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Chapter 5

ELEMENTS OF GROUP 5

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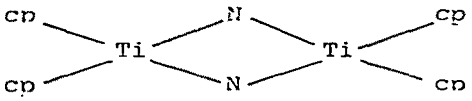
5.1 NITROGEN

5.1.1 Bonds to Hydrogen

Ammonia and fluorine do not react below -120°C but in the gas phase above this temperature reaction is very vigorous; the products, identified mainly by n.m.r. and mass spectrometry, include ammonium fluoride, NF_3, N_2F_4, FN:NF, and N_2 in addition to fluoramine, NH_2F.[1] This compound, which is isoelectronic with HOF, is not known as a stable species.

The cyclopentadiene-bridged titanium compound, $(cp_2Ti)_2$, reacts with ammonia, primary and secondary amines consuming two mols of ammonia per Ti_2 unit.[2] One mol. of hydrogen is eliminated giving a red compound in which the titanium atoms are tetrahedrally coordinated as shown in (1). The nitrogen atoms are not nitridic



(1)

and three hydrogen atoms should be included in the structure. Compound (1) is highly reactive converting carbon monoxide and carbon dioxide to respectively isocyanate and carbamate, with nitrogen there is initial coordination and then reduction can be achieved with potassium naphthalene.[3] The compound also serves as a low pressure homogeneous catalyst for olefin hydrogenation.

Equilibrium constants for the reactions shown in equations (1) and (2) have been evaluated at temperatures between 25 and 70°C

$$NH_3 + HCO_3^- \longrightarrow NH_2COO^- + H_2O \qquad \ldots (1)$$
$$NH_2COOH \longrightarrow NH_2COO^- + H^+ \qquad \ldots (2)$$

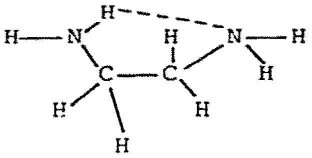
giving pK values of -0.328 and 6.76 respectively and ΔH values of -10 and 11kJ mol^{-1} respectively.[4]

On heating with ammonia under pressure at between 300 and 500°C, various mixtures of potassium and europium metals give the compounds EuN, $Eu(NH_2)_2$, $KEu(NH_2)_3$ and $K_3Eu(NH_2)_6$ as crystalline samples.[5] The nitride has a sodium chloride structure and is a thermal decomposition product of $Eu(NH_2)_2$ which has the anatase structure.

The ternary compounds are isotypic with respectively $KCa(NH_2)_3$ and $K_3La(NH_2)_6$. In liquid ammonia, the auride ion results when metallic gold dissolves in solutions containing potassium, rubidium or caesium,[6] auride formation was confirmed electrochemically and by the observation of the characteristic band at 289nm.

The compound between ammonium iodide and dioxan is a 1:1 rather than a 1:2 complex as previously reported, and from Raman spectroscopy NH ... O hydrogen bonds are important in stabilizing the structure.[7]

Microwave data for ethylenediamine have been analysed[8] in terms of the two gauche forms, (2) and (3), previously calculated to be the more stable rotamers. Both are stabilized by hydrogen bonds and because it is possible to interchange the acceptor and donor amino groups, double minimum potentials for the appropriate transformations are expected. Splittings caused by the double minima are observed experimentally and the data give a value of 63 ± 2° for the NCCN torsion angles in both conformers whereas CCN angles of 109.0 and 111.5° are obtained for (2) and (3) respectively. Vibrational studies on the isotopically substituted ethylenediammonium ion in the tetrachlorocadmate salt can be interpreted on the basis of a trans, centrosymmetric conformation for the cation;[9] hydrogen bonding is important here but is much weaker in the hexachloroplatinate and -stannate salts.



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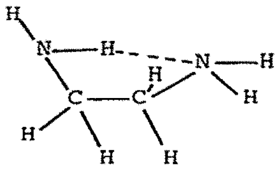


(3)

Hydroxylamine with perchloryl fluoride in ethanol solution gives in addition to $(NH_3OH)F$ the chlorate, $(NH_3OH)ClO_3$, with liberation of oxygen and nitrogen.[10] The mixture presents a serious explosion hazard if attempts are made to separate and isolate the products. N-substitution occurs when hydroxylamine is treated with alkylsulphonyl chlorides[11] or dimethylaminosulphonyl chloride[12] to give respectively $Me(CH_2)_nSO_2NHOH$ and Me_2NSO_2NHOH. N-methyl-hydroxylamine reacts similarly with methyl- or phenyl-sulphonyl chlorides.[13] The products, $RSO_2N(Me)OH$ where R=Me or Ph, are relatively stable in strongly acid solution, but in alkaline solution hydrolysis via a monomeric nitrosamine occurs. Other aspects of hydroxylamine sulphonate chemistry are discussed in Chapter 6.

