine group. In disubstituted compounds, the relative arrangement of the amine groups affects the reactivity towards aziridine with, for example, there being no reaction with the cis isomeric forms.

The hexa-aziridinyl derivative crystallises as a clathrate $2N_3P_3$(aziridinyl)$_6$.C_6H_6 from benzene solution[346] and as ansolvous monoclinic and orthorhombic forms from carbon disulphide and m-xylene solutions respectively.[347] In the benzene compound, an X-ray structure shows that all three molecules lie on a crystallographic three fold axis, the two phosphazene groups being related by a centre of inversion. The N_3P_3 ring is slightly puckered and unusually the geminal aziridinyl groups adopt a cis conformation. The more usual trans arrangement of substituents is found in the other two forms, where the molecules have no significantly different structural parameters. Again the ring is non planar, showing a slight crown conformation, with ring P-N distances in the range 1.585 and 1.600Å.

Two new cationic cyclotriphosphazenes, i.e. $N_3P_3Me_6H^+$ $SnMe_2X_3^-$ where X = Cl or Br, have been isolated when $N_3P_3Me_6$ is treated with Me_2SnX_2.[348] At room temperature, n.m.r. spectroscopy shows equivalent methyl groups but on cooling to -30°C, the single signal splits into two doublets in the ratio 1:2 indicating dynamic proton exchange via intermolecular scrambling of the N-H proton.

Tautomerism in hydroxy-phosphazene systems (see equation (54)) has been investigated by ^{31}P n.m.r. spectroscopy.[349] Depending

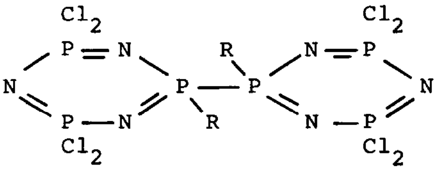


...(54)

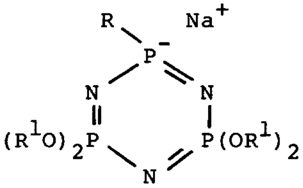
on the nature of the substituentsR, the following three different types of behaviour have been identified; (a) no exchange detected and only one tautomer is present, (b) exchange occurs between equivalent sites but only one form is observed and (c) exchange occurs between non-equivalent sites and two forms are present.

^{15}N labelled phosphazenes in which the label is included at the exocyclic nitrogen have been synthesised for $N_3P_3Cl_5X$ and $N_3P_3Cl_4X_2$ where X = NH_2, NHMe, NMe_2 and NHPh;[350] the fully labelled oxycyclophosphazanes, $[NRP(OR)(O)]_3$ where R = Me or Et and $[NMeP(OMe)(O)]_4$ have also been prepared.[351] The compounds were required for detailed n.m.r. investigations.

Nucleophilic attack on the bicyclotriphosphazene (105) by $NaOCH_2CF_3$ or NaOPh can lead to either cleavage of the P-P bond and substitution of the chlorine atoms or cleavage of P-Cl bonds without change in the P-P system.[352] The first path gives organocyclotriphosphazenes and the latter, organodi(cyclotriphosphazenes). In addition it is possible to generate anionic species such as (106), which with alcohols can be converted to the



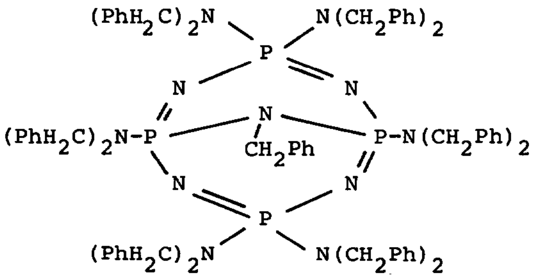
(105, R = Me or Ph)



(106, R = Me or Ph
R^1 = Ph or CH_2CF_3)

corresponding hydride.

The tetrameric chlorocyclophosphazene, $N_4P_4Cl_8$, reacts with sodium phenoxide by a non-geminal route to give $N_4P_4Cl_{8-n}(OPh)_n$ where n = 1 to 6 and 8.[353] The products for n = 2 to 6 are isomer mixtures and, although separation attempts were unsucessful, structures were assigned from ^{31}P n.m.r. data on the mixtures and both ^1H and ^{31}P data for the dimethylamino- or methoxy-substituted derivatives. The replacement pattern at the distribution stage appears to give both 2,4- and 2,6- forms while at the hexakis stage all four non-geminal isomers are formed but with predominance of the 2,trans-6-isomer. The corresponding dibenzylamine reaction leads to mono, bis and tetrakis products, again with non-geminal structures, and although the tris products could not be isolated pure, there is evidence for the formation of two compounds with the formula $N_4P_4Cl_5[N(CH_2Ph)_2]_3$.[354] Perhaps of greater interest is the isolation of the bicyclic compound (107) from $N_4P_4Cl_8$ and an excess of dibenzylamine in refluxing acetonitrile, the product resulting from transannular attack and dealkylation. Such products may be characteristic features of

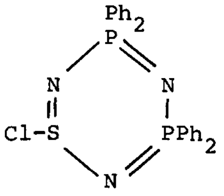


(107)

reactions with bulky secondary amines.

An X-ray structure of the molybdenum carbonyl complex obtained with the permethylated tetraphospha(III)azane, $(MePNMe)_4$, shows coordination of the metal to three carbon monoxide molecules and three of the four phosphorus atoms of the phosphazane.[355] Mo-P distances are 2.467, 2.513 and 2.537Å.

A number of new P-N-S systems have been identified. The first (108) is a hybrid between the cyclotriphosphazenes and the trithiazyl halides and results when Ph_2PCl and S_4N_4 react in acetonitrile solution.[356] The N_3P_2 segment is planar but the sulphur atom lies some 0.3Å from this plane. Hydrolysis leads to the linear phosphazene, $(H_2N.PPh_2{:}N{:}PPh_2.NH_2)^+Cl^-$, while with $Me_3Si.NSN.SiMe_3$ the product is the tricyclic compound (109) containing two eight membered $P_2N_4S_2$ ring fused at a tetrahedral spirocyclic sulphur atom. S_4N_4 reactions with tetramethyl- or tetraphenyl-diphosphine or with triphenylphosphite give phosphadithiatriazenes (110) and in this case the N_3S_2 segment is planar with the phosphorus atom 0.28Å from the plane.[357] From ab initio calculations on the model compound $H_2PS_2N_3$ there is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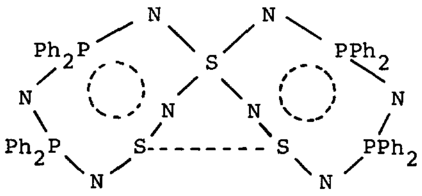
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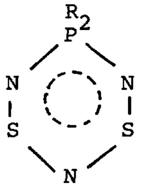
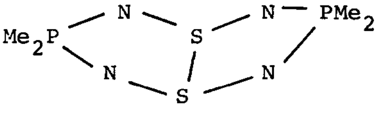

(110, R = Me, Ph or OPh)

extensive delocalisation of the eight π-electrons over the N_3S_2 fragment. These heterocycles readily form addition compounds with norbornadiene and the structure of the complex with (110, R = Ph) shows that cycloaddition of the hydrocarbon takes place across the two sulphur atoms to give the exo-β-isomer. Compound (110, R = Me) decomposes at room temperature to give in addition to S_4N_4 and the well known methyl cyclophosphazenes, $(NPMe_2)_{3 \text{ and } 4}$, a yellow solid identified by n.m.r. spectroscopy and X-ray crystallography as the new eight membered bicyclic (111).[358] The compound has a folded "butterfly" type structure



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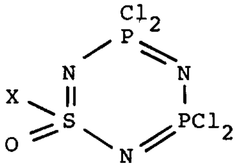

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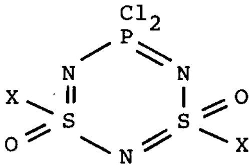


(113)

with a cross-ring S···S contact of 2.551Å; P-N and S-N distances are 1.630, 1.642 and 1.594, 1.597Å respectively.

Spirocyclic compounds can be isolated from reactions between N,N'-dimethylethylenediamine and either $N_3P_3Cl_6$ or the two sulphur containing analogues (112) and (113).[359] Although the triphosphazene gives mono-, bis- and tris-derivatives, only mono- and bis- derivatives can be isolated with (112, X = Ph) and the mono-spiro compound only for (112, X = Cl). In these cases reaction occurs at the PCl_2 groups. With compound (113, X = Ph or Cl) again a mono-substituted derivative only was isolated.

Reactions of (112, X = Cl) with both pyrrolidine and dimethylamine follow a non-geminal substitution route with the following order of reactivity: PCl_2>SOCl>PCl(amine).[360] In the mono- and di-substituted compounds, the amine groups occupy positions cis to the oxygen ligand. Reactivity in the related system (cis-113, X = Cl) follows the sequence : S(1)Cl>PCl>S(2)Cl>PCl(amine for attack by dimethylamine in acetonitrile solution;[361] problems due to isomerisation in the presence of Me_2NH_2Cl or catalytic amounts of antimony(V) chloride were also considered. The cis-isomer (113, X = Cl) with sodium methoxide in a 1:2.2 molar ratio leads to the disubstituted product $[NP(OMe)_2(NSOCl)_2]$ using a methanol-ether mixture as solvent, but a mono-substituted compound as a mixture of isomers can be isolated when methyl acetate is the solvent.[362] Methanolysis of the related trans-isomer (113, X = Ph) does not follow the same path and products apparently containing P(O)R groups are formed.

5.2.5 Bonds to Oxygen

The +3 Oxidation State. A number of new molybdenum, tungsten, rhenium[363] and cobalt[364] complexes with the ligand trimethyl phosphite have been isolated. In the presence of the phosphite, molybdenum and tungsten chlorides as their pyridine adducts are reduced giving $M[P(OMe)_3]_6$, but with related rhenium halide complexes, products such as $Re_2[P(OMe)_3]_{10}$, $HRe[P(OMe)_3]_5$, $H_3Re[P(OMe)_3]_4$, etc. can be isolated depending on the detailed experimental conditions.[363] It is also possible to produce cationic and hydridic compounds from these binary phosphites on reaction with protonic acids. Although trimethyl phosphite typically gives simple donor-acceptor complexes examples have recently been formed where bond cleavage occurs.[365] A specific case is the reaction with $[CpCr(CO)_2P(OMe)_3]_2$ which leads to $[CpCr(CO)_2P(OMe)_3P(O)(OMe)_2]$. This formula and that for a second example, $\{(MeO)_2PMo[P(OMe)_3]_5\}^+PF_6^-$, have been confirmed by X-ray crystallography.

Phosphites, $(RO)_3P$ where R = Me, Et or Ph, also react with $(CF_3S)_3N$ to give substituted phosphinimines $CF_3SN{=}P(OR)_3$ and $(CF_3S)_2$,[366] but whereas the phenyl derivative is stable to 100°C, rearrangement of the alkyl derivatives to $(RO)_2P(O)NR(SCF_3)$ occurs on heating. Treatment of triphenylarsine with $(CF_3S)_3N$ leads to $CF_3SN{=}AsPh_3$.

Molecular phosphites, MPO_2, and the corresponding arsenites and antimonites have been generated and trapped in N_2 matrices, and show the i.r. bands listed in Table 1.[367] Together with data for the ^{18}O enriched species, analysis points to a C_{2v} ring structure for all three compounds.

Table 1. I.r. bands (cm^{-1}) for MEO_2 (E = P, As or Sb).

Compound	ν(E-O)	ν(E-O)	σ(EO_2)
$NaPO_2$	1062.1	1151.6	523.0
$CsAsO_2$	863.0	851.5	393.0
$KSbO_2$	764.6	744.8	339.0

Full structures have been determined for the following phosphites: $NaCo(H_2PO_3)_3.H_2O$,[368] $(NH_4)_2Sn(HPO_3)_2$,[369] $(NH_4)_2HPO_3.H_2O$,[370] and $MnH(PO_3)_2.2H_2O$.[371] In the ammonium phosphite structure,[370] the mean P-O distance is 1.514Å with a P-H distance of 1.34Å; comparison of the volume of the HPO_3^{2-} with those of PO_3F^{2-} and SO_3^{2-} indicates a decrease in volume in the order F>H>lone pair. Each phosphorus tetrahedron in the structure of $Na_{0.5}H_{2.5}PO_3$ is connected by strong hydrogen bonds to three others giving infinite sheets with the composition $(H_{2.5}PO_3)_n^{n/2-}$ parallel to the xy plane.[372]

Hydrogen phosphite complexes, $MH_3[O_2P(O)H]_3$ where M = Fe(III) or Cr(III), have been isolated and i.r. and electronic spectra measured.[373]

Acetic anhydride reactions with hydrogen phosphites, $MH(HPO_3)$ where M = K or NH_4, lead to diphosphites $M_2(H_2P_2O_5)$ and although there is n.m.r. evidence for the intermediate formation of acetylphosphite species, they could not be isolated[374] (see also reference 394).

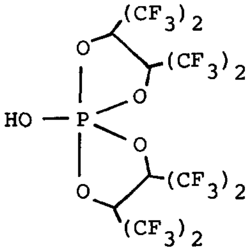
<u>The +5 Oxidation State</u>. Analysis of the structures of phosphorus oxides in the series P_4O_7 to P_4O_{10} show that they can be related to a common, almost body centred "pseudo unit cell" containing two molecules; these similarities are probably a consequence of similarity in molecular packing.[375]

Arsenic(III) oxide and phosphorus(V) oxide in a 1:1 ratio on heating to 673K gives arsenic(III) phosphate $AsPO_4$, which has an infinite layer structure isostructural with AsO_2.[376] Each arsenic atom is pyramidally coordinated to three oxygen atoms at distances of 1.794 and 1.800Å while the phosphorus atoms are in tetrahedral coordination (P-O distances 1.561, 1.570 and 1.476Å). Heating the hydrolysis product of arsenic phosphate to 593K in an evacuated quartz tube gives crystals of a new oxide hydroxide, $As_2PO_5(OH)$.[377] This compound also has an infinite layer structure with arsenic and phosphorus atoms in respectively pyramidal and tetrahedral coordination but from X-ray diffractometry it is not isostructural with $As_3O_5(OH)$.

On refluxing with pyridine, P_4O_{10} is converted into a solid less hygroscopic than the starting material which is considered to be the diphosphoric acid bis(pyridinium)betaine.[378] The trihydrogen diphosphate, $Me_3S(H_3P_2O_7)$, can be isolated after methanolysis of

$P_4O_6S_4$.[379]

The hydroxyphosphorane (114), which results from hydrolysis of the corresponding bromide or chloride, has high stability probably as a result of the specific electron withdrawing and spacial requirements of the perfluoropinacol group.[380] Reaction between silver phenylphosphate and cis-$(Coen_2Cl_2)ClO_4$ in dimethylsulphoxide gives a mixture of two isomers each containing the cyclic cation (115).[381] An X-ray structure of the less soluble form as the triflate salt identified it as the meso-(ΔΛ) form, with substantial deviations from tetrahedral geometry at the bridging phenylphosphate groups (O-P-O angles fall between 98.9 and 115.6°). This is most probably a consequence of geometrical constraints in the novel eight membered ring system. The more soluble isomer is the racemic (ΔΔ and ΛΛ) mixture which can be resolved by cation exchange chromatography with $(+)_D$-sodium antimonyl tartrate as eluent.



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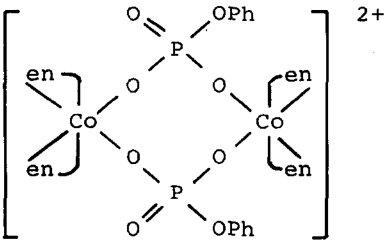


(115)

Complex formation between diphenylphosphate[382] or the phenyl ester of phenylphosphonic acid[383] and a range of di- and tri-organotin compounds has been studied. For one of these compounds i.e. $Ph_3Sn[O_2P(OPh)_2]$, an X-ray structure indicates the formation of an unusual centrosymmetric cyclic hexamer with O-P-O bridges between planar Ph_3Sn groups.[384] The tin atoms are in trigonal bipyramidal coordination (O-Sn-O angles are 175.7, 176.7 and 178.6°) while the O-P-O angle in the ring is 118.5° (see also reference 434).

A new two stage process has been described for preparing Co(II), Ni(II) and Cu(II) complexes with respectively trimethyl-, triethyl- and triallyl-phosphate, dimethyl- and di-i-propyl methylphosphonates, dibutyl butylphosphonate and O,P-dimethyl-P-phenylphosphinate.[385] The procedure involves treating the hydrated metal tetrafluoroborate with trimethyl orthoformate to give the methanol complex, followed by addition of the ligand. X-ray crystallography on the thorium(IV) nitrate complex with two mols of carbamyl-methylenephosphonate, $(EtO)_2P(O)CH_2C(O)NEt_2$, shows the metal in 12-fold coordination from both the carbonyl and phosphoryl oxygen atoms and two oxygens from each of the four nitrate groups.[386] In the $(PhO)_3PO.BCl_3$ adduct the P-O distance is increased to 1.499Å from that (1.432Å) found in the uncomplexed phosphine oxide.[387] The imidodiphosphate complex, $Yb\{N[P(O)(OPh)_2]_2\}_3$, with ca. D_3 symmetry about the central atom is coordinated to six oxygen atoms of three bidentate ligands.[388] Restriction of the coordination number to six here is thought to be a consequence of the bulkiness of the ligand.

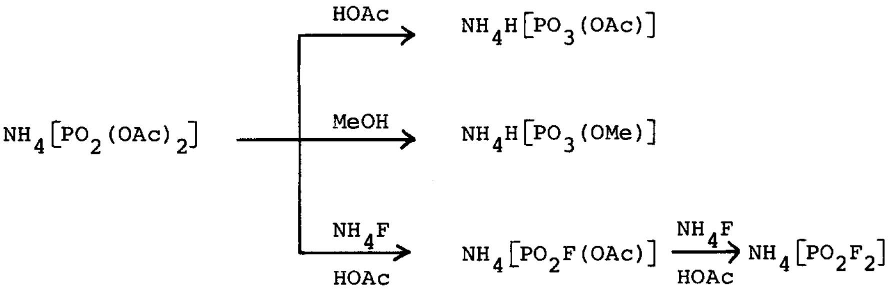
M.o. calculations on complexes between $(HO)_2PO_2^-$ and the cations Li^+, Na^+, Be^{2+} and Mg^{2+} have been carried out to elucidate the problem of cation binding to nucleic acids.[389] In all cases the most stable situation is that where the cation interacts symmetrically with the two phosphate oxygen atoms.

Structures for the tetraurea complexes of $Ca(H_2PO_4)_2$ and $Mg(H_2PO_4)_2$ are based on sheets of $M(H_2PO_4)_2[OC(NH_2)_2]_2$ units separated by layers containing only urea molecules.[390] The Group 2 metal is in six fold coordination to oxygen atoms from bridging H_2PO_4 groups and two trans urea molecules. The reactions which occur when urea and $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ are heated, as well as similar processes with the urea-phosphoric acid adduct, have been followed by ^{31}P n.m.r. spectroscopy.[391] Overall the process is a condensation and although di- and tri-phosphates are initially formed, the major final product is ammonium cyclohexaphosphate which is presumably the most stable polymer under these specific conditions. The rhodium complex, $Rh_2(H_2PO_4)_4(H_2O)_2$, has the characteristic discrete dimeric structure with four bridging phosphate groups, a short Rh-Rh bond and water molecules in axial positions.[392] The compound reacts with KOH to give $K_4[Rh_2(HPO_4)_4(H_2O)_2].8H_2O$ as the major product, but with CsOH two products, i.e. $Cs_4[Rh_2(HPO_4)_4(H_2O)_2].6H_2O$ and $Cs_{1.5}H_{0.5}[Rh_2(H_2PO_4)_2(H_2O)_2].2H_2O$, were isolated.[393] The final hydrolysis product of the bridged compound, which results after heating an aqueous solution, is formulated as $Rh_4(HPO_4)(PO_4)_2(H_2O)_{12}$, but at room temperature under argon $Rh_2(HPO_4)_2(H_2O)_{7.5}$ can also be isolated. The parent compound also reacts with KCl and KSCN to give respectively $K_3Rh_2(H_2PO_4)_2(HPO_4)_2Cl.5H_2O$ and $K_3Rh_2(H_2PO_4)_2(HPO_4)_2(NCS).4H_2O$.

Room temperature reactions between acetic anhydride and ammonium phosphate follow equation (55) and lead to diacetyl phosphates; the corresponding lithium and potassium salts can also

$$NH_4H_2PO_4 + 2Ac_2O \rightarrow NH_4[PO_2(OAc)_2] + 2HOAc \qquad \ldots(55)$$

be isolated.[394] Some aspects of the reactivity of the ammonium salt are summarised in Scheme 7.