The nitrogen 1s binding energy has been measured by X-ray p.e.s. for a number of compounds containing NH_2 and NO_2 groups.[14] Values for the amino-nitrogen in urea, thiourea, urethane, $H_2NSO_3^-$ and $H_2NCO_2^-$ are close to 400 eV; data are also available showing that with perchloric acid protonation occurs at a nitrogen atom with urea but at the sulphur atom with thiourea.[15]

A new preparation for nitroxyl, HNO, involves dissociation of 9,10-dihydro-9,10-epoxyimino-9,10-dimethylanthracene at 70°C under mild non-photochemical conditions.[16] Nitroxyl has also been shown to be important as an intermediate in the reduction of hydroxylamine by nitrogen (II) oxide and in the decomposition of the trioxodinitrate anion $HN_2O_3^-$.[17]

5.1.2 Bonds to Carbon

Microwave data for nitrosyl cyanide, ONCN, and a number of ^{15}N, ^{13}C, and ^{18}O substituted species establish planarity for the molecule and give values of 1.163(5), 1.418(5), and 1.217(5)Å for respectively the N-C(N), C-N(O), and N-O distances.[18] The N-C-N fragment is however distinctly non-linear (170°) and the C-N-O angle is 113.5°.

Thermal decomposition of a solution of potassium methylamide in methylamine, shown in equation (3), is a method for preparing N,N'-dimethylformamidine,[19] the free base being liberated by

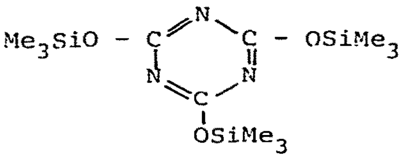
$$2MeNH_2 + MeNHK \rightarrow \underset{(\underline{4})}{MeN{:}CHN(K)Me} + 2H_2 + NH_3 \qquad \ldots (3)$$

treatment of (4) with n-dodecanol. On heating to 100° the base loses methylamine forming bis-N-(N'-methylmethylimino)methylamine, $MeN(CH{:}NMe)_2$. From ^1H n.m.r. and i.r. spectra the pure substituted formamidine exists exclusively in the *cis* isomeric form.[20] It is stable in acid solution, probably a function of the difficulty in eliminating methylamine from the tetrahedral intermediate formed at low pH.[21] When hydrolysis does occur however, the *cis* form of N-methylformamide is one of the first products but this converts slowly to the more stable *trans* isomer.

A crystalline sample of dilithium cyanamide, Li_2NCN, has been obtained for the first time in a reaction between dilithium acetylide and lithium nitride in liquid lithium at 600°C and has been characterised by i.r. spectroscopy and single crystal X-ray diffraction.[22] The NCN^{2-} ion is centrosymmetric with an N-C distance of 1.230Å; lithium ions are in distorted tetrahedral coordination by nitrogen atoms. In the structure of monosodium cyanamide, the N-C distances are 1.279 and 1.183Å, pointing to the presence of a delocalized π-system, but a hydrogen atom is attached to the nitrogen at the longer distance from carbon.[23] The compound results when cyanamide is treated with a solution of sodium ethoxide in ethanol; there is perhaps surprisingly no evidence for hydrogen bonding.

Structures have also been reported for biguanide, $H_2NC(:NH)NHC(:NH)NH_2$ and its mono- and di-protonated cations.[24] The unsymmetrical structure of the free base is confirmed but the bond distances point to extensive π-delocalization and the molecule is almost planar. In each of the protonated forms there are two almost planar sections twisted relative to each other by respectively 47.6 and 48.4° in the mono- and di-protonated species, and again there is a strong π-contribution to all the bonds. Lack of planarity is probably due to steric interactions between the hydrogen atoms. Major effects of protonation are an increase in the length of the C-N bridge bonds while the $C-N(H_2)$ distances decrease.

A tris(trimethylsilyl) derivative of cyanuric acid to which is ascribed the O-bonded structure (5) is the product when cyanuric



(5)

acid reacts with trimethylsilyl cyanide,[25] and the same compound results when either Me_3SiCN or Me_3SiNSO reacts with $(ClNCO)_3$. In the latter cases the only by-products are ClCN and ClNSO respectively and the reactions serve as convenient preparative methods for the two pseudo-halogen chlorides.

I.r. and Raman spectra have been obtained for compounds in the series Et_3M, Et_2MeM, and $EtMe_2M$ where M=N,P or As.[26] In general simple spectra are obtained in the M-C stretching region for solid samples while in the liquid state mixtures of conformers are present. A C_3 conformation appears to be adopted for the Et_3M species although this form is not predominant in the liquid. Similarly a single form is obtained on crystallization of the $EtMe_2M$ species, and it is considered that the preferred solid state conformations are those in which all the C-Me groups are gauche to the lone pair of electrons on the central atom. Normal vibrations and a force field have been calculated for $N(CN)_2^-$ and $C(CN)_3^-$.[27]

Group 5 sulphinate derivatives have been obtained according to equation (4), the general properties varying with the Group 5

$$R^1_4EX + R^2SO_2M \rightarrow MX + R^1_4EO_2SR^2 \quad \ldots (4)$$

R^1 = Me or Ph; E = N,P,As,Sb or Bi; X = Cl, Br or I;
R^2 = Me,Ph, or p-tolyl; M = Na or Ag.