<u>Scheme 7</u>

The structure of the phosphoric acid - 2-aminoethanol adduct involves an extensive hydrogen bonded network with one P-O distance (1.610Å) appreciably longer than the others (1.530, 1.510 and 1.500Å).[395]

A new family of molecular sieves containing no silicon atoms but based on aluminophosphate materials has recently been discussed.[396] Of the 20 examples, 14 are microporous and six are two dimensional layer species. The compounds are synthesised hydrothermally at 100-250°C from mixtures containing an organic amine or a quaternary ammonium salt (R) which becomes trapped in a product with the general composition $xR.Al_2O_3.P_2O_5.yH_2O$.

Phase transitions in $Na_2Zr(PO_4)_2.3H_2O$, obtained from α-zirconium phosphate,[397] and the uptake of aminoacids on the latter[398] have been investigated. A direct precipitation method for the preparation of θ-zirconium phosphate has been discovered;[399] the product is a more highly hydrated form, i.e. $Zr(HPO_4)_2.8H_2O$, with an interlayer spacing of 10.4Å and is useful in the exchange of larger cations. Lamellar zirconium phosphonates, e.g. the bis(3-sulphopropyl) and bis(2-sulphophenyl)ethylphosphonates, show utility from the accessibility of the sulphonic acid groups as both strong acid ion exchangers and Bronsted acid catalysts.[400]

As part of a comprehensive study on the thermal dehydration of orthophosphates, data have been reported for $Rb_2HPO_4.2H_2O$,[401] RbH_2PO_4,[402] CsH_2PO_4,[403] $M(H_2PO_4)_2.2H_2O$ where M = Mg, Ca or Mn,[404] $TlPO_4.2H_2O$,[405] $ScPO_4.2H_2O$,[406] and $Zn(H_2PO_4)_2.2H_2O$.[407] In many cases the upper temperature limit was 900°C and among the techniques used were d.t.a., t.g.a., i.r. spectroscopy and X-ray powder diffraction.

Strong hydrogen bonds are present in the structures of $CsH_5(PO_4)_2$[408] and $KMgH(XO_4)_2.15H_2O$ where X = P or As;[409] the former is best described as $CsH(H_2PO_4)_2$.

Crystalline calcium magnesium phosphates over the whole concentration range have been successfully prepared from aqueous solutions,[410] and defect hydroxyapatites with Ca:P molar ratios between 1.40 and 1.62 can be isolated.[411] From analyses, the formulae are represented by $Ca_{10-x-y}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x-2y}$ with the OH content falling between 0 and 1.13. The structures contain two types of calcium vacancies; the first, which involves loss of OH and addition of H to the lattice, appears to depend on the conditions of preparation while in the second, the vacancy is electrically compensated by two vacant OH positions. Site occupancy factors in a series of cadmium substituted fluoroapatites have been assessed by X-ray diffraction[412] and powder diffraction and vibrational spectroscopic data have been collected for the oxoapatites, $Ca_8Ln_2(PO_4)_6O_2$, where Ln = La and Pr-Ho.[413]

The topotactic reaction, see equation (56), has been investigated

$$Pb(H_2PO_4)_2 \rightarrow PbHPO_4 + H_3PO_4 \qquad ...(56)$$

and structures determined for the two lead phosphates.[414] Single crystal X-ray data for YPO_4, $ScPO_4$ and $LuPO_4$ show the presence of isolated distorted PO_4 tetrahedra with the metal atoms in eight fold coordination.[415] The previously unknown titanium hydroxyorthophosphate, $Ti(OH)PO_4$, and the corresponding arsenate have been synthesised from an aqueous solution of $TiCl_4$ and the appropriate acid heated in a sealed quartz ampoule at 250°C.[416] The compounds, which are isostructural with $Ge(OH)PO_4$, are converted to

$Ti_2O(XO_4)_2$ on heating.

Neutron powder diffraction on $VOPO_4.2D_2O$ shows the presence of infinite $VOPO_4$ layers with one water molecule coordinated to vanadium and the second hydrogen bonded to two layers.[417] This layer phosphate gives a pyridine intercalation product, $VOPO_4$.py, on long refluxing with an excess of the base and X-ray powder data point to coordination of pyridine to vanadium with the ligand perpendicular to the phosphate layers.[418] Similar intercalates can be isolated with 4-phenylpyridine and 4,4'-bipyridine together with a related 1:1 pyridine complex with $VOAsO_4$.

Synthesis of the tantalum oxyphosphates and arsenates, $TaOPO_4.H_2O$, $TaOPO_4$, $TaOAsO_4$ and Ta_9AsO_{25}, has been reported,[419] i.r., electronic, and e.s.r. spectra have been measured for $CuHPO_4.H_2O$ and $Cu_4H(PO_4)_3.3H_2O$,[420] and the crystallographic properties of solid solutions of $M_3(PO_4)_2$, where M = Mg, Mn, Fe, Ni, Cu, Zn or Cd, in $Co_3(PO_4)_2$ have been investigated.[421] A full structure determination for $SrNaPO_4.9H_2O$ shows coordination of all nine water molecules to strontium in a tricapped trigonal prismatic arrangement, coordination number six for sodium, and an extensive hydrogen bonded network associated with the phosphate anion.[422] In the related,new struvite analogue, $MgNaPO_4.7H_2O$, the cations and anions are again completely surrounded by water molecules.[423] The lithium magnesium phosphate, $LiMgPO_4$, has an ordered olivine structure,[424] while in $CaKNd(PO_4)_2$ the structure is an isotype of hexagonal $LnPO_4$, except that the potassium atoms occupy a tunnel in the lattice and the Ln positions are occupied statistically by Nd and Ca atoms.[425]

Two compounds belonging to a new class of phosphates, containing both mono- and di-phosphate groups, have been isolated. The first is $K_2H_8(PO_4)_2(P_2O_7)$, which crystallises on slow evaporation of an aqueous solution of KH_2PO_4 and diphosphoric acid.[426] Two independent monophosphate groups are present together with a $P_2O_7^{2-}$ group which has bridge bonds of 1.57 and 1.59Å and an angle of 135° at the bridging oxygen. All three phosphorus units are linked by hydrogen bonds. The second example, $Na_6[Th(PO_4)(P_2O_7)]_2$, results from a high temperature reaction between $Th(PO_3)_4$ and $NaPO_3$ at 1090K followed by addition of a 1:1 mixture of ThO_2 and $Na_4P_2O_7.10H_2O$.[427] The structure contains a binuclear thorium unit in which the metal has a coordination number of nine from bidentate bridging diphosphate groups and PO_4 units.

X-ray p.e. spectra for a number of mono-, di- and tri-phosphates have been analysed showing among other conclusions a relationship between the P(2p) binding energy and the log of the corresponding stability constant.[428]

Among diphosphate structures recently determined are those for $Mg_2P_2O_7.2H_2O$,[429] $MnHP_2O_7$,[430] and $Fe_2P_2O_7$.[431] The latter, which also contains two different types of distorted FeO_6 octahedra, has the P_2O_7 unit in a skew arrangement with bridge P-O distances of 1.621 and 1.575Å and a P-O-P angle of 153°. In the hydrated magnesium diphosphate, for example, the P-O-P angle shows a more usual value of 125.7°.[429]

Thermal transformations in $(NH_4)_2MgP_2O_7.4H_2O$ and $(NH_4)_2Mg_3(P_2O_7)_2.4H_2O$ have been examined showing that at high temperatures it is possible to obtain magnesium tetrametaphosphate.[432] High temperature reactions have also been used to prepare the vanadyl diphosphate, $KVOP_2O_7 \cdot 0.2H_2O$,[433] and members of the series $M_2UO_2P_2O_7$, where M = Na, K, Rb or Cs.[434] V_2O_5 is reduced by ammonium dihydrogen phosphate at 375°C to give vanadium(III) trimetaphosphate.[435]

As in related telluric acid adducts, a structure determination on the compound $Rb_3P_3O_9.Te(OH)_6.H_2O$ shows that the two anions are independent.[436] Ammonolysis of trimetaphosphate in aqueous solution to yield monoamidotrimetaphosphate has an activation energy of 13.6 kcal mol^{-1} from rate data obtained by h.p.l.c.[437] Hydrolysis of both tri- and tetra-metaphosphates is affected by the addition of various cations with, for example, the rate being retarded by alkali metal cations in acidic media but accelerated in basic media.[438] The efficiency is in the order $Li^+ > Na^+ > K^+$. With magnesium and copper ions, hydrolysis is retarded in the pH range 1.0 to 2.0 but above pH 2.7 these ions lead to an accelerated rate of hydrolysis.

An amorphous double triphosphate, $NH_4Mg_2P_3O_{10}.7H_2O$, has been isolated,[439] and its thermal behaviour together with that for the related manganese and zinc compound has been determined.[440] Full X-ray structural information is now available for $Na_5P_3O_{10}.6H_2O$,[441] and two new products, $Na_2KCr_2P_3O_{12}$ and $K_6Cr_2P_6O_{21}$, have been identified in the $K_2Cr_2O_7$-$NaPO_3$ glass and $K_2Cr_2O_7$-$K_4P_2O_7$ systems respectively at ca. 400°C.[442]

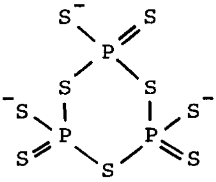
Protonation constants have been determined for the tetra- to hepta-polyphosphates and a given polyphosphate can be identified using ^{31}P n.m.r. spectroscopy by comparing the signal intensities due to middle and end group phosphorus atoms.[443]

Two new thermodynamically stable phosphates, $K_4Pb(P_3O_9)_2$ melting incongruently at 582°C and the polymeric $K_2Pb(PO_3)_4$ melting at 578°C, have been identified in the KPO_3-$Pb(PO_3)_2$ system but the tetrametaphosphate, $K_2Pb(P_4O_{12})$ could not be obtained by thermal methods.[444] A new form of Kurrol's salt, $(NaPO_3)_n$, has been identified by X-ray powder diffraction on a sample of the B-form which had been finely ground.[445] The helical structure in the new form is closely related to that in the starting B-form but the relative positions of the helices in the [101] direction are different.

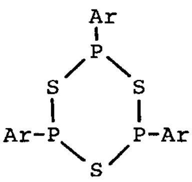
5.2.6 Bonds to Sulphur

The previously unknown phosphorus sulphide P_4S_8 has been identified by ^{31}P n.m.r. spectroscopy as the initial desulphurisation product of P_4S_9 with triphenylphosphine at room temperature.[446] The compound has apparently only limited stability even in dilute solution and is thought to be formed by extraction of one terminal sulphur from P_4S_9 leaving the cage intact. A multicomponent system containing all molecules of the type $P_4S_nSe_{3-n}$, where n = 0-3, is obtained according to an investigation of the P_4S_3-P_4Se_3 system by X-ray diffractometry, mass spectrometry and ^{31}P n.m.r. spectroscopy.[447] The compounds are all considered to have cage structures, and during the course of the work a new modification of P_4S_3, probably isostructural with γ-P_4Se_3, was identified.

Treatment of either P_4S_9 or P_4S_{10} with liquid ammonia at below -33°C leads to formation of the ammonium salt of the perthiocyclotriphosphate (<u>116</u>);[448] further reaction with ammonia leads to $(NH_4)_2PS_3(NH_2)$ while with PCl_3 or $PSCl_3$ at 150°C, the ammonium salt



(<u>116</u>)

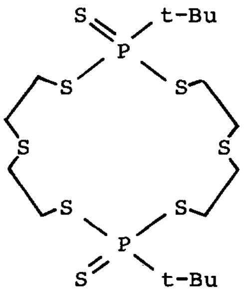


(<u>117</u>)

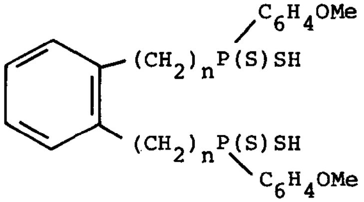
of (<u>116</u>) is reconverted to P_4S_9. Hydrolysis of (<u>116</u>) at room temperature gives the monomeric thiophosphate but with Tl^+, the primary product is the linear thiotriphosphate, $Tl_5P_3OS_9$. A six-membered phosphorus-sulphur ring compound (<u>117</u>) is the product when lithium sulphide reacts with tri(t-butyl)phenylphosphorus dichloride.[141]

Treatment of a suspension of $P_2S_5.py_2$ in benzene with gaseous hydrogen chloride gives $pyH(PS_2Cl_2)$, but this can be converted to a salt of the difluoropentathiodiphosphate anion, $(Pr_4N)_2P_2S_5F_2$ on reaction with successively KHF_2 in acetonitrile and Pr_4NI.[449]

The ring structure of the 16-membered macrocycle (<u>118</u>) is asymmetric and conforms to neither of the two forms calculated to be the most favourable for a cyclohexadecane system; this may however be a consequence of the short intermolecular S···C contacts.[450] Among the new dithiophosphinic acids synthesised from perthiophosphonic anhydrides and a bis-Grignard reagent are compounds (<u>119</u>) with n = 2 or 3; their use as ligands with Ni(II) and Co(II) was also investigated.[451]



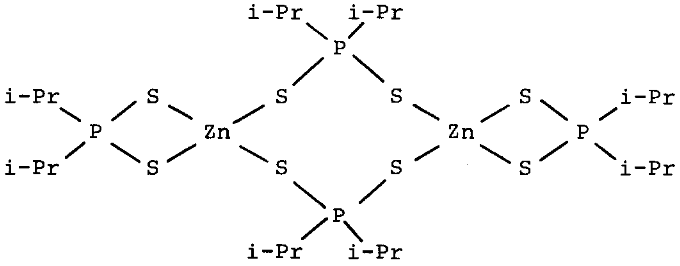
(<u>118</u>)



(<u>119</u>)

New tin-dithiophosphato complexes, $Sn[S_2P(OR)_2]_2$ where R = Me, Et, i-Pr or Ph, have been synthesised and the structure of the phenyl compound shows a centrosymmetric dimer in which one ligand simultaneously behaves as an unsymmetrical chelate and as a bridging group.[452] The second ligand is a normal chelating group (see also references 382-384). Structures are also available for the 2:1 adduct of hexamethylenetetramine with cadmium bis(O,O'-diethyldithiophosphate)[453] and the 1:1 adduct between triphenylphosphine and the related cobalt complex, $Co[S_2P(OMe)_2]_2$.[454]

In the lanthanoid dimethyldithiophosphinate complexes, $Ph_4As[Ln(S_2PMe_2)_4]$ where Ln = Ce or Tm, the lanthanoid is in eight fold coordination to sulphur with distances in the thulium complex ranging from 2.789 to 2.961Å.[455] An eight membered ring (120) containing two bridging dithiophosphinate groups is present in the structure of zinc di-n-propyldithiophosphinate.[456]



(120)

Vibrational spectra have been obtained for the potentially bidentate diphosphanes, $R(Et_2N)P(S)-P(S)(NEt_2)R$ where $R = Et_2N$, C_6H_{11} or Ph, and an X-ray structure for the diethylamino compound shows an inversion centre midway between the phosphorus atoms leading to a trans conformation similar to that already observed for the analogue with $R = C_6H_{11}$.[457] The bidentate ligand, $HN[PPh_2(S)]_2$, gives a new tellurium(II) complex which has a structure based on a planar centrosymmetric TeS_4 unit.[458]

Both phosphorus and sulphur atoms in $Na_3PO_3S.12H_2O$ lie on the three fold axis (space group R$\bar{3}$c) and the anion is disordered with equal occupancy over two orientations related by rotation about any one of the three equivalent diad axes normal to the P-S bond.[459] The P-S and P-O distances are 1.992 and 1.519Å respectively. The mean P-S bond distance in the tetrahedral anion of Li_3PS_4 has been found to be 2.050Å.[460]

A silver compound containing both PS_4^{3-} and $P_2S_7^{4-}$ groups has been obtained from the elements in calculated proportions at 823K.[461] According to X-ray data, the PS_4^{3-} units form layers which alternate with double layers of $P_2S_7^{4-}$ units.

The structure of $Ag_4P_2S_6$ contains two independent $P_2S_6^{4-}$ units with P-P distances of 2.268 and 2.247Å and a mean P-S distance of 2.03Å.[462] The related thiohypodiphosphates, ZrP_2S_6 and ThP_2S_6, isolated from reactions between the elements in stoichiometric proportions at 500-800°C, also contain the P_2S_6 units in the staggered conformation.[463] For the zirconium compound the P-P distance is 2.218Å.

5.3 ARSENIC

5.3.1 Arsenic, Polyarsines and Arsenides.

The Raman spectrum of the As_4 molecule in a krypton matrix at 10K shows bands at 352, 207 and 265 cm^{-1}, values which are to higher energy than the corresponding bands in the gas phase spectra.[464] The structure of the polymeric arsenic structure with puckered graphite-like sheets has been investigated by Hückel m.o. calculations and compared with results for graphite and polymeric selenium.[465] Stabilisation of pyramidal coordination at arsenic is considered to result from relieving π-antibonding effects in the HOMO.

An unusual compound $As_2[W(CO)_5]_3$, in which an As_2 unit behaves as a six electron donor, results when arsenic(III) chloride reacts with either $Na_2W_2(CO)_{10}$ or $(CO)_5W(THF)$.[466] The structure, illustrated in Figure 9, shows a D_{3h} framework for the As_2W_3 unit; the As-As distance is 2.279Å (see references 516 and 569 for the related Sb_2 and Bi_2 compounds).

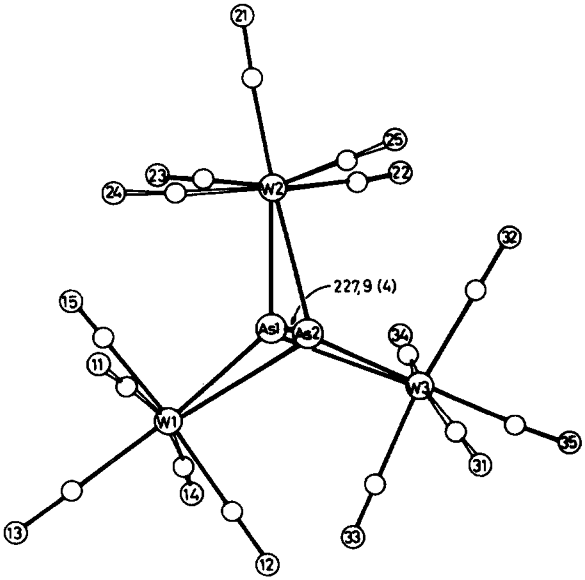
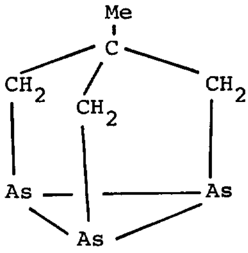


Figure 9. Structure of $As_2[W(CO)_5]_3$ (reproduced by permission from J. Organomet. Chem., 226(1982)C5).

The pale yellow, silyldiarsine $(Me_3Si)_4As_2$, which results when 1,2-dibromoethane reacts with the lithium salt of bis(trimethylsilyl)arsine, has an overall gauche conformation with a Si-As-As-Si torsion angle of -125.7°.[467] The two $AsSi_2$ units are related by a crystallographic two fold axis and important parameters are: As-As 2.458, As-Si 2.365 and 2.362Å, Si-As-Si 100.90 and As-As-Si 93.87 and 113.63°.

Among the products isolated from reactions between $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Co_2(CO)_8$ and a number of iridium complexes and the tricyclic triarsine (121)(≡L) are $Os_6(CO)_{21}L$, $Co_2(CO)_6L$ and $Ru(CO)_4L$.[468] Reaction appears to involve oxidative addition and structures are proposed on the basis of vibrational and n.m.r. data.



(121)

Cyclo-tetra(t-butylarsine) which has been prepared as shown in equation (57) is isotypic with the corresponding tetrastibine,

$$2t\text{-}BuAsCl_2 + 2Li_2Ast\text{-}Bu \rightarrow (t\text{-}BuAs)_4 + 4LiCl \qquad \ldots(57)$$

obtained by reduction of t-$BuSbCl_2$ with magnesium.[469] In both compounds the four-membered rings are folded with the substituents occupying pseudo equatorial positions in an all trans configuration. Mean molecular parameters are given in Table 2 for the two species.

Table 2. Molecular parameters for $(t\text{-}BuM)_4$, where M = As or Sb.

	M = As	M = Sb
M-M (Å)	2.44	2.82
M-C (Å)	2.02	2.21
M-M-M (°)	86	85
M-M-C (°)	101	99

Deuterated pentaethylpentaarsine has been synthesised from $CD_3CH_2AsH_2$ and dibenzylmercury and variable temperature ^1H n.m.r. spectra are interpreted in terms of fast pseudorotation on the n.m.r. time scale at temperatures between -65 and 75°C.[470] Either 2:3 or 2:2:1 patterns occur in the spectra depending on dilution implying the presence of either a permanent or time averaged plane of symmetry. The structure of an unusual triple decker sandwich molecule containing an As_5 unit, which was obtained as one of the products from a reaction between $[CpMo(CO)_3]_2$ and pentamethylcyclopentaarsine, is illustrated in Figure 10.[471] From bond distance data and the relative arrangements of the three rings, the As_5 group is considered to coordinate as both a μ-(η^2-As_3) and a μ-(η^2-As_2) ligand. As-As distances fall between 2.389 and 2.762Å with a mean As-As-As angle of 108.0°.

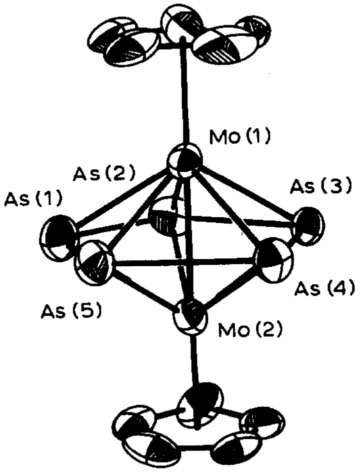


Figure 10. Molecular structure of $(CpMo)_2[\mu$-$(\eta^4$-$As_5)]$ (reproduced by permission from J. Am. Chem. Soc., 104(1982)4727).

In addition to producing a cyclotetraarsine and t-Bu_6As_8, the magnesium reduction of t-$BuAsCl_2$ in either THF or ether solution has been reinvestigated showing that the pentaarsine (t-BuAs)$_5$ is also formed.[472] Full details are now available on the structure of the octaarsine t-Bu_6As_8, mentioned in last year's report (p.306).[473]

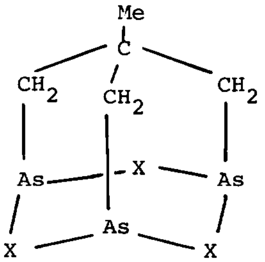
New ternary phases Ca_3AlAs_3, Ba_3AsSb_3,[474] $Ca_3Si_2As_4$, $Ca_3Ge_2As_4$, $Sr_3Si_2As_4$ and $Sr_3Ge_2As_4$,[475] have been obtained from high temperature reactions on stoichiometric mixtures of the elements. In Ca_3AlAs_3, the structure is based on chains of corner sharing $AlAs_4$ tetrahedra (As-Al 2.503 and 2.539Å) but in the related antimony compound, two $AlSb_4$ tetrahedra share a common edge to give discrete Al_2Sb_6 units (bridging and terminal Al-Sb distances are 2.724 and 2.709Å respectively).[474] The silicon and germanium arsenides each contain polymeric $M_2As_4{}^{6-}$ anions which are linked differently depending on the cation.[475] A calcium copper ternary, $CaCu_4As_2$ has been prepared from an equimolar mixture of Cu, Cu_3As and CaAs.[476]

Ca_3AsCl_3, which is an isotype of Mg_3NF_3, can be prepared from high temperature reactions of either a 3:2:3 mixture of Ca, As and $CaCl_2$ or a 1:3 mixture of Ca_3As_2 and $CaCl_2$.[477] On heating to 1025°C, the compound decomposes giving calcium chloride and $Ca_{2-x}As_{1-x}Cl_{1+x}$ with $x = 0.1_3$.

5.3.2. Bonds to Carbon or Silicon

Reactions of a range of lanthanoid(III) chlorides with $LiAs({}^tBu)_2$ in THF solution lead to compounds of the type $M[As(t\text{-}Bu)_2]_3$ which may be solvated depending on M.[478] In the presence of tetramethylethylenediamine (tmed), the complexes for M = Y, La, Pr, Er or Lu are converted into $M[As(t\text{-}Bu)_2]_3(tmed)_x$, with x varying between 0.5 and 3 depending again on M.

Reaction of the adamantane-like compound (122, X = $NC_6H_4p\text{-}Me$) with hydrogen chloride leads to the tris(dichloroarsine)



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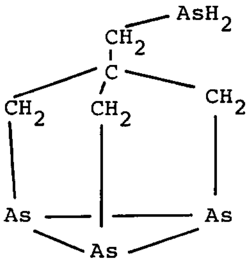


(123)

$MeC(CH_2AsCl_2)_3$, which is also the product when (122, X = O) is chlorinated with either PCl_3 or $AsCl_3$.[479] Oxidation of (122, X = O or S) with hydrogen peroxide leads to the triarsonic acid, $MeC[CH_2As(O)(OH)_2]_3.H_2O$. Two new hydrides, i.e. $MeC(CH_2AsH_2)_3$

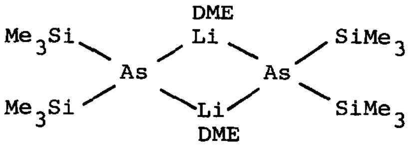
and $C(CH_2AsH_2)_4$, are the reduction products of $MeC(CH_2AsI_2)_3$ and $C(CH_2AsI_2)_4$ respectively with $LiAlH_4$ and on oxidation these hydrides are converted to the triarsine derivatives (121) and (123) respectively.

Compounds of the type cis-$Cp(CO)_2[E(CH_2R)_3]MBr$, where E = As or Sb, R = Ph or Me_3Si and M = Mo or W, result when $Cp(CO)_3MBr$ is treated with the appropriate arsine or stibine.[480] With $(RCH_2)_3AsBr_2$ and $Na[Mo(CO)_3Cp]$, there is an initial redox reaction to give $(RCH_2)_3As$ but at higher temperatures there is further reaction to give the same type of complex, i.e. cis-$Cp(CO)_2$-$[As(CH_2R)_3]MoBr$.

The lithium salt $LiCH_2As(O)Ph_2$, prepared by treating methyl diphenylarsine oxide with lithium isopropylamide in THF at -40°C, is a useful intermediate for preparing a range of new compounds.[481] With copper(II) chloride in THF, for example, it is converted to the diarsine oxide $Ph_2As(O)CH_2CH_2As(O)Ph_2$,[482] which in turn can be reduced with $LiBH_4$ to the mono- and di-arsine.

The crystal structure of $Ph_4As^+HCl_2^-$, obtained by passing hydrogen chloride into a solution of Ph_4AsCl in dichloromethane, shows the HCl_2^- ion lying on a centre of inversion with a Cl---Cl separation of 3.09Å.[483]

Lithiation of tris(trimethylsilyl)arsine in 1,2-dimethoxyethane (DME) yields the salt $LiAs(SiMe_3)_2.DME$, which is dimeric (see 124) in both the solid state and in solution.[484] The As_2Li_2 ring is planar with As-Si and As-Li distances of 2.307 and 2.59Å respectively (for the related antimony compounds see reference 530).



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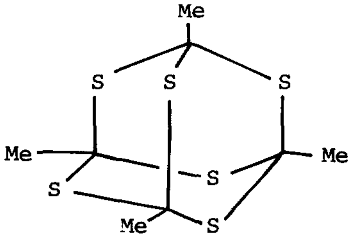

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5.3.3 Bonds to Halogens

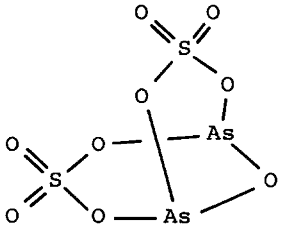
N.q.r. spectra for the arsenic(III) and antimony(III) chloride complexes $MCl_3.L$, where L = Me_3N, $PhNH_2$ and tetramethylthiourea, have been measured.[485] Reaction of AsI_3 with thioacetic acid gives among other products a 1:1 adduct of the triiodide with tetramethylhexathioadamantane (125).[486] The arsenic coordination number is increased to six with contacts to three sulphur atoms of the ligand (As-I 2.575 to 2.577, As---S 3.274 to 3.310Å). Formation of the ligand may proceed via rearrangement of thioacetic acid to the dithio analogue followed by condensation to MeC(S)SC(S)Me.

The oxidising power of both arsenic and antimony pentafluorides continues to be exploited and the new species $(S_7I)_4S_4(AsF_6)_6$ and $[(S_7I)_2I](SbF_6)_3.2AsF_3$ have been isolated from reactions with mixtures of elementary sulphur and iodine[487] (see also reference 545). Similarly, intercalates of the two pentafluorides into graphite continue to arouse interest. From recent work, the product richest in AsF_5 has the approximate composition $C_{8.4}AsF_5$ but it is found that $C_{10.4}AsF_5$ species are relatively stable toward further intercalation.[488] Infrared investigation shows the process is accompanied by C-F bond formation and liberation of AsF_3. Similar reactions with antimony pentafluoride are much slower and contrary to the situation with arsenic, the ratio F:Sb is close to six. Fluorination at carbon is also more pronounced and the richest compound has the composition $C_{7.3}SbF_6$.

Three types of hexafluoroarsenate salts, i.e. $MF_2.2AsF_5$ for M = Mg, Ca, Sr, Mn, Co, Ni, Cd, Hg and Pb, $2MF_2.3AsF_5$ for M = Fe, Cu and Zn and $MF_2.AsF_5$ for M = Ag or Sn, have been identified in a study of the interaction of metal(II) fluorides with AsF_5 in liquid hydrogen fluoride.[489,490] In all cases loss of AsF_5 occurs on heating but the most complex behaviour is observed with the 2:3 compounds where there is successive formation of $MF_2.AsF_5$ and $2MF_2.AsF_5$.

5.3.4 Bonds to Oxygen

Structures have been determined for two of the products, i.e. $As_2O_3.3SO_3$[491] and $As_2O_3.2SO_3$,[492] isolated from solutions of arsenic(III) oxide in oleum and that for a third compound, $As_2O_3.SO_3$, has been refined.[493] The first compound is formulated as $As_2(SO_4)_3$ and consists of SO_4 bridges between two pyramidal AsO_3 units leading to chains parallel to the a axis.[491] Bridging and terminal S-O distances are ca. 1.54 and 1.42Å respectively while the mean As-O distance at 1.83Å implies a weakening over those in As_4O_6. The compound, $As_2O_3.2SO_3$ as shown in (126), consists of discrete $As_2O(SO_4)_2$ molecules, with one As_2O group linked to two bridging sulphate groups.[492] As-O distances in the As_2O unit are stronger (ca. 1.75Å) but those to the sulphate groups average 1.84Å. The chlorodioxarsenane (127) structure shows a twist-boat conformation for the ring with the As-Cl bond in an axial position;[494] As-Cl and As-O distances are 2.258 and 1.738, 1.743Å respectively.



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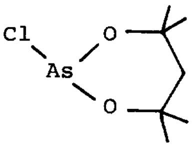


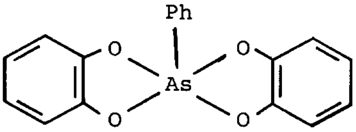
(127)

Arsenic(III) and antimony(III) complexes with (±)- and meso-1,2-dihydroxycyclohexane-1,2-dicarboxylate have the formula $Na_2[M_2(C_8H_8O_6)_2].xH_2O$ where M = As or Sb.[495] ^{13}C n.m.r. data point to their being dimers in solution and an X-ray structure for $Na_2[As_2(\pm-C_8H_8O_6)_2].6H_2O$ shows a racemic mixture of the binuclear ΔΔ(RR,RR) and ΛΛ(SS,SS) complexes.

A macrocyclic arsa-aza-oxa-crytand, $[N(CH_2CH_2)_3]_8(As_4O_4)_6$ has been isolated from a reaction between $[HN(CH_2CH_2AsI_2)_3]I$ and concentrated aqueous ammonia in THF solution.[496] From X-ray diffraction, the compound consists of six eight-membered As_4O_4 rings interconnected by triethylamine units attached to the arsenic atoms. The eight nitrogen atoms are at the corners of a distorted cube and the six As_4O_4, which have crown conformations, are close to the surfaces of the cube. Overall the molecule has C_{3v} symmetry and the short (mean 1.79Å) As-O bond lengths point to partial double bond character.

A new mixed As(III)-As(IV) compound, $As_3O_5(OH)$, can be obtained when the hydrolysis products of As_2O_4 are heated to 593K.[497] Its structure is based on infinite layers containing two independent pyramidal $As(III)O_3$ units (As-O 1.784 and 1.838Å) and tetrahedral $As(V)O_4$ groups (As-O 1.593, 1.646, 1.666 and 1.669Å). The oxygen attached by the shortest distance has some double bond character and participates in hydrogen bonding to an oxygen on a symmetry related As(V) atom; angles at bridging oxygen atoms fall in the range 126.1 to 132.3°.

In continuation of investigations into the geometry at five coordinate Group 5 elements, full crystal structures have been carried out for the two arsoranes (<u>128</u>) and (<u>129</u>).[498] In (<u>128</u>), the two independent molecules in the structure are displaced 99 and 95% respectively along the Berry coordinate linking the trigonal bipyramid and square pyramid extremes, while the structure of (<u>129</u>) lies only 23% from the ideal trigonal bipyramid. These observations, supplemented by molecular mechanics calculations, indicate that the general structural principles governing spirophosphorane chemistry can also be applied to the analogous arsenic derivatives.



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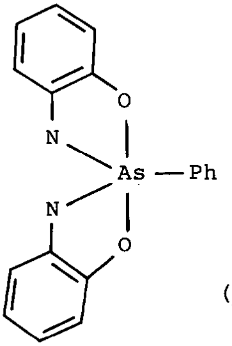


(<u>129</u>)

The arsonates of a series of diorganotin compounds, $XC_6H_4AsO_3SnR_2$ where R = Me, n-Bu, $PhCH_2$ etc and X = H, p-Me, p-Cl, o-NH_2 etc., are high melting solids, insoluble in organic solvents.[499] A chromium pentammine complex, $[Cr(NH_3)_5(H_2AsO_4)](ClO_4)_2$, can be obtained by treating the corresponding aquo complex with concentrated arsenic acid.[500]

A single crystal structure has been determined for $CuAgH_3(AsO_4)_2$,[501] and powder data for α-Cs_3AsO_4, α-$Cs_4As_2O_7$ and $Cs_5As_3O_{10}$ have been indexed.[502] α-$BiAsO_4$, a synthetic form of the mineral rooseveltite obtained from bismuth nitrate and arsenic acid in aqueous solution, has the $CePO_4$, monazite structure.[503]

The arsenic atom is in distorted tetrahedral coordination while the bismuth is irregularly coordinated to eight oxygen atoms in the range 2.332 to 2.646Å. Asymmetry in coordination is probably associated with steric activity of the bismuth lone pair of electrons.

Powder neutron diffraction data for $UO_2DAsO_4.4D_2O$[504] and $LiUO_2AsO_4.4D_2O$[505] show chains of H_4O_2 and $H_5O_2^+$ units alternating with layers of UO_2^{2+} and AsO_4^{3-} ions for the former while in the lithium salt each linear UO_2^{2+} ion makes contact with four oxygen atoms from four different AsO_4 units. The new zinc arsenate mineral, prosperite $Ca_2Zn_4[H_2O(AsO_4)_4]$, has a complicated framework of cation polyhedra supported by a hydrogen bonded network involving AsO_4 tetrahedra.[506]

5.3.5 Bonds to Sulphur, Selenium or Tellurium

A series of dithioarsinic acid derivatives, e.g. $R_2Sn(S_2AsMe_2)_2$ and $R'_3Sn(S_2AsMe_2)$ where R = Me, Bu or Ph and R' = Ph or cyclohexyl, has been prepared using the sodium salt, NaS_2AsMe_2 and the appropriate organotin halide.[507] With $SnCl_4$ itself, only the di- and tetra-substituted compounds, $Cl_2Sn(S_2AsMe_2)_2$ and $Sn(S_2AsMe_2)_4$ could be isolated, there being no evidence for the formation of the mono- or tri-substituted species even when reactions in 1:1 and 1:3 ratios were carried out.

Structures for two alkylarylarsine sulphides, $(p\text{-}MeC_6H_4)Et_2AsS$ and Ph_2EtAsS, in which the As-S bond lengths are 2.090 and 2.081Å respectively, confirm that increasing the number of aryl substituents leads to a decrease in the electron density at arsenic and a strengthening of the As-S π-bonding.[508] Both X-ray and neutron diffraction data have been used to investigate, in particular, hydrogen bonding in the tetrathioarsenate, $Na_3AsS_4.8D_2O$.[509]

Structure determinations have been carried out on $(LaO)_4As_2S_5$ and its isotype $(CeO)_4Ga_2S_5$[510] and on the new sulpho-salt, $Tl_2MnAs_2S_5$, recently synthesised by a hydrothermal method.[511] The mineral rebulite, $Tl_5Sb_5As_8S_{22}$, has a three dimensional structure in which all arsenic atoms are trigonally bonded to three sulphur atoms (mean As-S 2.29Å).[512] Sulphur coordination to antimony is of three types: a) octahedral with one split vertex and three short (2.4-2.6) and four long (2.9-3.9Å) Sb-S bonds, b) as above but with four short (2.5-2.8Å) and three longer bonds and c) pseudo-trigonal bipyramidal (2.4-2.9Å). There is a measure of arsenic-antimony disorder.

The selenides, $(PhSe)_3As$ and $(PhSe)_3Bi$, have been prepared from the appropriate trichloride and PhSeNa and, together with $(PhS)_3Sb$ and $(PhS)_3Bi$, their thermal decomposition has been studied.[513] Initiation is by oxygen and a radical chain mechanism leads to the products $(PhS)_2$ or $(PhSe)_2$ and the appropriate metalloid.

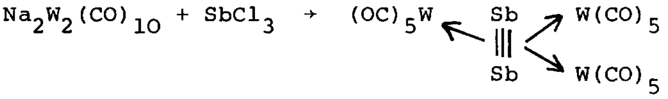
The intermediate phases, As_5Te_7I and α-AsTeI, have been identified in the As_2Te_3-AsI_3 system; the former contains chains of edge sharing octahedra condensed further into ribbons.[514]

5.4 ANTIMONY

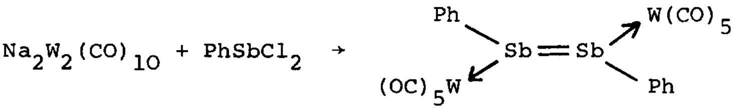
5.4.1 Antimony and Polystibines

Chemical transport of antimony by the trichloride, water or gallium(III) chloride has been investigated showing that with the latter the rate is larger than that calculated thermodynamically for diffusion only.[515]

The unstable Sb_2 and PhSb=SbPh species can be generated by reductive dehalogenation and stabilised as tungsten carbonyl complexes as shown in equations (58) and (59).[516] X-ray structures for both have been carried out showing that the former contains the same D_{3h} heavy atom structure as was observed for the analogous arsenic compound.[466]



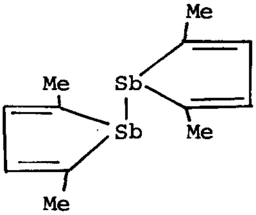
...(58)



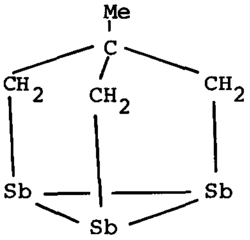
...(59)

Dehalogenation of Pr_2SbBr and Ph_2SbBr with magnesium in THF leads to the distibines $Pr_2SbSbPr_2$ and $Ph_2SbSbPh_2$ respectively, which with oxygen and sulphur give the corresponding bridged species, $R_2SbXSbR_2$ where X = O or S.[517] Detailed investigation of the vibrational spectra of such distibines shows Sb-Sb stretching modes at 145 and 175 cm^{-1} for the tetramethyl compound, indicating the presence of both trans and gauche conformers, and at 163 and 141 cm^{-1} respectively for the ethyl and phenyl compounds.[518] Although treatment of a mixture of n-Bu_2SbBr and Me_3SiCl with magnesium leads to only the distibine, n-Bu_4Sb_2, similar reactions with Ph_2SbBr or t-Bu_2SbBr do give the silyl-stibines $Ph_2SbSiMe_3$ and t-$Bu_2SbSiMe_3$ respectively.[519] Polymeric $(RSb)_n$ is sometimes formed when dihalogenostibines are used but with Me_3SiCl and $PhSbBr_2$, the magnesium dehalogenation reaction also gives $PhSb(SiMe_3)_2$. On the other hand, a mixture of t-$BuSi(SiMe_3)_2$, $Sb(SiMe_3)_3$ and (t-$BuSb)_4$ results when t-$BuSbCl_2$-Me_3SiCl mixtures are dehalogenated.

An alternative preparative route to tetrakis(trimethylsilyl)-distibine, $(Me_3Si)_4Sb_2$, an intensely red solid, involves treatment of the lithium salt $Li[Sb(SiMe_3)_2].2THF$ with 1,2-dibromoethane.[520] The R_2Sb groups occupy transoid positions in the solid state with the following major structural parameters: Sb-Sb 2.867, Sb-Si 2.594Å, Si-Sb-Si 94.46, Sb-Sb-Si 98.68, 94.43°. The sequence of Sb-Sb groups is almost linear and their separation (3.99Å) is substantially less than the sum of the van der Waals' radii; this is probably an important factor in the development of the intense colour in the solid. A related problem, the thermochromic effect in 2,2',5,5'-tetramethyl-bistibole (<u>130</u>), can also be accounted for on the basis of a one dimensional electronic band structure according to extended Hückel calculations.[521] Although antimony d orbitals were not included in the calculations, they are probably important as the d_{xz} and d_{z^2} orbitals are of correct symmetry to interact with the π_u^* LUMO and so lower its energy.



(<u>130</u>)

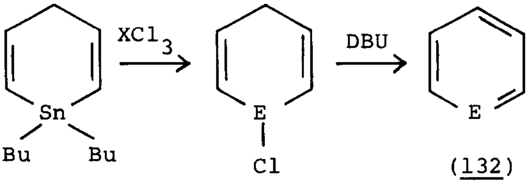


(<u>131</u>)

The substituted cyclotristibine (<u>131</u>) has been synthesised by the reaction of sodium in THF with $MeC(CH_2SbCl_2)_3$ and yields a $Cr(CO)_5$ complex on treatment with $Cr(CO)_5.THF$.[522] As mentioned earlier,[469] the cyclotetrastibine, t-Bu_4Sb_4, has been synthesised and its structural parameters are summarised in Table 2 (page 350).

5.4.2 Bonds to Carbon or Silicon

Organo-antimony chemistry for 1980 has been surveyed.[523] The gold derivative, $[(Ph_3Sb)_4Au][(C_6F_5)_2Au]$, contains three independent cations according to a recent crystal structure determination with one of the Au-Sb bonds in each lying along a crystallographic three fold axis.[524] Each $AuSb_4$ has approximately $\bar{4}$ symmetry with Au-Sb bond distances in the range 2.585 to 2.669Å. Both stibabenzene and bismabenzene (132, E = Sb or Bi) can be isolated from the reactions outlined in (60).[525] Both compounds



(132)

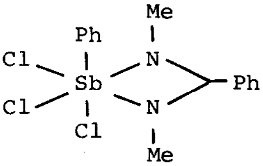
...(60)

polymerise almost immediately at room temperature but recently it has been shown that the analogues carrying an alkyl substituent in the 4-position are considerably more stable. 4-Methylstibabenzene, for example, is unchanged after 1hr. at 25°C but still polymerisation occurs within 24hr.

Gas phase p.e.s. for Me_5Sb, Me_3SbX_2 where X = Cl, Br or I and $SbCl_5$ have been measured and assigned on the basis of a D_{3h} model; d orbitals appear not to be involved in the bonding in these compounds.[526] One mol of methane is liberated when pentamethyl antimony and carboxylic acids react in a 1:2 ratio to give the tetramethylstibonium salt of the corresponding hydrogen dicarboxylate.[527] Among the compounds isolated are those from benzoic, o-phthalic, 4-ethoxysalicylic, oxalic and malic acids and crystal structures for the first three products have been determined. The anions are characterised by strong hydrogen bonds, e.g. the O---O separation is 2.32Å in the hydrogen diphthalate; in the dibenzoate there is also a residual Sb---O interaction leading to cation distortion.

Thermolysis of thioaryl derivatives, Ph_4SbSAr, in organic solvents are radical processes, as are the corresponding reactions on neat samples investigated earlier.[528] The products isolated are based on radical attack on carbon tetrachloride or cyclohexane, used as solvents.

Analysis of the ^{121}Sb Mössbauer data for the N,N'-dimethylbenzamidine (≡LH) complexes $Ph_nSbCl_{4-n}L$ points to structures (133), (134) and (135) for the products with n = 1, 2 and 3 respectively;[529] structure (134) has been confirmed by X-ray



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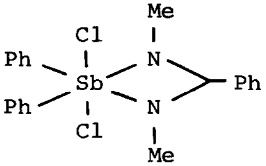

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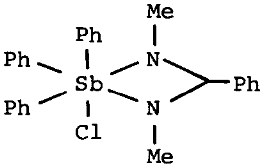


(135)

crystallography showing a distorted octahedral arrangement with Sb-Cl and Sb-N distances of 2.426, 2.454 and 2.125, 2.167Å respectively. The N-Sb-N angle is closed to 60.6° from constraints imposed by the four membered ring.

Tetramethylsilane is eliminated on treatment of tris(trimethylsilyl)stibine with methyl lithium in dimethoxyethane (DME) with formation of the lithium derivative $(Me_3Si)_2SbLi(DME)$.[530] This product has a polymeric structure with both lithium and antimony atoms in distorted tetrahedral coordination; some bond distances and angles determined are: Sb-Si 2.532, Sb-Li 2.933, Li-O 2.011Å, Si-Sb-Si 94.2, Li-Sb-Si 106.3, 97.6, Sb-Li-Sb 130.7 and Li-Sb-Li 144.6°.

5.4.3 Bonds to Halogens

The following compounds, KSb_4F_{13}, KSb_2F_7, $KSbF_4$ and K_2SbF_5, all with incongruent melting points, have been identified in a d.t.a. and X-ray diffraction study of the $KF\text{-}SbF_3$ system.[531] In the $MF\text{-}SbF_3$ systems for M = Rb or Cs in anhydrous formic acid solution there is evidence for $RbSb_2F_7$, $RbSbF_4$, $Rb_3Sb_2F_9$ and Rb_2SbF_5 and the caesium compounds $CsSb_4F_{13}$, $CsSb_2F_7$ and Cs_2SbF_5.[532] $Rb_3Sb_2F_9$, which has a diffraction pattern showing high symmetry, has been isolated for the first time; it cannot be obtained from either aqueous or acetic acid solutions.

Antimony trifluoride and potassium sulphate solutions in water give a new 1:1 complex with the structure illustrated in Figure 11.[533] Coordination about the antimony atom is pseudo-octahedral with bonds to three fluorine atoms (1.940, 1.983 and 1.995Å) and two oxygens (2.346 and 2.450Å); the O-Sb-O angle is 96.4°.

The structure of the 1:1 adduct, produced when antimony

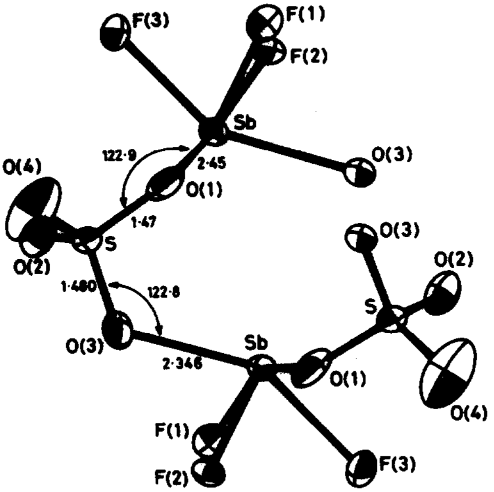


Figure 11. Part of the $(SbF_3.SO_4)_x^{2x-}$ helix in the structure of $K_2SO_4.SbF_3$ (reproduced by permission from J. Chem. Soc. Dalton Trans., (1982)2313).

trichloride and gallium trichloride react in liquid sulphur dioxide, consists of $SbCl_2^+$ and $GaCl_4^-$ ions which strongly interact to produce infinite chains parallel to the b axis.[534] The cation is angular (Sb-Cl 2.295 and 2.299Å, Cl-Sb-Cl 97.4°) but there are two longer contacts (2.713 and 2.772Å) to chlorine atoms of adjacent $GaCl_4^-$ groups. If the lone pair is active, coordination about antimony could be described as very distorted trigonal bipyramidal. The $GaCl_4^-$ anions are substantially distorted from tetrahedral symmetry. The $SbCl_3$ adduct with dithiooxamide (≡L), i.e. $SbCl_3.L_{1.5}$, is also polymeric with the ligands bridging between pairs of antimony atoms.[535] The central atom is in six fold, distorted octahedral, coordination to three chlorine atoms at 2.340, 2.381 and 2.388Å and three sulphur atoms with a fac-arrangement at 3.165, 3.212 and 3.396Å. 2-Aminobenzothiazole (≡L) gives the following antimony(III) and bismuth(III) halide complexes: $SbCl_3.2L$, $SbBr_3.1.5L$, $SbI_3.L$ and $BiX_3.L$ where X = Cl, Br or I;[536] coordination is via the endocyclic nitrogen atom.

Structures have been determined for three compounds each with the stoichiometry $R_4N^+SbCl_4^-$.[537] When R = Et, the product contains discrete tetrameric $Sb_4Cl_{16}^{4-}$ anions in which the antimony is in six fold coordination to three terminal and three bridging chlorine atoms at 2.394 to 2.504 and 2.780 to 3.268Å respectively.

The anion with R = n-Pr and n-Bu is in each case a doubly chlorine bridged dimer, $Sb_2Cl_8^{2-}$, with pseudo-octahedral coordination about each antimony. The two species differ however as for R = n-Pr the apical atoms occupy trans position while with R = n-Bu, these atoms are cis to each other.

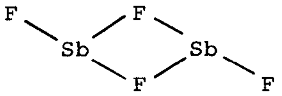
The complex $2SbBr_3$.biphenyl is centrosymmetric with pyramidal $SbBr_3$ molecules (mean Sb-Br 2.509Å) coordinated to the phenyl groups of a planar biphenyl molecule at a distance of 3.23Å.[538] A further Sb---Br contact at 3.695Å completes pseudo-octahedral geometry about antimony.

The enthalpy and entropy of polymerisation of gaseous SbF_5 have been estimated as -18.5 kJ mol^{-1} and -35.5 JK^{-1} respectively from vapour phase molecular weight data on the assumption that only monomers and tetramers are present.[539] Enthalpies of formation are available from hydrolysis data for liquid SbF_5 and the solids $MSbF_6$, where M = Li, Na, K, Cs or Ag.[540] New ^{19}F n.m.r. data show that both the band position and line width for the SbF_5-graphite intercalation compounds are strongly orientation dependent.[541]

Both 1:2 and 1:3 adducts of UO_2F_2 with SbF_5 have been isolated from solutions in liquid hydrogen fluoride.[542] In the latter, the heavy atoms form part of a fluorine bridged network with uranium in pentagonal pyramidal coordination to two axial oxygens and five equatorial fluorines all of which bridge to antimony atoms. One antimony is bonded to three bridging and three terminal fluorines but for the other two, only two of the attached fluorines form bridges. The structure can be thought of as consisting of UO_2^{2+} ions surrounded by pairs of SbF_6^- and $Sb_2F_{11}^-$ ions. The slow reaction which takes place when $UOF_4.2SbF_5$ is dissolved in anhydrous hydrogen fluoride gives the hexafluoride and the new compound $UO_2F_2.4SbF_5$.[543] On heating at 70°C, the latter is converted to $UO_2F_2.3SbF_5$ whose structure was described above.

A structural study of the mercury compound, $Hg_{3-x}SbF_6$ where x = 0.10, shows the presence of chains of mercury atoms and slightly flattened SbF_6 octahedra;[544] the compound is isostructural with the AsF_6^- salt. Oxidation of either a 1:3 sulphur-selenium alloy or selenium itself with SbF_5 in liquid sulphur dioxide solution gives a species formulated as $(Se_4^{2+})(Sb_2F_4^{2+})(Sb_2F_5^+)(SbF_6^-)_5$ on the basis of X-ray crystallography.[545] The cationic antimony species have respectively two and one bridging fluorine atoms,

(136) and (137), but the effective coordination numbers are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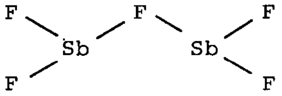
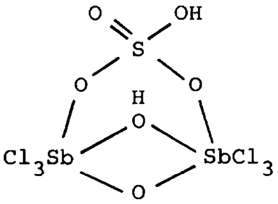

(137)

increased if contacts out to ca. 3.2Å are included. Similar reactions with tellurium yield $Te_4(SbF_6)_2$.

Treatment of $Ru_3(CO)_{12}$ with $SbCl_5$ and HCl in dichloromethane gives a product formulated as $H_5O_2[Ru(CO)_3Cl_3].SbCl_3$ but the antimony trichloride is not coordinated to the metal.[546] Instead it forms three longer contacts to three chlorine atoms from different anions at distances between 3.19 and 3.42Å.

Further examples of the dimeric triply bridged diantimony structure, first identified in carboxylate species, have been obtained from reactions with sulphuric acid. Reaction with $2SbCl_5.H_2O$ in dichloromethane solution, for example, leads to compound (138) containing a novel hydrogen sulphate bridge.[547] This product can be hydrated with 1.5 and 2 mols of water, and structures are available for both these species. Reaction with sulphuric acid in methanol leads to compound (139), which can also be obtained by treatment of $(Cl_4SbOMe)_2$ with the acid in dichloromethane solution.[548] A perchlorate analogue of (138) with the structure (140) has also been isolated as a product from the $SbCl_5$-Cl_2O_6 reaction.[549] Initially a perchlorato-complex, formulated as $Sb_8Cl_{24}O_5(ClO_4)_6$, is formed but on standing in contact with antimony(V) chloride this is converted to (140). It is interesting to note that compounds (138) to (140) can be considered as two molecules of the unknown antimony(V) chloride, Cl_3SbO, stabilised by protonation (or methylation) by the acid.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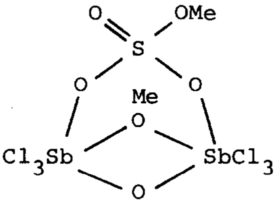
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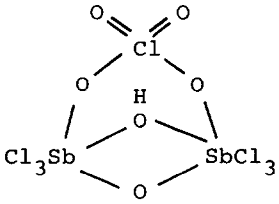
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Raman spectra and X-ray powder diffraction data have been collected for a series of hexachloroantimonates, $MSbCl_6$ where M = Na, K, Rb, Cs, Tl and NH_4 obtained by reactions between stoichiometric amounts of $SbCl_5$ and MCl in phosphoryl chloride solution.[550]

5.4.4 Bonds to Oxygen

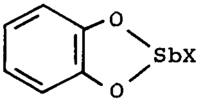
On heating together stoichiometric mixtures of $SbCl_3$ and $Sb(OMe)_3$ to 130° in an inert atmosphere, reorganisation takes place to give the mixed species, $SbCl(OMe)_2$ and $SbCl_2(OMe)$, which have been characterised by i.r., n.m.r. and mass spectrometry.[551] A new antimony(III) monomethylcarbonate has been obtained following the preparation in equation (61) and a related carbonate results from the reaction in equation (62).[552] The carbonate is unstable,

$$Ph_2SbCl + LiO_2COMe \rightarrow Ph_2SbO_2COMe + LiCl \qquad ...(61)$$

$$Ph_2SbCl + Na_2CO_3 \rightarrow (Ph_2Sb)_2CO_3 + 2NaCl \qquad ...(62)$$

decomposing between 0 and 10° with loss of carbon dioxide to give the oxide $(Ph_2Sb)_2O$. A range of stibylcarbonates, $M(O_2COSbPh_2)$ where M = Li, Na, K, Rb, Cs, Tl or NH_4, has also been isolated when Ph_2SbCl is treated with the appropriate carbonate or hydrogen carbonate in a water-methanol mixture at 0^oC. Again the compounds are unstable and lose carbon dioxide at ca. 35^oC to produce stibyl oxides, $M(OSbPh_2)$.

1,10-Phenanthroline complexes of the catecholates (141, X = F, Cl, Br or I) have been isolated[553] and the monomeric structure of



(141)

the fluoride complex, suggested from i.r. data has been confirmed by X-ray crystallography.[554] The central atom is in pseudo-octahedral coordination with the following bond distances: Sb-F 1.965, Sb-O 2.063, 2.007, Sb-N 2.448, 2.569Å. There is evidence that ionisation takes place with the heavier halide analogues and in methanol solution their conductance is that of a 1:1 electrolyte.

Single crystals of $ZnSb_2O_4$ can be obtained when zinc oxide and a large excess of antimony(III) oxide are heated in a sealed system to 1023K for 24hr.[555] The structure consists of chains of twisted and elongated ZnO_6 octahedra linked by antimony atoms in trigonal pyramidal coordination to oxygen atoms. X-ray powder data suggest a defect pyrochlore structure for $CeSbO_3$ obtained from a high temperature reaction between CeO_2 and Sb_2O_3,[556] and a structure based on the stacking of perovskite units and partial ordering of the cation vacancies is suggested for the rhenium compound, $Ba_3ReSb\square O_9$.[557]

Compounds of the type $Ba_3M(II)Sb_2O_9$ where M = Mg, Mn, Co, Ni, Cu or Zn, can be obtained from reactions between the metal oxide, Sb_2O_3 and $BaCO_3$.[558] From crystallographic data all the products, with the exception of the copper compound, contain Sb_2O_9 units formed from two face sharing $Sb(V)O_6$ units linked further by MO_6 octahedra. In the copper compound, the face sharing octahedra contain both Sb(V) and Cu(II) atoms whilethe single linking octahedral group is occupied by an Sb(V) atom. These structural differences lead to differences in the vibrational and electronic spectra.

The formation of vanadium antimonate, $VSbO_4$, from V_2O_5 and Sb_2O_3 has been reinvestigated to show that it is possible to produce a monophasic species with a tetragonal rutile type structure.[559] On heating to >800°C, it is converted to β-Sb_2O_4.

An amorphous form of Sb_2O_5 can be obtained by heating powdered antimony with concentrated nitric acid,[560] but recent ^{121}Sb Mössbauer data on pure Sb_2O_5 produced by hydrothermal methods differ significantly from those obtained previously on "Sb_2O_5" samples.[561] Differences were also observed in the i.r. and Raman spectra of different samples of Sb_2O_5.

5.4.5 Bonds to Sulphur or Selenium

Tris(di-n-propyldithiocarbamato)antimony(III) contains three asymmetrically bidentate ligands (Sb-S distances range between 2.465 and 2.857Å) but here the usual D_3 symmetry of the MS_6 core in this type of compound is reduced to ca. C_s.[562] The reason is the close approach of a centrosymmetrically related molecule (Sb---S' 3.471Å), but there is still space to accommodate the antimony lone pair.

Structures of thio- and seleno-antimonates, together with the related arsenic and bismuth compounds, have been reviewed, and the influence of factors such as cation size and stoichiometry assessed.[563] In particular attention has been paid to the longer range contacts in these types of compound with interesting electrical and semiconducting properties.

High temperature preparations from the elements have been used to prepare the isotypes $Sr_3Sb_4S_9$ and $Sr_3Sb_4Se_9$.[564] In the sulphur compounds, a full structure determination shows the presence of SbS_5 and SbS_3 units with pseudo-octahedral and pseudo-tetrahedral geometry respectively. The former are connected by common edges to give ribbons parallel to the b axis and the latter give chains by corner sharing. Sb-S distances fall in the ranges 2.427 to 2.820 and 2.419 to 2.934 for the SbS_3 and SbS_5 units respectively. Pseudo-tetrahedral, trigonal pyramidal units condensed to form Sb_3S_5 layers are present in the structure of the new black sulphosalt, $TlSb_3S_5$,[565] while ribbon-like $(Bi,Sb,Sn)_8S_{10}$ sheets occur in the $Bi_xSb_{2-x}Sn_2S_5$ structure, where x lies between 0.2 and 0.4.[566]

^{121}Sb Mössbauer data for Me_3SbO and $Me_3Sb(OH)_2$ agree with trigonal bipyramidal coordination about the antimony atom but the small quadrupole splitting observed for Ph_3SbS indicates a tetrahedral structure.[567] This has been confirmed by an X-ray determination showing discrete molecules with Sb-C distances of 2.098Å; the short Sb-S distance, 2.244Å, points to the possibility of there being a degree of Sb-S π-bonding.

The anion in the new selenoantimonite, $Baen_4(SbSe_2)_2$, which is produced when $Ba_4Sb_4Se_{11}$ is dissolved in ethylenediamine, consists of infinite $SbSe_2^-$ chains formed by the interconnection of $SbSe_3$ pyramids.[568] Bridging Sb-Se distances lie between 2.591 and 2.624Å while the mean Sb-Se terminal distance is 2.455Å; angles at the bridging selenium atoms are 96.7 and 102.5°.

5.5 BISMUTH

The bismuth analogue, $Bi_2[W(CO)_5]_3$, of the arsenic[466] and antimony[516] compounds mentioned earlier can be obtained by a similar method using bismuth trichloride;[569] the same type of structure is observed with a short Bi-Bi bond distance (2.818Å). Pure, single crystals of $Bi_8(AlCl_4)_2$ have been produced by treating elemental bismuth with a $BiCl_3$-$AlCl_3$ melt.[570] A square antiprismatic structure, deviating only slightly from D_{4h} symmetry, is found for the Bi_8^{2+} cluster (see Figure 12) with a

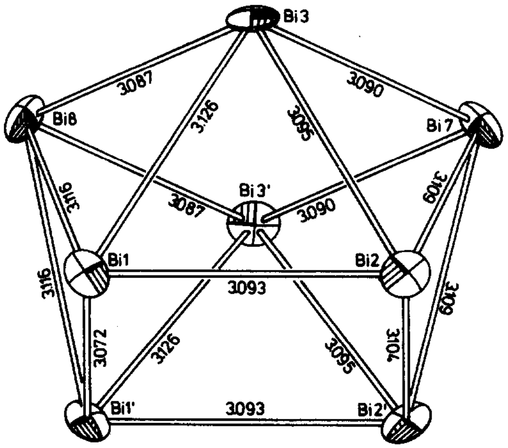


Figure 12. Structure of the Bi_8^{2+} cation (reproduced by permission from Angew. Chem. Int. Ed. Engl., 21(1982)445).

mean Bi-Bi bond distance of 3.100Å and Bi-Bi-Bi angles of 88.1 to 91.8° in the square faces and 59.3 to 60.7° in the triangular faces. The new anion, $Sn_2Bi_2^{2-}$, has been isolated as the potassium-cryptate salt (2,2,2-crypt $K)_2Sn_2Bi_2$.en from reactions of KSn_2 and K_3Bi_2 with the cryptate in ethylenediamine solution.[571] The metal atoms in the tetrahedral anion are disordered equally over the four sites. This compound is the first heteroatomic example of the tetrahedral, 20 electron cluster.

The dibismuthine, $Et_2BiBiEt_2$, can be isolated as an oily red liquid by the reactions outlined in equations (63) and (64).[572]

$$Et_3Bi + 2Na \rightarrow Et_2BiNa + EtNa \qquad ...(63)$$

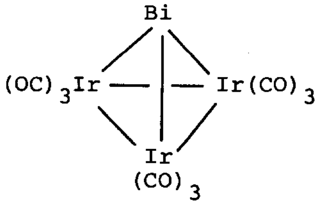
$$2Et_2BiNa + Cl(CH_2)_2Cl \rightarrow Et_2BiBiEt_2 + C_2H_4 + 2NaCl \qquad ...(64)$$

The compound darkens in colour to decompose at 0°C to Et_3Bi and polymeric EtBi. The related tetrasilyldibimuthine, $(Me_3Si)_2BiBi(SiMe_3)_2$, has also been isolated from a similar reaction using the lithium salt, $LiBi(SiMe_3)_2$.2THF and 1,2-dibromoethane.[573] Although the compound is unstable with respect to hydrolysis, light and oxidation, it can be crystallised from pentane as green needles with a metallic lustre. The lithium salt used in this preparation can be obtained from a reaction between methyllithium and $(Me_3Si)_3Bi$; the latter compound when treated with Me_3SnCl successively replaces the trimethylsilyl groups finally yielding $(Me_3Sn)_3Bi$.

Bismuth organometallic chemistry for 1980 has been reviewed.[574] Polymeric structures with bridging carboxylate groups are proposed on the basis of i.r. data for a series of diphenyl bismuth carboxylates $Ph_2BiOOCR$, which result from reactions between either Ph_2BiCl and the sodium carboxylate or Ph_2BiOEt and the free carboxylic acid.[575] Compounds with R = Me, Et, Pr, Me_2CH, t-Bu, Ph and $MeCOCH_2CH_2$ were prepared. The deuterated compound $(o\text{-}C_6H_4D)_3Bi$ has been prepared by a Grignard reaction on bismuth tribromide it can be converted to $(o\text{-}C_6H_4D)_2BiBr$.[576] ^1H n.m.r. spectra of the two products have been used to aid the assignment of the spectra of phenyl derivatives.

A new high pressure BiF_3 phase with a tysonite structure has been identified,[577] and conditions for the solid phase and solution preparations of Rb_2BiF_5, $RbBiF_4$ and $RbBi_3F_{10}$ have been defined.[578]

A novel iridium cluster compound (<u>142</u>) with a mean Bi-Ir distance of 2.734Å and Ir-Bi-Ir angle of 59.7° results when bismuth trichloride is treated at -20°C with $NaIr(CO)_4$ in THF solution.[579] Bismuth chloride, bromide, nitrate or perchlorate complexes can be prepared with 3,4,5,6-tetrahydropyrimidine-2(1H)-thione (≡L) and benzimidazole-2(3H)-thione (≡L') and a crystal structure for $BiCl_3.3L$ shows distorted octahedral coordination about bismuth.[580] Distances to the three chlorine atoms are 2.669, 2.757 and 2.784Å and to three sulphur atoms of the ligands are 2.741, 2.779 and 2.876Å. The 6s pair of electrons appears to be inert. I.r. spectra indicate that in the perchlorate and



(<u>142</u>)

nitrate complexes, i.e. $Bi(ClO_4)_3.5L$, $Bi(ClO_4)_3.5L'$, $Bi(NO_3).4L'.4H_2O$, etc., both ionic and covalent groups are present.

Hydrolysis of the bismuth(III) sulphate leads successively to $Bi_2(H_2O)_2(SO_4)_2(OH)_2$ and $[Bi_2O(OH)_2]SO_4$, the latter often formulated as $(BiO)_2SO_4.H_2O$, and their structures have been reinvestigated.[581,582] The former contains planar $Bi_2(OH)_2{}^{4+}$ units with each bismuth atom coordinated further to oxygen atoms from a sulphate group and a water molecule.[581] Distorted octahedral coordination is completed by longer contacts to two oxygen atoms of different neighbouring sulphate groups. The second compound contains infinite $[Bi_2O(OH)_2{}^{2+}]_n$ chains, as shown in Figure 13, which result when two $[Bi(OH)^{2+}]_n$ chains are interconnected via oxygen atoms.[582] Of the two bismuth atoms in the asymmetric unit, one is pyramidally coordinated to one oxygen and two hydroxy groups while the second is attached to two oxygens and two hydroxy groups.

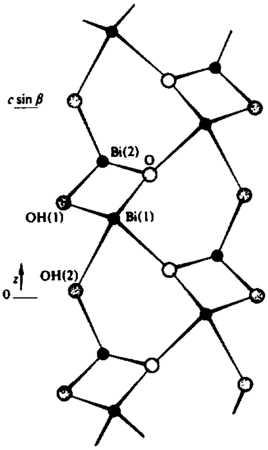


Figure 13. Projection of the $[Bi_2O(OH)_2{}^{2+}]_n$ chain along the a axis (reproduced by permission from Acta Crystallogr., B38(1982)2881).

Mixed complexes containing a unidentate group, such as Br^-, I^-, SCN^-, NO_2^- and thiourea, in addition to edta have been produced in aqueous solution, and there is evidence that the central bismuth atom is seven-fold coordinated.[583] The Na_2SO_4-$Bi_2(SO_4)_3$ system shows the formation of $NaBi(SO_4)_2$ but there is no evidence for a second species $Na_3Bi(SO_4)_3$, the potassium analogue of which is known from the corresponding K_2SO_4 system.[584] Three new compounds, $Bi_2Ru_2O_{7+x}$, $Bi_2Ru_2O_7$ and a sillenite phase $Bi_{12}RuO_{20}$, have been isolated during an investigation of the Bi_2O_3-RuO_2 system.[585]

The compound $SrBiSe_3$ recently isolated from the elements has a structure based on edge sharing of distorted $BiSe_6$ octahedra to give $[Bi_8Se_{10}]_n^{12-}$ chains.[586] Bi-Se distances fall in the range 2.641 to 3.418Å and the structure is completed by Se_3^{2-} anions and Sr^{2+} cations.

The ligands in the methylxanthate complex, $PhBi(S_2COMe)_2$, are asymmetrically bidentate with two short (2.649 and 2.670Å) and two long (2.961 and 3.079Å) Bi-S bonds.[587] The overall geometry is pseudooctahedral, a structure which in comparison with that for $RTl(S_2CNEt_2)_2$ for example implies lone pair activity. Distorted octahedral geometry is observed for the bismuth complex with P,P,P',P'-tetraphenylamidobis(phosphine sulphide) but although there are two sets of Bi-S lengths, i.e. 2.728 to 2.772 and 2.832 to 2.986Å, the distortion does not follow the C_{3v} model.[588] Contrary to the situation above, the Bi-S distances and the S···S contacts do not suggest stereochemical activity for the lone pair of electrons.

Both Eu(II) and Eu(III) in respectively eight- and seven-fold coordination are found in the structure of Eu_2BiS_4 obtained by heating a mixture of Eu_3S_4 and Bi_2S_3 to 1223K.[589] The bismuth atoms are in a distorted octahedron of sulphur atoms at 2.615, 2.704(x2), 2.982(x2) and 3.133Å. A new phase, Tl_9BiTe_6, with a Cr_5B_3 type structure has been identified in the Tl-Bi-Te system.[590]

REFERENCES.

1 W.E.Jones and M.G.Ahmed, Can. J.Chem., 60(1982)2629.
2 W.B.Maier,M.Poliakoff, M.Simpson and J.J.Turner, J. Mol. Struct., 80(1982)83.
3 K.I.Goldberg, D.M.Hoffman, and R.Hoffman, Inorg. Chem., 21(1982)3863.
4 S.M.Rocklage and R.R.Schrock, J. Am. Chem. Soc., 104(1982)3077.
5 J.A.Creighton, R.D.Pergolla, B.T.Heaton, S.Martinengo, L.Strona and D.A.Willis, J. Chem. Soc. Chem. Commun., (1982)864.
6 N.D.Feasey, S.A.R.Knox and A.G.Orpen, J. Chem. Soc. Chem. Commun., (1982)75.
7 J.Hamada, S.Tsunashima and S.Sato, Bull. Chem. Soc. Jpn, 55(1982)1739.
8 N.D.Spencer and G.A.Somorjai, J. Phys. Chem., 86(1982)3493.
9 R.L.Mills, D.H.Liebenberg and P.Pruzan, J. Phys. Chem., 86(1982)5219.
10 C.Scher, B.Ravid and E.A.Halevi, J. Phys. Chem., 86(1982)654.
11 A.I.Ryumin, I.I.Smirnov and G.A.Sorkinova, Russ. J. Inorg. Chem., 27(1982)301.
12 P.P.Edwards, Adv. Inorg. Radiochem., 25(1982)135.
13 F.A.Uribe and A.J.Bard, Inorg. Chem., 21(1982)3160.
14 E.Desimoni and P.G.Zambonin, J. Chem. Soc. Faraday Trans. 1, 78(1982)89.
15 G.L.Johnson and L.Andrews, J. Am. Chem. Soc., 104(1982)3043.
16 B.Nelander and L.Nord, J. Phys. Chem., 86(1982)4375.
17 J.Motonaka, S.Ikeda and N.Tanaka, Bull. Chem. Soc.Jpn., 55(1982)2396.
18 K.Trueblood, C.B.Knobler, D.S.Lawrence and R.V.Stevens, J. Am. Chem. Soc., 104(1982)1355.
19 I.G.Krasil'nikova, Z.L.Leneva, S.V.Mel'nikova, V.N.Nosov, L.N.Ryadneva and E.E.Shpinel, Russ. J. Inorg. Chem., 27(1982)776.
20 A.Fox, J.S.Hartman and R.E.Humphries, J. Chem. Soc. Dalton Trans., (1982)1275.
21 L.R.Thorne and W.D.Gwinn, J. Am. Chem. Soc., 104(1982)3822.
22 W.Kafitz, F.Weller and K.Dehnicke, 490(1982)175.
23 O.D.Krogh, C.H.Ward and J.M.Hollenbeck, J. Phys. Chem., 86(1982)2892.
24 I.R.Dunkin and P.C.P.Thomson, J. Chem. Soc. Chem. Commun., (1982)1192.
25 J.C.Brand, M.D.Cook, A.J.Price and B.P.Roberts, J. Chem. Soc. Chem. Commun., (1982)151.
26 H.Henle and R.Mews, Chem. Ber., 115(1982)2935.
27 R.S.Hosmane, M.A.Rossman and N.J.Leonard, J. Am. Chem. Soc., 104(1982)5497.
28 H.M.Colquhoun, A.E.Crease, S.A.Taylor and D.J.Williams, J. Chem. Soc. Chem. Commun., (1982)736.
29 R.R.Schrock, M.L.Listemann, and L.G.Sturgeoff, J. Am. Chem. Soc., 104(1982)4291.
30 K.Tanaka, Y.Imasaka, M.Tanake, M.Honjo and T.Tanaka, J. Am. Chem. Soc., 104(1982)4258.
31 J.D.Goddard, Can. J. Chem., 20(1982)1250.
32 M.D.Rozeboom, K.N.Houk, S.Searles and S.E.Seyedrezai, J. Am. Chem. Soc., 104(1982)3448.
33 A.Waterfeld and R.Mews, J. Chem. Soc. Chem. Commun., (1982)839.
34 A.Sekiya and D.D.DesMarteau, J. Org. Chem., 46(1981)1277.

35 D.Christen, H.Oberhammer, R.M.Hammaker, S.-C.Chang and D.D.DesMarteau, J. Am. Chem. Soc., 104(1982)6186.
36 J.Berthelot, M.Jubault and J.Simonet, J. Chem. Soc. Chem. Commun., (1982)759.
37 G.D.Price, J.J.Pluth, J.V.Smith, J.M.Bennett and R.L.Patton, J. Am. Chem. Soc., 104(1982)5971.
38 T.Yamabe, K.Hori and K.Fukui, Inorg. Chem., 21(1982)2046.
39 A.Bossi, F.Garbassi, G.Petrini and L.Zanderighi, J. Chem. Soc. Faraday Trans. 1, 78(1982)1029.
40 K.-I.Aika, H.Midorikawa and A.Ozaki, J. Phys. Chem., 86(1982)3263.
41 G.N.Schrauzer, N.Strampach and L.A.Hughes, Inorg. Chem., 21(1982)2184.
42 W.Hussain, G.J.Leigh and C.J.Pickett, J. Chem. Soc. Chem. Commun., (1982)747.
43 G.L.Hillhouse, G.V.Goeden and B.L.Haymore, Inorg. Chem., 21(1982)2064.
44 P.T.Bishop, J.R.Dillworth, J.Hutchinson and J.A.Zubieta, J. Chem. Soc. Chem. Commun., (1982)1052.
45 T.Kemmerich, J.H.Nelson, N.E.Takach, H.Boehme, B.Jablonski and W.Beck, Inorg. Chem., 21(1982)1226.
46 H.Siebert and R.Macht, Z. Anorg. Chem., 489(1982)77.
47 K.Kohata, T.Fukuyama and K.Kuchitsu, J. Phys. Chem., 86(1982)602.
48 M.Ferriol, R.Abraham, H.Delalu and M.-T.Saugier-Cohen-Adad, J. Chim. Phys., 79(1982)725.
49 Y.Oosawa, J. Chem. Soc. Chem. Commun., (1982)221.
50 K.G.Phelan and G.Stedman, J. Chem. Soc. Dalton Trans., (1982)1603.
51 J.P.Calfa, K.G.Phelan and F.T.Bonner, Inorg. Chem., 21(1982)521.
52 M.Veith and G.Schlemmer, Z. Anorg. Chem., 494(1982)7.
53 P.Overbosch, G. van Koten and O.Overbeek, Inorg. Chem., 21(1982)2373; J.Ashley-Smith, M.Green and F.G.A.Stone, J. Chem. Soc. Dalton Trans., (1982)1805.
54 P.Overbosch, G. van Koten and O.Overbeek, J. Am. Chem. Soc., 102(1980)2091.
55 P.Overbosch, G. van Koten, D.M.Grove, A.L.Spek and A.J.M.Duisenberg, Inorg. Chem., 21(1982)3253.
56 H.Huber, Angew. Chem. Int. Ed. Engl., 21(1982)64.
57 R.N.Butler and V.C.Garvin, J. Chem. Res. (S), (1982)183.
58 (a) R.D.Bardo, J. Phys. Chem., 86(1982)4658; (b) S.G.Kukolich, J. Am. Chem. Soc., 104(1982)4715.
59 G.D.Mendenhall, L.C.Stewart and J.C.Scaiano, J. Am. Chem. Soc., 104(1982)5109.
60 C.A.Ogle, K.A.Vander Kooi, G.D.Mendenhall, V.Lorprayoon and B.C.Cornilsen, J. Am. Chem. Soc., 104(1982)5114.
61 C.A.Casewit and W.A.Goddard, J. Am. Chem. Soc., 104(1982)3280.
62 S.G.Kukolich, J. Am. Chem. Soc., 104(1982)6927.
63 R.G.Orth, H.T.Jonkman and J.Michl, J. Am. Chem. Soc., 104(1982)1834.
64 A.R.Ravishankara, F.L.Elsele and P.H.Wine, J. Phys. Chem., 86(1982)1854.
65 A.Bahta, R.Simonaitis and J.Heicklen, J. Phys. Chem., 86(1982)1849.
66 M.Fowles, D.N.Mitchell, J.W.L.Morgan and R.P.Wayne, J. Chem. Soc. Faraday Trans. 2, 78(1982)1239.
67 F.Yao, I.Wilson and H.Johnston, J. Phys. Chem., 86(1982)3611.
68 Y.Kosaki, A.Miyamoto and Y.Murakami, Bull. Chem. Soc. Jpn., 55(1982)1719.

69 A.Miyamoto, K.Kobayashi, M.Inomata and Y.Murakami, J. Phys. Chem., 86(1982)2945.

70 S.Naito and K.Tamaru, J. Chem.Soc. Faraday Trans. 1, 78(1982)735.

71 W.A.Pryor, J.W.Lightsey and D.F.Church, J. Am. Chem. Soc., 104(1982)6685.

72 I.R.Slagle and D.Gutman, J. Am. Chem. Soc., 104(1982)4741.

73 G.J.Audley, D.L.Baulch and I.M.Campbell, J. Chem. Soc. Chem. Commun., (1982)1053.

74 A.B.Kyte, R.Jones-Parry and D.Whittaker, J. Chem. Soc. Chem. Commun., (1982)74.

75 A.S.Nazarov, A.F.Antimonov and I.I.Yakovlev, Russ. J. Inorg. Chem., 26(1981)1753.

76 B.Masci, J. Chem. Soc. Chem. Commun., (1982)1262.

77 L.R.Dix and D.L.H.Williams, J. Chem. Res. (S), (1982)190.

78 A.J.Frank and M.Graetzel, Inorg. Chem., 21(1982)3834.

79 M.R.Bennett, G.M.Brown, L.Maya, and F.A.Posey, Inorg. Chem., 21(1982)2461.

80 G.Rabai and M.T.Beck, J. Chem. Soc. Dalton Trans., (1982)573.

81 M.J.Akktar, J.A.Balschi and F.T.Bonner, Inorg. Chem., 21(1982)2216.

82 V.V.Aleshin, G.N.Shirokova and V.Ya.Rosolovskii, Russ. J. Inorg. Chem., 26(1981)1106.

83 G.G.Bikbaeva, Y.E.Nikitin and E.M.Baranovskaya, Russ. J. Inorg. Chem., 26(1981)1188.

84 (a) V.A.Kulikov, V.V.Ugarov and N.G.Rambidi, J. Struct. Chem., 22(1981)796; (b) N.I.Tuseev, E.Z.Zasorin and V.P.Spiridonov, J. Struct. Chem., 20(1979)499.

85 M.Jansen, Z. Naturforsch., 37a(1982)1457.

86 M.Jansen, Z. Anorg. Chem., 491(1982)175.

87 A.Gleizes, A.Meyer, M.A.Hitchman and O.Kahn, Inorg. Chem., 21(1982)2257.

88 W.G.Jackson, G.A.Lawrence, P.A.Lay and A.M.Sargeson, J. Chem. Soc. Chem. Commun., (1982)70.

89 F.T.Bonner and K.A.Pearsall, Inorg. Chem., 21(1982)1973.

90 K.A.Pearsall and F.T.Bonner, Inorg. Chem., 21(1982)1978.

91 W.R.Murphy, K.J.Takeuchi and T.J.Meyer, J. Am. Chem. Soc., 104(1982)5817.

92 R.E.Stevens and W.L.Gladfelter, J. Am. Chem. Soc., 104(1982)6454.

93 B.Haymore, J.C.Huffman, A.Dobson and S.D.Robinson, Inorg. Chim. Acta, 65(1982)L231.

94 D.Braga, B.F.G.Johnson, J.Lewis, J.M.Mace, M.McParthin, J.Puga, W.J.H.Nelson, P.R.Raithby and K.H.Whitmire, J.Chem. Soc. Chem. Commun., (1982)1081.

95 D.Braga, K.Hendrick, B.F.G.Johnson, J.Lewis, M.McParthin, W.J.H.Nelson and J.Puga, J. Chem. Soc. Chem. Commun., (1982)1083.

96 N.D.Feasey and S.A.R.Knox, J. Chem. Soc. Chem. Commun., (1982)1062.

97 S.M.Burnett, C.S.Feigerle, A.E.Stevens and W.C.Lineberger, J. Phys. Chem., 86(1982)4486.

98 T.Bojes, T.Chivers, W.G.Laidlaw and M.Trsic, J. Am. Chem. Soc., 104(1982)4837.

99 T.Chivers and C.Lau, Inorg. Chem., 21(1982)453.

100 H.W.Roesky and J.Anhaus, Chem. Ber., 115(1982)3682.

101 A.J.Banister, R.G.Hey, G.K.MacLean and J.Passmore, Inorg. Chem., 21(1982)1679.

102 R.J.Gillespie, J.F.Sawyer, D.R.Slim and J.D.Tyrer, Inorg. Chem., 21(1982)1296.

103 F.A.Kennett, G.K.MacLean, J.Passmore and M.N.S.Rao, J. Chem. Soc. Dalton Trans., (1982)851, 1879.

104 M.C.Caserio and J.K.Kim, J. Am. Chem. Soc., 104(1982)3231.

105 A.J.Morris, C.H.L.Kennard, J.R.Hall and G.Smith, Inorg. Chim. Acta, 62(1982)247.

106 A.J.Morris, C.H.L.Kennard, J.R.Hall, G.Smith and A.H.White, Inorg. Chim. Acta, 62(1982)L153.

107 M.Herberhold and W.Ehrenreich, Angew. Chem. Int. Ed. Engl., 21(1982)633.

108 R.D.Tiwari, K.K.Pandey and U.C.Agarwala, Inorg. Chem., 21(1982)845.

109 H.Guenther, H.Oberhammer, R.Mews and I.Stahl, Inorg. Chem., 21(1982)1872.

110 A.Waterfeld and R.Mews, Angew. Chem. Int. Ed. Engl., 21(1982)354.

111 A.Waterfeld, H.Oberhammer and R.Mews, Angew. Chem. Int. Ed. Engl., 21(1982)355.

112 J.S.Thrasher, J.L.Howell and A.F.Clifford, Inorg. Chem., 21(1982)1616.

113 W.Storzer, D.Schomburg, G.V.Roeschenthaler and R.Schmutzler, Chem. Ber., 116(1983)367.

114 N.Burford, T.Chivers, A.W.Cordes, W.G.Laidlaw, M.C.Noble, R.T.Oakley and P.N.Swepston, J. Am. Chem. Soc., 104(1982)1282.

115 H.Brunner, M.Muschiol and M.F.A.Dove, J. Chem. Soc. Dalton Trans., (1982)1527.

116 T.Palmesen, Acta Chem. Scand., A36(1982)183.

117 J.F.Sawyer, G.J.Schrobilgen and S.J.Sutherland, (a) J. Chem. Soc. Chem. Commun., (1982)21; (b) Inorg. Chem., 21(1982)4064.

118 J.Foropoulos and D.D.DesMarteau, J. Am. Chem. Soc., 104(1982)4260.

119 D.A.Brown, A.L.Roche, T.A.Pakkanen, T.T.Pakkanen and K.Smolander, J. Chem. Soc. Chem. Commun., (1982)676.

120 W.Kafitz, F.Weller and K.Dehnicke, Z. Anorg. Chem., 490(1982)175.

121 L.R.Groeneveld, G.Vos, G.C.Verschoor and J.Reedijk, J. Chem. Soc. Chem. Commun., (1982)620.

122 W.W.Wilson and K.O.Christe, Inorg. Chem., 21(1982)2091.

123 K.O.Christe and W.W.Wilson, Inorg. Chem., 21(1982)4113.

124 R.Bougon, T.B.Huy, J.Burgess, K.O.Christe and R.D.Peacock, J. Fluorine Chem., 19(1982)263.

125 P.B.Davies, C.J.Kho, W.K.Leong and W.Lewis-Bevan, J. Chem. Soc. Chem. Commun., (1982)690.

126 R.Minkwitz and R.Nass, Z. Naturforsch., 37b(1982)1558.

127 S.-C.Chang and D.D.DesMarteau, Polyhedron, 1(1982)129.

128 J.Fawcett, R.D.Peacock and D.R.Russell, J. Chem. Soc. Chem. Commun., (1982)958.

129 D.D.DesMarteau, H.H.Eysel, H.Oberhammer and H.Gunther, Inorg. Chem., 21(1982)1607.

130 M.P.Snyder and D.W.Margerum, Inorg. Chem., 21(1982)2545.

131 H.H.Sisler and J.C.Barrick, Polyhedron, 1(1982)535.

132 C.K.Kohlmiller and L.Andrews, Inorg. Chem., 21(1982)1519.

133 R.Kerbachi, R.Minkwitz and U.Engelhardt, Z. Anorg. Chem., 486(1982)129.

134 R.Kerbachi, R.Minkwitz and U.Engelhardt, Inorganica Chim. Acta, 65(1982)L103.

135 K.Lehr, K.Hestermann and G.Heymer, Z. Anorg. Allg. Chem., 490(1982)197.

136 O.Ohms, G.Grossmann and H.-A.Lehmann, Z. Anorg. Allg. Chem., 486(1982)22.

137 M.DiVaira and L.Sacconi, Angew. Chem. Int. Ed. Engl., 21(1982)330.
138 W.E.Lindsell, J. Chem. Soc. Chem. Commun., (1982)1422.
139 M. DiVaira, M.Peruzzini and P.Stoppioni, J. Chem. Soc. Chem. Commun., (1982)894.
140 J.Chatt, P.B.Hitchcock, A.Pidcock, C.R.Warrens and K.R.Dixon, J. Chem. Soc. Chem. Commun., (1982)932.
141 B.Cetinkaya, P.B.Hitchcock, M.F.Lappert, A.J.Thorne and H. Goldwhite. J. Chem. Soc. Chem. Commun., (1982)691.
142 B.Cetinkaya, A.Hudson, M.F.Lappert and H.Goldwhite, J. Chem. Soc. Chem. Commun., (1982)609.
143 A.H.Cowley, J.E.Kilduff, T.H.Newman and M.Pakulski, J. Am. Chem. Soc., 104(1982)5820.
144 J.Escudié, C.Couret, J.D.Andriamizaka and J.Satgé, J. Organomet. Chem., 228(1982)C76.
145 A.Schmidpeter, S.Lochschmidt and W.S.Sheldrick, Angew. Chem. Int. Ed. Engl., 21(1982)63.
146 M.Baudler and T.Pontzen, Z. Anorg. Allg. Chem., 491(1982)27.
147 R.Fröhlich and K.-F.Tebbe, Acta Crystallogr., B38(1982)115.
148 M.Baudler and F.Saykowski, Z. Anorg. Allg. Chem., 486(1982)39.
149 M.Baudler, C.Gruner, H.Tschäbunin and J.Hahn, Chem. Ber., 115(1982)1739.
150 M.Baudler and J. Hellmann, Z. Anorg. Allg. Chem., 490(1982)11.
151 M.Baudler, J.Hellmann and J.Hahn, Z. Anorg. Allg. Chem., 489(1982)11.
152 M.Baudler and G.Kupprat, Z. Naturforsch., 37b(1982)527.
153 J.Hahn, M.Baudler, C.Krüger and Y.-H.Tsay, Z. Naturforsch., 37b(1982)797.
154 G.Fritz, J.Härer and K.H.Scheider, Z. Anorg. Allg. Chem., 487(1982)44.
155 G.Fritz, R.Uhlmann, K.D.Hoppe, W.Hönle and H.G. von Schnering, Z. Anorg. Allg. Chem., 491(1982)83.
156 K.-F.Tebbe and R.Fröhlich, Z. Naturforsch., 37b(1982)534.
157 K.-F.Tebbe and T.Heinlein, Z. Kristallogr., 160(1982)285.
158 D.Weber, C.Mujica and H.G. von Schnering, Angew. Chem. Int. Ed. Engl., 21(1982)863.
159 M.Feher, R.Fröhlich and K.-F.Tebbe, Z. Kristallogr., 158(1982)24
160 M.Baudler, Y.Aktalay, T.Heinlein and K.-F.Tebbe, Z. Naturforsch., 37b(1982)299.
161 D.Weber, E.Fluck, H.-G. von Schnering and K.Peters, Z. Naturforsch., 37b(1982)594.
162 H.Quast, M.Heuschmann, W. von der Saal, W.Buchner, K.Peters, and H.G. von Schnering, Chem. Ber., 115(1982)1154.
163 A.J.Blake, G.P.McQuillan, I.A.Oxton and D.Troy, J. Mol. Struct., 78(1982)265.
164 J.W.Gilje, W.S.Sheldrick, N.Weferling and R.Schmutzler, Angew. Chem. Int. Ed. Engl., 21(1982)379.
165 H.W.Roesky and H.Djarrah, Inorg. Chem., 21(1982)844.
166 H.W.Roesky, D.Amirzadeh-Asl and W.S.Sheldrick, J. Am. Chem. Soc., 104(1982)2919.
167 W.Klemm and H.G. von Schnering, Z. Anorg. Allg. Chem., 491(1982)9.
168 A.Zschunke, E.Bauer, H.Schmidt and K.Issleib, Z. Anorg. Allg. Chem., 495(1982)115.
169 H.G. von Schnering and G.Menge, Z. Anorg. Allg. Chem., 491(1982)286.

170 M.H.Möller and W.Jeitschko, Z. Anorg. Allg. Chem., 491(1982)225.
171 B.Süss, K.Hein and J.Korb, Z. Anorg. Allg. Chem., 494(1982)115.
172 B.Eisenmann, H.Jordan and H.Schäfer, Z. Naturforsch., 37b(1982)1221.
173 B.Eisenmann, H.Jordan and H.Schäfer, Z. Naturforsch., 37b(1982)1564.
174 W.Carrillo-Cabrera, Acta Chem. Scand., A36(1982)563, 571.
175 R.Rühl and W.Jeitschko, Acta Crystallogr., B38(1982)2784.
176 R.Rühl and W.Jeitschko, Inorg. Chem., 21(1982)1886.
177 C.Hadenfeldt and W.Fester, Z. Anorg. Allg. Chem., 490(1982)25.
178 B.Solouki, H.Bock, A.Westerhaus, G.Becker and G.Uhl, Chem. Ber., 115(1982)3747.
179 J.C.T.R.Burckett-St.Laurent, P.B.Hitchcock, H.W.Kroto, M.F.Meidine and J.F.Nixon, J. Organomet. Chem., 238(1982)C82.
180 B.Bak, N.A.Kristiansen and H.Svanholt, Acta Chem. Scand., A36(1982)1.
181 B.Bak, N.A.Kristiansen and H.Svanholt, J. Mol. Struct., 78(1982)63.
182 H.W.Kroto, J.F.Nixon, M.J.Taylor, A.A.Frew and K.W.Muir, Polyhedron, 1(1982)89.
183 K.Issleib, H.Schmidt and C.Wirkner, Z. Anorg. Allg. Chem., 488(1982)75.
184 R.Appel, S.Korte, M.Halstenberg and F.Knock, Chem. Ber., 115(1982)3610.
185 R.Appel and U.Kündgen, Angew. Chem. Int. Ed. Engl., 21(1982)219.
186 R.Appel, M.Halstenberg, K.Knock and H.Kunze, Chem. Ber., 115(1982)2371.
187 G.Becker, M.Rössler and G.Uhl, Z. Anorg. Allg. Chem., 495(1982)73.
188 A.Marinetti, F.Mathey, J.Fisher and A.Mitschler, J. Am. Chem. Soc., 104(1982)4484.
189 A.H.Cowley, R.A.Kemp and J.C.Wilburn, J. Am. Chem. Soc., 104(1982)331.
190 G.Becker, W.Massa, O.Mundt and R.Schmidt, Z. Anorg. Allg. Chem., 485(1982)23.
191 W.Clegg, M.Haase, M.Hesse, U.Klingbiel and G.M.Sheldrick, Angew. Chem. Int. Ed. Engl., 21(1982)445.
192 R.Batchelor and T.Birchall, J. Am. Chem. Soc., 104(1982)674.
193 R.Thamm and E.Fluck, Z. Naturforsch., 37b(1982)965.
194 N.Auner and J.Grobe, Z. Anorg. Allg. Chem., 489(1982)23.
195 N.Auner and J.Grobe, Z. Anorg. Allg. Chem., 490(1982)38.
196 J.Eichbichler and P.Peringer, J. Chem. Soc. Chem. Commun., (1982)193.
197 H.H.Karsch,Chem. Ber., 115(1982)823.
198 T.Allman and R.G.Goel, Can. J. Chem., 60(1982)716.
199 E.E.Wille, D.S.Stephenson, P.Capriel and G.Binsch, J. Am. Chem. Soc., 104(1982)405.
200 D.Dakternieks, Aust. J. Chem., 35(1982)469.
201 G.Bandoli, D.A.Clemente, U.Mazzi and E.Roncari, J. Chem. Soc. Dalton Trans., (1982)1381.
202 E.C.Alyea, G.Ferguson and A.Somogyvari, Inorg. Chem., 21(1982)1369.
203 Y.Inoguchi, B.Milewski-Mahrla and H.Schmidbaur, Chem. Ber., 115(1982)3085.
204 N.W.Alcock, P.Moore, P.A.Lampe and K.F.Mok, J. Chem. Soc. Dalton Trans., (1982)207.

205 D.G.Allen, G.M.McLaughlin, G.B.Robertson, W.L.Steffen, G.Salem and S.B.Wild, Inorg. Chem., 21(1982)1007.
206 D.G.Allen and B.F.Taylor, J. Chem. Soc. Dalton Trans., (1982)51.
207 G.V.Gribunova, V.E.Shklover, Yu. T.Struchkov, V.D.Vilchevskaya, N.L.Podobedova and A.I.Krylova, J. Organomet. Chem., 238(1982)297.
208 H.-P.Abaicht, U.Baumeister, H.Hartung, K.Issleib,R.A.Jacobson, J.Richardson, S.M.Socol and J.G.Verkade, Z. Anorg. Allg. Chem., 494(1982)55.
209 S.Hietkamp, H.Sommer and O.Stelzer, Angew Chem. Int. Ed. Engl., 21(1982)376.
210 H.H.Karsch and U.Schubert, Z. Naturforsch., 37b(1982)186.
211 M.M.Olmstead, C.-L.Lee and A.L.Balch, Inorg. Chem., 21(1982)2712.
212 I.J.Colquhoun, C.E.McFarlane and W.McFarlane, J. Chem. Soc. Chem. Commun., (1982)220.
213 I.J.Colquhoun and W.McFarlane, J. Chem. Soc. Dalton Trans., (1982)1915.
214 M.Camalli, F.Caruso and L.Zambonelli, Acta Crystallogr., B38(1982)2468.
215 R.L.Cook and J.G.Morse, Inorg. Chem., 21(1982)4103.
216 E.H.Wong, L.Prasad, E.J.Gabe and F.C.Bradley, J. Organomet. Chem., 236(1982)321.
217 E.H.Wong, R.M.Ravenelle, E.J.Gabe, F.L.Lee and L.Prasad, J. Organomet. Chem., 233(1982)321.
218 C.S.Kraihanzel, J.M.Ressner and G.M.Gray, Inorg. Chem., 21(1982)879.
219 K.Diemert, W.Kuchen and J.Kutter, Z. Naturforsch., 37b(1982)841.
220 T.Costa and H.Schmidbaur, Chem. Ber., 115(1982)1367.
221 T.Costa and H.Schmidbaur, Chem. Ber., 115(1982)1374.
222 W.E.Hill, J.G.Taylor, C.A.McAuliffe, K.W.Muir and L.Manojlovic-Muir, J. Chem. Soc. Dalton Trans., (1982)833.
223 L.G.Scanlon, Y.-Y.Tsao, K.Toman, S.C.Cummings and D.W.Meek, Inorg. Chem., 21(1982)2707.
224 H.H.Karsch, Z. Naturforsch, 37b(1982)282.
225 H.H.Karsch, Chem. Ber., 115(1982)1956.
226 C.Mealli, Acta Crystallogr., B38(1982)1040.
227 M.Baacke, S.Hietkamp, S.Morton and O.Stelzer, Chem. Ber., 115(1982)1389.
228 H.Schmidbaur and T.Costa, Z. Naturforsch., 37b(1982)677.
229 B.N.Diel, R.C.Haltiwanger and A.D.Norman, J. Am. Chem. Soc., 104(1982)4700.
230 R.Bartsch, S.Hietkamp, S.Morton and O.Stelzer, Angew. Chem. Int. Ed. Engl., 21(1982)375.
231 M.Ciampolini, P.Dapporto, A.Dei, N.Nardi and F.Zanobini, Inorg. Chem., 21(1982)489.
232 C.Bianchini, A.Meli, A.Orlandini, Inorg. Chem., 21(1982)4161.
233 C.Bianchini, A.Meli and A.Orlandini, Inorg. Chem., 21(1982)4166.
234 C.Bianchini, P.Innocenti, A.Meli, A.Orlandini and C.Scapacci, J. Organomet. Chem., 233(1982)233.
235 S.Voran, H.Blau, W.Malisch and U.Schubert, J. Organomet. Chem., 232(1980)C33.
236 Y.Yamamoto, Bull. Chem. Soc. Jpn., 55(1982)3025.
237 H.Schmidbaur, A.Schier, B.Milewski-Mahrla and U.Schubert, Chem. Ber., 115(1982)722.
238 A.Schier and H.Schmidbaur, Z. Naturforsch., 37b(1982)1518.
239 H.Schmidbaur, U.Deschler and B.Milewski-Mahrla, Chem. Ber., 115(1982)3290.

240 H.Schmidbaur, U.Deschler and D.Seyferth, Z. Naturforsch., 37b(1982)950.
241 H.Schmidbaur, C.E.Zybill and D.Neugebauer, Angew. Chem. Int. Ed. Engl., 21(1982)310.
242 R.Appel, J.Peters and A.Westerhaus, Angew. Chem. Int. Ed. Engl., 21(1982)80.
243 E.Bye, W.B.Schweizer and J.D.Dunitz, J. Am. Chem. Soc., 104(1982)5893.
244 K.B.Dillon, M.P.Nisbet, and T.C.Waddington, J. Chem. Soc. Dalton Trans., (1982)465.
245 G.Paul and E.Herrmann, Z. Chem., 22(1982)307.
246 S.O.Grim, S.A.Sangokoya, I.J.Colquhoun and W.McFarlane, J. Chem. Soc. Chem. Commun., (1982)930.
247 H.H.Karsch, Chem. Ber., 115(1982)818.
248 I.Bkouche-Waksman, P.L'Haridon, Y.Leroux and R.Burgada, Acta Crystallogr., B38(1982)3024.
249 C.Piccinni-Leopardi, G.Germain, J.P.Declercq, M. van Meerssche,J.B.Robert and K.Jurkschat, Acta Crystallogr., B38(1982)2197.
250 S.M.Bowen, E.N.Duesler, R.T.Paine and C.F.Campana, Inorg. Chim. Acta, 59(1982)53.
251 H.Schumann and F.W.Reier, J. Organomet. Chem., 235(1982)287.
252 E.Lindner, M.Steinwand and S.Hoehne, Chem. Ber., 115(1982)2181.
253 E.Lindner, M.Steinwand and S.Hoehne, Angew. Chem. Int. Ed. Engl., 21(1982)355.
254 E.Lindner, M.Steinwand and S.Hoehne, Chem. Ber., 115(1982)2478.
255 E.Lindner and M.Steinwand, Z. Naturforsch., 37b(1982)407.
256 U.Klingebiel and N.Vater, Angew. Chem. Int. Ed. Engl., 21(1982)857.
257 K.Hassler, Monatsh., 113(1982)421.
258 A.J.Downs, G.P.Gaskill and S.B.Saville, Inorg. Chem., 21(1982)3385.
259 A.H.Cowley, R.A.Kemp, M.Lattman and M.L.McKee, Inorg. Chem., 21(1982)85.
260 M.J.Buckingham, G.E.Hawkes, I.M.Ismail and P.J.Sadler, J. Chem. Soc. Dalton Trans., (1982)1167.
261 M.Watanabe and J.R. van Wazer, Bull. Chem. Soc. Jpn., 55(1982)2902.
262 K.B.Dillon, A.W.G.Platt, A.Schmidpeter, F.Zwaschka and W.S.Sheldrick, Z. Anorg. Allg. Chem., 488(1982)7.
263 K.Drewehes and H.P.Latscha, Angew. Chem. Int. Ed. Engl., 21(1982)638.
264 K.Diemert, W.Kuchen and J.Kutter, Chem. Ber., 115(1982)1947.
265 A.Hinke and W.Kuchen, Z. Naturforsch., 37b(1982)1543.
266 R.Bartsch, O.Stelzer and R.Schmutzler, J. Fluorine Chem., 20(1982)85.
267 A.Lopusinski and J.Michalski, J. Am. Chem. Soc., 104(1982)290.
268 H.Oberhammer, J.Grobe and D.Le Van, Inorg. Chem., 21(1982)275.
269 D.Robert, C.Demay and J.G.Riess, Inorg. Chem., 21(1982)1805.
270 D.W.H.Rankin, M.R.Todd and M.Fild, J. Chem. Soc. Dalton Trans., (1982)2079.
271 H.D.B.Jenkins, K.P.Thakur, A.Finch and P.N.Gates, Inorg. Chem., 21(1982)423.
272 J.Gloede, Z. Anorg. Allg. Chem., 484(1982)231.
273 J.Gloede, Z. Chem., 22(1982)126.
274 G.-U.Wolf and H.Grunze, Z. Chem., 22(1982)212.

275 K.B.Dillon and A.W.G.Platt, J. Chem. Soc. Dalton Trans., (1982)1199.

276 H.-D.Dörner, K.Dehnicke and D.Fenske, Z. Anorg. Allg. Chem., 486(1982)136.

277 M.El Essawi, F.Weller and K.Dehnicke, Z. Anorg. Allg. Chem., 486(1982)147.

278 G.Trinquier, J. Am. Chem. Soc., 104(1982)6969.

279 W.W.Schoeller and E.Niecke, J. Chem. Soc. Chem. Commun., (1982)569.

280 E.Niecke and H.-G.Schäfer, Chem. Ber., 115(1982)185.

281 O.J.Scherer, R.Konrad, E.Guggolz and M.L.Ziegler, Angew. Chem. Int. Ed. Engl., 21(1982)297.

282 A.H.Cowley and R.A.Kemp, J. Chem. Soc. Chem. Commun., (1982)319.

283 E.Niecke and R.Rüger, Angew. Chem. Int. Ed. Engl., 21(1982)62.

284 H.Maisch, Z. Naturforsch., 37b(1982)61.

285 A.Tarassoli, R.C.Haltiwanger and A.D.Norman, Inorg. Chem., 21(1982)2684.

286 M.L.Thompson, R.C.Haltiwanger, A.Tarassoli, D.E.Coons and A.D.Norman, Inorg. Chem., 21(1982)1287.

287 H.-J.Chen, A.Tarassoli, R.C.Haltiwanger, V.S.Allured and A.D.Norman, Inorg. Chim. Acta Lett., 65(1982)L69.

288 E.Niecke and R.Rüger, Z. Naturforsch., 37b(1982)1593.

289 P.H.Neilson and P.Wisian-Neilson, Inorg. Chem., 21(1982)3568.

290 J.L.Atwood, A.H.Cowley, W.E.Hunter and S.K.Mehrotra, Inorg. Chem., 21(1982)1354.

291 J.Ellermann, M.Lietz and K.Geibel, Z. Anorg. Allg. Chem., 492(1982)122.

292 G.M.Brown, J.E.Finholt, R.B.King, J.W.Bibber and J.H.Kim, Inorg. Chem., 21(1982)3790.

293 R.B.King and T.W.Lee, Inorg. Chem., 21(1982)319.

294 G.-V.Röschenthaler and W.Storzer, Z. Naturforsch., 37b(1982) 281.

295 F.A.Cotton, J.G.Riess, C.E.Rice and B.R.Stults, Inorg. Chem., 21(1982)3123.

296 L.D.Hutchins, R.W.Light and R.T.Paine, Inorg. Chem., 21(1982)266.

297 A.H.Cowley, R.A.Kemp and C.A.Stewart, J. Am. Chem. Soc., 104(1982)3239.

298 O.J.Scherer, J.Kerth, B.K.Balbach and M.L.Ziegler, Angew. Chem. Int. Ed. Engl., 21(1982)136.

299 C.Romming and J.Songstad, Acta Chem. Scand., A36(1982)665.

300 K.Maartmann-Moe, C.Romming and J.Songstad, Acta Chem. Scand., A36(1982)757.

301 M.P.du Plessis, T.A.Modro and L.R.Nassimbeni, Acta Crystallogr., B38(1982)1504.

302 E.Fluck, S.Kleemann, H.Hess and H.Riffel, Z. Anorg. Allg. Chem., 486(1982)187.

303 J.C.J.Bart, I.W.Bassi and M.Calcaterra, Acta Crystallogr., B38(1982)1932.

304 A.H.Cowley, M.Lattman, P.M.Stricklen and J.G.Verkade, Inorg. Chem., 21(1982)543.

305 T.Bünger and U.Engelhardt, Z. Naturforsch., 37b(1982)24.

306 U.Engelhardt, B.Friedrich and B.Stromburg, Acta Crystallogr., B38(1982)753.

307 U.Engelhardt and I.Kirner, Z. Naturforsch., 37b(1982)190.

308 T.Bünger, H.J.Merrem and U.Engelhardt, Z. Anorg. Allg. Chem., 494(1982)125.

309 E.-P.Flindt, Z. Anorg. Allg. Chem., 487(1982)119.

310 D.W.H.Rankin, M.D.Walkinshaw and H.Schmidbaur, J. Chem. Soc. Dalton Trans., (1982)2317.

311 C.Glidewell and H.D.Holden, J. Organomet. Chem., 226(1982) 171.

312 R.Bartsch, O.Stelzer and R.Schmutzler, Z. Naturforsch., 37b(1982)267.

313 H.Nöth, Z. Naturforsch., 37b(1982)1491.

314 H.Richter, E.Fluck, H.Riffel and H.Hess, Z. Anorg. Allg. Chem., 491(1982)266.

315 G.Schilling, C.W.Rabener and W.Lehr, Z. Naturforsch., 37b(1982)38.

316 B.Thomas, D.Scheller and G.Grossmann, Z. Anorg. Allg. Chem., 489(1982)126.

317 R. de Jaeger, T.Abouchaccra, A.Ouassini and J.Heubel, Z. Anorg. Allg. Chem., 489(1982)204.

318 A.Pflützner, E.Herrmann and L.Riesel, Z. Chem., 22(1982)104.

319 J.-M.Dupart, A.Grand, S.Pace and J.G.Riess, J. Am. Chem. Soc., 104(1983)2316.

320 G.L.Hillhouse, G.V.Goeden and B.L.Haymore, Inorg. Chem., 21(1982)2064.

321 R.Keat, D.S.Rycroft, E.Niecke, H.-G.Schäfer and H.Zorn, Z. Naturforsch., 37b(1982)1665.

322 O.J.Scherer and K.-D.Krieger, Z. Naturforsch., 37b(1982)1041.

323 R.Keat, L.Murray and D.S.Rycroft, J. Chem. Soc. Dalton Trans., (1982)1503.

324 H.Richter, E.Fluck, H.Riffel and H.Hess, Z. Anorg. Allg. Chem., 486(1982)177.

325 O.J.Scherer,M.Paüttmann, C.Krüger and G.Wolmershaüser, Chem. Ber., 115(1982)2076.

326 D.E.Coons, V.S.Allured, M.D.Noirot, R.C.Haltiwanger, and A.D.Norman, Inorg. Chem., 21(1982)1947.

327 P.G.Owston, L.S.Shaw, R.A.Shaw and D.A.Watkins, J. Chem. Soc. Chem. Commun., (1982)16.

328 R.O.Day, A.Schmidpeter and R.R.Holmes, Inorg. Chem., 21(1982)3916.

329 K.Ramachandran and C.W.Allen, J. Am. Chem.Soc., 104(1982)2396.

330 C.W.Allen, K.Ramachandran, R.P.Bright and J.C.Shaw, Inorg. Chim. Acta, 64(1982)L109.

331 P.R.Suszko, R.R.Whittle and H.R.Allcock, J. Chem. Soc. Chem. Commun., (1982)960.

332 R. D. Sharma, S.J.Rettig, N.L.Paddock and J.Trotter, Can. J. Chem., 60(1982)535.

333 I.Rayment, H.M.M.Shearer and H.W.Roesky, J. Chem. Soc. Dalton Trans., (1982)883.

334 S.S.Krishnamurthy and P.M.Sundaram, J. Chem. Soc. Dalton Trans., (1982)67.

335 A.A.Smaardijk, B. de Ruiter, A.A. van der Huizen and J.C. van de Grampel, Rec. Trav. Chim., 101(1982)270.

336 C.W.Allen, J.A.Mackay, J.J.McCormack, R.A.Newman and M.P.Hacker, Inorg. Chim. Acta, 67(1982)L17.

337 G.J.Bullen, J. Cryst. Molecular Struct., 12(1982)11.

338 R.Enjalbert, G.Guerch, J.-F.Labarre and J.Galy, Z. Kristallogr., 160(1982)249.

339 G.Guerch, J.-F.Labarre, R.Roques and F.Sournies, J. Mol. Struct., 96(1982)113.

340 P.R.Suszko, R.R.Whittle and H.R.Allcock, J. Chem. Soc. Chem. Commun., (1982)649.

341 K.D.Gallicano and N.L.Paddock, Can. J. Chem., 60(1982)521.

342 H.R.Allcock, T.J.Fuller and K.Matsumura, Inorg. Chem., 21(1982)515.

343 G.Guerch, J.-F.Labarre, F.Sournies, M.Manfait, F.Spreafico, and S.Filippeschi, Inorg. Chim. Acta, 66(1982)175.
344 G.Guerch, J.-F.Labarre, J.Oiry and J.-L.Imbach, Inorg. Chim. Acta, 67(1982)L5.
345 A.A. van der Huizen, A.P.Jekel, J.K.Bolhuis, D.Keekstra, W.H.Ouseman and J.C. van de Grampel, Inorg. Chim. Acta, 66(1982)85.
346 T.S.Cameron, J.-F.Labarre and M.Graffeuil, Acta Crystallogr., B38(1982)168.
347 T.S.Cameron, J.-F.Labarre and M.Graffeuil, Acta Crystallogr., B38(1982)2000.
348 V.Ramamoorthy, T.N.Ranganathan, G.S.Rao and P.T.Manoharan, J. Chem. Res.(S), (1982)316.
349 K.S.Dhathathreyan, S.S.Krishnamurthy, A.R.V.Murthy, R.A.Shaw and M.Woods, J. Chem. Soc. Dalton Trans., (1982)1549.
350 B.Thomas, A.John and G.Grossmann, Z. Anorg. Allg. Chem., 489(1982)139.
351 B.Thomas, G.Grossmann and H.Meyer, Z. Anorg. Allg. Chem., 490(1982)121.
352 H.R.Allcock, M.S.Connolly and P.J.Harris, J. Am. Chem. Soc., 104(1982)2482.
353 K.S.Dhathathreyan, S.S.Krishnamurthy and M.Woods, J. Chem. Soc. Dalton Trans., (1982)2151.
354 S.S.Krishnamurthy, P.M.Sundaram and M.Woods, Inorg. Chem., 21(1982)406.
355 K.D.Gallicano, N.L.Paddock, S.J.Rettig and J.Trotter, Can. J. Chem., 60(1982)2415.
356 T.Chivers, M.N.S.Rao and J.F.Richardson, J. Chem. Soc. Chem. Commun., (1982)982.
357 N.Burford, T.Chivers, A.W.Cordes, W.G.Laidlaw, M.C.Noble, R.T.Oakley and P.N.Swepston, J. Am. Chem. Soc., 104(1982)1282.
358 N.Burford, T.Chivers, P.W.Codding and R.T.Oakley, Inorg. Chem., 21(1982)982.
359 B. de Ruiter, G.Kuipers, J.H.Bijlaart and J.C. van de Grampel, Z. Naturforsch., 37b(1982)1425.
360 B. de Ruiter, H.H.Baalmann and J.C. van de Grampel, J. Chem. Soc. Dalton Trans., (1982)2337.
361 B. de Ruiter and J.C van de Grampel, J. Chem. Soc. Dalton Trans., (1982)1773.
362 D.M.Kok, A.M.G.Kok-Hettinga and J. C. van de Grampel, Inorg. Chim. Acta, 59(1982)105.
363 H.W.Choi and E.L.Muetterties, J. Am. Chem. Soc., 104(1982)153.
364 E.L.Muetterties, J.R.Bleeke, Z.-Y.Yang and V.W.Day, J. Am. Chem. Soc., 104(1982)2940.
365 V.W.Day, I.Tavanaiepour, S.S.Abdel-Meguid, J.F.Kirner and L.-Y.Goh, Inorg. Chem., 21(1982)657.
366 A.Haas and J.Hahne, Z. Anorg. Allg. Chem., 490(1982)230.
367 J.S.Ogden and S.J.William, J. Chem. Soc. Dalton Trans., (1982)825.
368 B.Kratochvil, J. Podlahova, S.Habibpur, V.Petricek and K.Maly, Acta Crystallogr., B38(1982)2436.
369 T.Yamaguchi and O.Lindqvist, Acta Crystallogr., B38(1982)1441.
370 M.Rafiq, J.Durand and L.Cot, Z. Anorg. Allg. Chem., 484(1982)187.
371 I.Cisarova, C.Novak, V.Petricek, B.Kratochvil and J.Loub, Acta Crystallogr., B38(1982)1687.

372 R.G.Hazell, A.C.Hazell and B.Kratochvil, Acta Crystallogr., B38(1982)1267.

373 R.N.Puri and R.O.Asplund, Inorg. Chim. Acta, 57(1982)57.

374 A.Piehl, J.Neels and M.Meisel, Z. Chem., 22(1982)53.

375 M.Jansen and M.Möbs, Z. Kristallogr., 159(1982)283.

376 D.Bodenstein, A.Brehm, P.G.Jones, E.Schwarzmann and G.M.Sheldrick, Z. Naturforsch., 37b(1982)136.

377 D.Bodenstein, A.Brehn, P.G.Jones, E.Schwarzmann and G.M.Sheldrick, Z. Naturforsch., 37b(1982)531.

378 G.-U.Wolf and M.Meisel, Z. Chem., 22(1982)54.

379 J.Neels and M.Meisel, Z. Chem., 22(1982)213.

380 G.-V.Röschenthaler and W.Storzer, Angew. Chem. Int. Ed. Engl ., 21(1982)208.

381 D.R.Jones, L.F.Lindoy, A.M.Sargeson and M.R.Snow, Inorg. Chem., 21(1982)4155.

382 K.C.Molloy, F.A.K.Nasser and J.J.Zuckerman, Inorg. Chem., 21(1982)1711.

383 D.Cunningham, L.A.Kelly, K.C.Molloy and J.J.Zuckerman, Inorg. Chem., 21(1982)1416.

384 K.C.Molloy, F.A.K.Nasser, C.L.Barnes, D. van der Helm and J.J.Zuckerman, Inorg. Chem., 21(1982)960.

385 M.W.G. de Bolster and R.J.F.Jans, Z. Anorg. Allg. Chem., 488(1982)207.

386 S.M.Bowen, E.N.Duesler and R.T.Paine, Inorg. Chem., 21(1982)261.

387 M.L.Levin, J.W.Fieldhouse and H.R.Allcock, Acta Crystallogr., B38(1982)2284.

388 S.Kulpe, I.Seidel, K.Szulzewsky and G.Kretschmer, Acta Crystallogr., B38(1982)2813.

389 P.Liebmann, G.Loew, A.D.McLean and G.R.Pack, J. Am. Chem. Soc., 104(1982)691.

390 T.D.Hayden, E.E.Kim and K.Eriks, Inorg. Chem., 21(1982)4054.

391 J.Emsley and S.Niazi, J.Chem. Soc. Dalton Trans., (1982)2527.

392 L.M.Dikareva, G.G.Sadikov, M.A.Porai-Koshits, I.B.Baranovskii, S.S.Abdullaev and R.N.Shchelokov, Russ. J. Inorg. Chem., 27(1982)417.

393 I.B.Baranovskii, S.S.Abdullaev, G.Ya.Mazo, I.F.Golovaneva, Ya.V.Salyn and R.N.Shchelokov, Russ. J. Inorg. Chem., 26(1981)925.

394 J.Neels and H.Grunze, Z. Anorg. Allg. Chem., 495(1982)65.

395 Z.Isabaev, B.T.Ibragimov, S.A.Talipov, M.T.Saibova and T.F.Aripov, Russ. J. Inorg. Chem., 26(1981)1086.

396 S.T.Wilson, B.M.Lok, C.A.Messina, T.R.Cannan and E.M.Flanigen, J. Am. Chem. Soc., 104(1982)1146.

397 Y.Inoue and Y.Yamada, Bull. Chem. Soc. Jpn., 55(1982)792.

398 T.Kijima, S.Ueno and M.Goto, J. Chem. Soc. Dalton Trans., (1982)2499.

399 T.Kijima, Bull. Chem. Soc. Jpn., 55(1982)3031.

400 P.M.DiGiacomo and M.B.Dines, Polyhedron, 1(1982)61.

401 B.M.Nirsha, E.N.Gudinitsa, V.A.Efremov, A.A.Fakeev, B.V.Zhadanov and V.A.Olikova, Russ. J. Inorg. Chem., 26(1981)1397.

402 B.M.Nirsha, E.N.Gudinitsa, V.A.Efremov, B.V.Zhadanova, V.A.Olikova and A.A.Fakeev, Russ. J. Inorg. Chem., 26(1981)1560.

403 B.M.Nirsha, E.N.Gudinitsa, A.A.Fakeev, V.A.Efremov, B.V.Zhadanov and V.A.Olikova, Russ. J. Inorg. Chem., 27(1982)770.

404 V.V.Pechkovskii, E.D.Dzyuba, R.Ya Melnikova, G.I.Salonets, V.I.Kovalishina and I.E.Malashonak, Russ. J. Inorg. Chem., 27(1982)1237.

405 T.V.Khomutova, A.A.Fakeev, B.M.Nirsha, O.I.Evstafeva, V.F.Chuvaev, V.M.Agre and N.P.Kozlova, Russ. J. Inorg. Chem., 27(1982)1671.
406 L.S.Eshchenko, R.N.Dvoskina, V.V.Pechkovskii and L.S.Strugach, Russ. J. Inorg. Chem., 26(1981)1726.
407 B.M.Nirsha, T.V.Khomutova, A.A.Fakeev, B.V.Zhadanov, V.M.Agre,N.P.Kozlova and V.A.Olikova, Russ. J. Inorg. Chem., 27(1982)630.
408 V.A.Efremov, V.K.Trunov, I.Matsichek, E.N.Gudinitsa and A.A. Fakeev, Russ. J. Inorg. Chem., 26(1981)1721.
409 S.Takagi, M.Mathew and W.E.Brown, Acta Crystallogr., B38(1982)44.
410 S.V.Chiranjeevirao, J.Hemmerle, J.C.Voegel and R.M.Frank, Inorg. Chim. Acta, 67(1982)183.
411 J.L.Meyer and B.O.Fowler, Inorg. Chem., 21(1982)3029.
412 O.E.Piro, M.C.Apella, E.J.Baran and B.E.Rivero, Rev. Chim. Min., 19(1982)11.
413 M.E.Escobar and E.J.Baran, Monatsh., 113(1982)43.
414 H.Worzala and K.H.Jost, Z. Anorg. Allg. Chem., 486(1982)165.
415 W.O.Milligan, D.F.Mullica, G.W.Beall and L.A.Boatner, Inorg. Chim. Acta, 60(1982)39.
416 N.G.Chernorukov, I.A.Korshunov and M.I.Zhuk, Russ. J. Inorg. Chem., 27(1982)3049.
417 M.Tachez, F.Theobald, J.Bernard and A.W.Hewat, Rev. Chim. Min., 19(1982)291.
418 J.W.Johnson, A.J.Jacobson, J.F.Brody and S.M.Rich, Inorg. Chem., 21(1982)3820.
419 N.G.Chernorukov, N.P.Egorov, E.V.Shitova and Yu.I. Chigirinskii, Russ. J. Inorg. Chem., 26(1981)1454.
420 S.B.Etcheverry, E.J.Baran, and E.Diemann, Z. Anorg. Allg. Chem., 486(1982)215.
421 A.G.Nord, Acta Chem. Scand., A36(1982)95.
422 S.Takagi, M.Mathew and W.E.Brown, Acta Crystallogr., B38(1982)1408.
423 M.Mathew, P.Kingsbury, S.Takagi and W.E.Brown, Acta Crystallogr., B38(1982)40.
424 F.Hanic, M.Handlovic, K.Burdova and J.Majling, J. Cryst. Mol. Struct., 12(1982)99.
425 M.Vlasse, P.Bochu, C.Parent, J.P.Chaminade, A.Daoudi, G.Le Flem and P.Hagenmuller, Acta Crystallogr., B38(1982)2328.
426 A.Larbot, A.Norbert, J.Durand, Z. Anorg. Allg. Chem., 486(1982)200.
427 B.Kojic-Prodic, M.Sljukic and Z.Ruzic-Toros, Acta Crystallogr., B38(1982)67.
428 E.N.Rizkalla, Inorg. Chim. Acta, 60(1982)53.
429 J.Oka and A.Kawahara, Acta Crystallogr., B38(1982)3.
430 A.Durif and M.T.Averbuch-Pouchot, Acta Crystallogr., B38(1982)2883.
431 T.Stefanidis and A.G.Nord, Z. Kristallogr., 159(1982)255.
432 Z.M.Zemtsova and V.V.Kokhanovskii, Russ. J. Inorg. Chem., 27(1982)2219.
433 A.I.Teterevkov and V.I.Poloiko, Russ. J. Inorg. Chem., 27(1982)604.
434 A.V.Laurov, A.B.Pobedina, I.A.Rozanov and I.V.Tananaev, Russ. J. Inorg. Chem., 26(1981)1001.
435 K.Schlesinger, G.Ladwig and I.Grunze, Z. Chem., 22(1982)214.
436 N.Boudjada and A.Durif, Acta Crystallogr., B38(1982)595.
437 T.Miyajima, Y.Miyahara and S.Ohashi, Polyhedron, 1(1982)425.
438 M.Watanabe, Bull. Chem. Soc. Jpn., 55(1982)3766.

439 T.N.Galkova and E.A.Prodan, Russ. J. Inorg. Chem., 26(1981)1144.
440 O.P.Olshevskaya, T.N.Galkova and E.A.Prodan, Russ. J. Inorg. Chem., 27(1982)1677.
441 D.M.Wiench, M.Jansen and R.Hoppe, Z. Anorg. Allg. Chem., 488(1982)80.
442 M.Hassanein, Rev. Chim. Min., 19(1982)116.
443 H.Waki and M.Hatano, Polyhedron, 1(1982)69.
444 F.Möwins and H.Grunze, Z. Anorg. Allg. Chem., 494(1982)43.
445 A.Immirzi and W.Porzio, Acta Crystallogr., B38(1982)2788.
446 J.-J.Barieux and M.C.Demarcq, J. Chem. Soc. Chem. Commun., (1982)176.
447 R.Blachnik and U.Wickel, Z. Naturforsch., 37b(1982)1507.
448 G.-U.Wolf and M.Meisel, Z. Anorg. Allg. Chem., 494(1982)49.
449 M.Meisel and C.Donath, Z. Chem., 22(1982)212.
450 A.Grand and J.Martin, Acta Crystallogr., B38(1982)3052.
451 K.Diemert, P.Haas and W.Kuchen, Z. Anorg. Allg. Chem., 292(1982)148.
452 J.L.Lefferts, K.C.Molloy, M.B.Hossain,D van der Helm and J.J.Zuckerman, Inorg. Chem., 21(1982)1410.
453 M.Shimoi, A.Ouchi, M.Aikawa, S.Sato and Y.Saito, Bull. Chem. Soc. Jpn., 55(1982)2089.
454 M.Shimoi, A.Ouchi, T.Uehiro, Y.Yoshino, S.Sato and Y.Saito, Bull. Chem. Soc. Jpn., 55(1982)2371.
455 S.Spiliadis, A.A.Pinkerton and D.Schwarzenbach, J. Chem. Soc. Dalton Trans., (1982)1809.
456 H.Wunderlich, Acta Crystallogr., B38(1982)614.
457 D.Troy, J.P.Legros and G.P.McQuillan, Inorg. Chim. Acta, 58(1982)217.
458 S.Bjornevag, S.Husebye and K.Maartmann-Moe, Acta Chem. Scand., A36(1982)195.
459 B.M.Goldstein, Acta Crystallogr., B38(1982)1116.
460 R.Mercier, J.-P.Malugani, B.Fahys, G.Robert and J.Douglade, Acta Crystallogr., B38(1982)1887.
461 P.Toffoli, P.Khodadad and N.Rodier, Acta Crystallogr., B38(1982)2374.
462 P.Toffoli, A.Michelet, P.Khodadad and N.Rodier, Acta Crystallogr., B38(1982)706.
463 A.Simon, K.Peters, E.-M.Peters and H.Hahn, Z. Anorg. Allg. Chem., 491(1982)295.
464 K.Manzel, W.Schulze, V.Wölfel and R.Minkwitz, Z. Naturforsch., 37b(1982)1127.
465 J.K.Burdett and J.-H.Lin, Acta Crystallogr., B38(1982)408.
466 B.Sigwarth, L.Zsolnai, H.Berke and G.Huttner, J. Organomet. Chem., 226(1982)C5.
467 G.Becker, G.Gutekunst and C.Witthauer, Z. Anorg. Allg. Chem., 486(1982)90.
468 J.Ellermann and L.Mader, Z. Anorg. Allg. Chem., 485(1982)36.
469 O.Mundt, G.Becker, H.-J.Wessely, H.J.Breunig, and H.Kischel, Z. Anorg. Allg. Chem., 486(1982)70.
470 A.L.Rheingold and S.Natarajan, J. Organomet. Chem., 231(1982)119.
471 A.L.Rheingold, M.J.Foley and P.J.Sullivan, J. Am. Chem. Soc., 104(1982)4727.
472 M.Baudler and P.Bachmann, Z. Anorg. Allg. Chem., 485(1982)129.
473 R.Fröhlich and K.-F.Tebbe, Z. Kristallogr., 158(1982)255.
474 G.Cordier, S.Savelsnerg and H.Schäfer, Z. Naturforsch., 37b(1982)975.

475 B.Eisenmann and H.Schäfer, Z. Anorg. Allg. Chem., 484(1982)142.
476 M.Pfisterer and G.Nagorsen, Z. Naturforsch., 37b(1982)420.
477 C.Hadenfeldt and H.O.Vollert, Z. Anorg. Allg. Chem., 491(1982)113.
478 H.Schumann and G.-M.Frisch, Z. Naturforsch., 37b(1982)168.
479 J.Ellermann and M.Lietz, Z. Naturforsch., 37b(1982)73.
480 A.Meyer, A.Hartl and W.Malisch, Z. Naturforsch., 37b(1982)845.
481 T.Kauffmann, H.Fischer and A.Woltermann, Chem. Ber., 115(1982)645.
482 T.Kauffmann and R.Joussen, Chem. Ber., 115(1982)654.
483 U.Müller and H.-D.Dörner, Z. Naturforsch., 37b(1982)198.
484 G.Becker and C.Witthauer, Z. Anorg. Allg. Chem., 492(1982)28.
485 T.Okuda, S.Gima, H.Ishihara and H.Negita, J. Mol. Struct., 81(1982)261.
486 R.Kniep and H.D.Reski, Inorg. Chim. Acta Lett., 64(1982)L83.
487 J.Passmore, G.Sutherland and P.S.White, Inorg. Chem., 21(1982)2717.
488 R.Pentenrieder and H.P.Boehm, Rev. Chim. Min., 19(1982)371.
489 B.Frlec, D.Gantar and J.H.Holloway, J. Fluorine Chem., 20(1982)217.
490 B.Frlec, D.Gantar and J.H.Holloway, J. Fluorine Chem., 20(1982)385.
491 J.Douglade and R.Mercier, Acta Crystallogr., B38(1982)720.
492 R.Mercier and J.Douglade, Acta Crystallogr., B38(1982)1731.
493 R.Mercier and J.Douglade, Acta Crystallogr., B38(1982)896.
494 P.Van Nuffel, A.T.H.Lenstra, H.J.Geise, L.K.Yuldasheva and N.A.Chadaeva, Acta Crystallogr., B38(1982)3089.
495 D.Marcovich, E.N.Duesler, R.E.Tapscott and T.F.Them, Inorg. Chem., 21(1982)3336.
496 J. Ellermann, A.Veit, E.Lindner and S.Hoehne, J. Chem. Soc. Chem. Commun., (1982)382.
497 D.Bodenstein, A.Brehn, P.G.Jones, E.Schwarzmann and G.M.Sheldrick, Z. Naturforsch., 37b(1982)138.
498 R.O.Day, J.M.Holmes, A.C.Sau, J.R.Devillers, R.R.Holmes and J.A.Deiters, J. Am. Chem. Soc., 104(1982)2127.
499 S.S.Sandhu, S.S.Sandhu Jr., G.K.Sandhu, R.V.Parish and O.Parry, Inorg. Chim. Acta, 58(1982)251.
500 A.Greix and M.Ferrer, Inorg. Chim. Acta, 59(1982)177.
501 A.Boudjada, R.Masse and J.C.Guitel, Acta Crystallogr., B38(1982)710.
502 B.K.Kasenov and S.M.Isabaev, Russ. J. Inorg. Chem., 26(1981)1679.
503 D.Bedlivy and K.Mereiter, Acta Crystallogr., B38(1982)1559.
504 A.N.Fitch, A.F.Wright and B.E.F.Fender, Acta Crystallogr., B38(1982)2546.
505 A.N.Fitch, B.E.F.Fender and A.F.Wright, Acta Crystallogr., B38(1982)1108.
506 P.Keller, H.Riffel and H.Hess, Z. Kristallogr., 158(1982)33.
507 I.Haiduc and L.Silaghi-Dumitrescu, J. Organomet. Chem., 225(1982)224.
508 V.E.Zavodnik, V.K.Belsky, Yu.G.Galyametdinov, J. Organomet. Chem., 226(1982)41.
509 K.Mereiter, A.Preisinger, O.Baumgartner, G.Heger, W.Mikenda and H.Steidl, Acta Crystallogr., B38(1982)401.
510 S.Jaulmes, E.Godlewski, M.Palazzi and J.Etienne, Acta Crystallogr., B38(1982)1707.
511 M.Gostojic, A.Edenharter, W.Nowacki and P.Engel, Z. Kristallogr., 158(1982)43.

512 T.Balic-Zunic, S.Scavnicar and P.Engel, Z. Kristallogr., 160(1982)109.

513 D.H.R.Barton, H.Dadoun and A.Gourdon, Nouv. J. Chim., 6(1982)53.

514 R.Kniep and H.D.Reski, Z. Naturforsch., 37b(1982)151.

515 H.Schäfer, Z. Anorg. Allg. Chem., 489(1982)154.

516 G.Huttner, U.Weber, B.Sigwarth and O.Scheidsteger, Angew. Chem. Int. Ed. Engl., 21(1982)215.

517 H.J.Breunig and H.Jawad, Z. Naturforsch., 37b(1982)1104.

518 H.J.Breunig, V.Breunig-Lyriti and W.Fichtner, Z. Anorg. Allg. Chem., 487(1982)111.

519 H.J.Breunig and T.Severengiz, Z. Naturforsch., 37b(1982)395.

520 G.Becker, H.Freudenblum and C.Witthauer, Z. Anorg. Allg. Chem., 492(1982)37.

521 T.Hughbanks, R.Hoffmann, M.-H.Whangbo, K.R.Stewart, O.Eisenstein and E.Canadell, J. Am. Chem. Soc., 104(1982) 3876.

522 J.Ellermann and A.Veit, Angew. Chem. Int. Ed. Engl., 21(1982)375.

523 G.O.Doak and L.D.Freedman, J. Organomet. Chem., 237(1982)21.

524 P.G.Jones, Z. Naturforsch., 37b(1982)937.

525 A.J.Ashe III, T.R.Diephouse and M.Y.El-Sheikh, J. Am. Chem. Soc., 104(1982)5693.

526 S.Elbel and H. tom Dieck, Z. Anorg. Allg. Chem., 483(1981)33.

527 B.Milewski-Mahrla and H.Schmidbaur, Z. Naturforsch., 37b(1982)1393.

528 B.S.Bedi, D.W.Grant, L.Tewnion and J.L.Wardell, J. Organomet. Chem., 239(1982)251.

529 F.Weller, J.Pebler, K.Dehnicke, K.Hartke and H.-M.Wolff, Z. Anorg. Allg. Chem., 486(1982)61.

530 G.Becker, A.Münch and C.Witthauer, Z. Anorg. Allg. Chem., 492(1982)15.

531 V.B.Sokolnikov, V.I.Shpanko and R.L.Davidovich, Russ. J. Inorg. Chem., 26(1981)1545.

532 A.A.Opalovskii, T.F.Gudimovich and G.P.Sokhranenko, Russ. J. Inorg. Chem., 26(1981)1799.

533 T.Birchall, B.Ducourant, R.Fourcade and G.Mascherpa, J. Chem. Soc. Dalton Trans., (1982)2313.

534 C.Peylhard, P.Teulon and A.Potier, Z. Anorg. Allg. Chem., 483(1981)236.

535 M.G.B.Drew, J.M.Kisenyi and G.R.Willey, J. Chem. Soc. Dalton Trans., (1982)1729.

536 A.Giusti, G.Peyronel and E.Giliberti, Polyhedron, 1(1982)655.

537 U.Ensinger, W.Schwarz and A.Schmidt, Z. Naturforsch., 37b(1982)1584.

538 A.Lipka and D.Mootz, Z. Naturforsch., 37b(1982)695.

539 J.Fawcett, J.H.Holloway, R.D.Peacock and D.K.Russell, J. Fluorine Chem., 20(1982)9.

540 J.Burgess, R.D.Peacock and R.Sherry, J. Fluorine Chem., 20(1982)541.

541 G.Roth, J.Goebbels, K.Lüders, P.Pfluger and H.-J.Guntherodt, Rev. Chim. Min., 19(1982)387.

542 J.Fawcett, J.H.Holloway, D.Laycock and D.R.Russell, J. Chem. Soc. Dalton Trans., (1982)1355.

543 J.H.Holloway, D.Laycock and R.Bougon, J. Chem. Soc. Dalton Trans., (1982)1635.

544 Z.Tun and I.D.Brown, Acta Crystallogr., B38(1982)2321.

545 G.Cardinal, R.J.Gillespie, J.F.Sawyer and J.E.Vekris, J. Chem. Soc. Dalton Trans., (1982)765.

546 P.Teulon and J.Roziere, Z. Anorg. Allg. Chem., 483(1982)219.

547 S.Blösl, W.Schwarz and A.Schmidt, Z. Anorg. Allg. Chem., 495(1982)165.

548 S.Blösl, W.Schwarz and A.Schmidt, Z. Anorg. Allg. Chem., 495(1982)177.

549 C.H.Belin, M.Chaabouni, J.L.Pascall and J.Potier, Inorg. Chem., 21(1983)3557.

550 H.-C.Gaebell, G.Meyer and R.Hoppe, Z. Anorg. Allg. Chem., 493(1982)65.

551 G.Gattow and F.-J.Kaesberger, Z. Anorg. Allg. Chem., 495(1982)193.

552 G.Gattow and F.-J.Kaesberger, Z. Anorg. Allg. Chem., 495(1982)186.

553 G.Alonzo, N.Bertazzi and A.Maccotta, Inorg. Chim. Acta, 62(1982)167.

554 H.Preut, F.Huber, G.Alonzo and N.Bertazzi, Acta Crystallogr., B38(1982)935.

555 E.G.Puebla, E.G.Rios, A.Monge and I.Rasines, Acta Crystallogr., B38(1982)2020.

556 P.G.Casado, A.Mendiola and I.Rasines, Inorg. Chem., 21(1982)2902.

557 S.Kemmler-Sack and U.Treiber, Z. Anorg. Allg. Chem., 484(1982)173.

558 U.Treiber and S.Kemmler-Sack, Z. Anorg. Allg. Chem., 487(1982)161.

559 F.J.Berry, M.E.Brett and W.R.Patterson, J. Chem. Soc. Chem. Commun., (1982)695.

560 W.D.Hill Jr., Inorg. Chim. Acta Lett., 64(1982)L255.

561 M.Jansen, J.Pebler and K.Dehnicke, Z. Anorg. Allg. Chem., 495(1982)120.

562 C.A.Kavounis, S.C.Kokkou, P.J.Rentzeperis and P.Karagiannidis, Acta Crystallogr., B38(1982)2686.

563 A.S.Kanishcheva, Yu.N.Mikhailov, V.B.Lazarev and A.F.Trippel, Russ. J. Inorg. Chem., 27(1982)1554.

564 G.Cordier, C.Schwidetzky and H.Schäfer, Rev. Chim. Min., 19(1982)179.

565 M.Gostojic, W.Nowacki and P.Engel, Z. Kristallogr., 159(1982)217.

566 V.Kupcik and M.Wendschuk, Acta Crystallogr., B38(1982)3070.

567 J.Pebler, F.Weller and K.Dehnicke, Z. Anorg. Allg. Chem., 492(1982)139.

568 T.König, B.Eisenmann and H.Schäfer, Z. Anorg. Allg. Chem., 488(1982)126.

569 G.Huttner, U.Weber and L.Zsolnai, Z. Naturforsch., 37b(1982)707.

570 B.Krebs, M.Huche and C.J.Brendel, Angew. Chem. Int. Ed. Engle., 21(1982)445.

571 S.C.Critchlow and J.D.Corbett, Inorg. Chem., 21(1982)3286.

572 H.J.Breunig and D.Müller, Angew. Chem. Int. Ed. Engl., 21(1982)439.

573 G.Becker and M.Rössler, Z. Naturforsch., 37b(1982)91.

574 G.O.Doak and L.D.Freedman, J. Organomet. Chem., 237(1982)51.

575 F.Huber and S.Bock, Z. Naturforsch., 37b(1982)815.

576 U.Praeckel and F.Huber, J. Organomet. Chem., 240(1982)C45.

577 E.I.Ardashnikova, M.P.Borzenkova, F.V.Kalinchenko and A.V.Novoselova, Russ. J. Inorg. Chem., 26(1981)931.

578 G.V.Zimina, A.Yu.Zamanskaya, L.A.Sadokhina, F.M.Spiridonov, P.P.Fedorov and P.I.Fedorov, Russ. J. Inorg. Chem., 27(1982)1596.

579 W.Kruppa, D.Bläser, R.Boese and G.Schmid, Z. Naturforsch., 37b(1982)209.

580 U.Praeckel, F.Huber and H.Preut, Z. Anorg. Allg. Chem., 494(1982)67.

581 M.Graunar and F.Lazarini, Acta Crystallogr., B38(1982)2879.

582 L.Golic, M.Graunar and F.Lazarini, Acta Crystallogr., B38(1982)2881.

583 S.D.Ershova, A.Ya Fridman, N.M.Dyatlova, B.V.Zhadanov, I.A.Polyakova, A.V.Kessenikh and N.A.Kaslina, Russ. J. Inorg. Chem., 27(1982)1418.

584 L.A.Kochubei, E.V.Margulis, F.I.Vershinina and L.V.Vorobeva, Russ. J. Inorg. Chem., 26(1981)1542.

585 I.I.Prosychev, V.B.Lazarev and I.S.Shaplygin, Russ. J. Inorg. Chem., 26(1981)1011.

586 R.Cook and H.Schäfer, Rev. Chim. Min., 19(1982)19.

587 C.Burschka, Z. Anorg. Allg. Chem., 485(1982)217.

588 D.J.Williams, C.O.Quicksall and K.M.Barkigia, Inorg. Chem., 21(1982)2097.

589 P.Lemoine, D.Carré and M.Guittard, Acta Crystallogr., B38(1982)727.

590 A.Pradel, J.-C.Tedenac, D.Coquillat and G.Brun, Rev. Chim. Min., 19(1982)43.