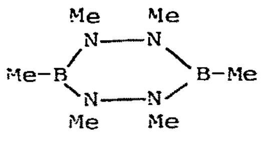
element.[28] The nitrogen compounds are purely ionic whereas those for antimony are penta-coordinated covalent molecules; with phosphorus and arsenic the bonding is intermediate with ready dissociation into ionic components. Methyl sulphinates are readily oxidized by air to the corresponding sulphonates, $R^1_4EO_3SMe$, while the antimony compounds, $Ph_4SbO_2SR^2$, lose SO_2 on refluxing in benzene to give the corresponding penta-organo antimony, Ph_4SbR^2.

5.1.3 Bonds to Nitrogen

Tetrahydrofuran can be displaced from $W(CO)_5.THF$ by hydrazine to give $W(CO)_5.N_2H_4$ or $[W(CO)_5]_2.N_2H_4$ and the former on oxidation with hydrogen peroxide gives the analogue containing coordinated N_2H_2.[29] A zirconium(III)-dinitrogen complex, for which a structure containing a sideways bonded nitrogen molecule is suggested by i.r. and e.s.r. measurements, is obtained when nitrogen reacts with $(\eta\text{-}C_5H_5)_2ZrCl[CH(SiMe_3)_2]$ in tetrahydrofuran.[30] Under reduced pressure, half the nitrogen is lost with probable formation of a dinitrogen bridged dimer. Molybdenum(V) chloride in tetrahydrofuran can be reduced in a nitrogen atmosphere by sodium amalgam in the presence of 1,2-bis(diphenylphosphino)ethane giving a one-step preparation of the compound $Mo(N_2)_2(phosphine)_2$.[31]

Anodic oxidation of ammonia or amines usually give poor yields of hydrazines and substituted hydrazines but new data show that amide ions can be oxidized efficiently, probably via aminyl radicals $R'R^2N\cdot$ which then dimerize.[32] As an example a 45% current yield of Bu_4N_2 was obtained on oxidation of $LiNBu_2$ at a platinum electrode in tetrahydrofuran solution.

The thioborane, $MeB(SMe)_2$, reacts with both 1,1- and 1,2-dimethylhydrazine to give with the former the solvolysis product $MeB(NHNMe_2)_2$ via the monosubstituted compound $MeB(SMe)(NHNMe_2)$.[33] Compounds (6) and (7) result with the symmetrically substituted hydrazine, while the sole product using monomethylhydrazine is the 6π-electron triazadiborolidine (8). Fluorosilyl substituted hydrazines can be prepared by elimination of hydrogen fluoride between $RSiF_3$ or $R'R^2SiF_3$ and hydrazine derivatives such as $PhNHNHSiMe_3$ and $Me_3SiNHNHSiMe_3$.[34]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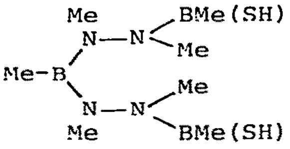
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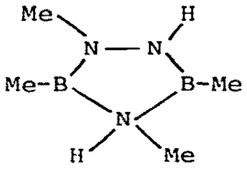
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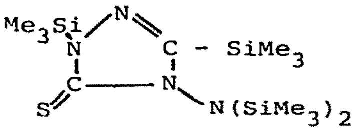
Full X-ray crystal structures are now available for 1,2-dimethyl-1,2-diformyl hydrazine,[35] $[N(Me)CH{:}O]_2$, and acetyl hydrazonium chloride[36] $[MeC(O)NHNH_3]^+Cl^-$. The symmetry of the former is very close to C_2 and the torsion angle about the N-N bond is -91.2°, compared with a planar structure for 1,2-diformyl hydrazine. The angle between the planes of the two NC:O groups is 90.0° and the N-N bond length is 1.386Å. The acetyl hydrazonium cation is non planar with an N-N bond distance of 1.415Å.

The silyl hydrazides, $LiN_2(SiMe_3)_3$ and $Li_2N_2(SiMe_3)_2$ react with phosgene and carbon disulphide to give the amino-isocyanate and amino-isothiocyanates, $(Me_3Si)_2NN{:}C{:}O$ and $(Me_3Si)_2NN{:}C{:}S$, respectively.[37] The former is a temperature stable dimer while the isothiocyanate is a monomer which decomposes into a mixture of (9) and (10) at room temperature. In ether solution on the other hand the decomposition products are sulphur and the carbodiimide $Me_3SiN{:}C{:}NSiMe_3$.



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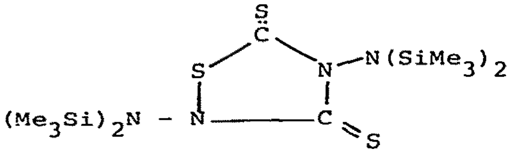

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Nitramide $NH_2.NO_2$ is considered from ^{15}N tracer studies to be the major precursor of the nitrogen(I) oxide obtained when nitric and sulphamic acids react in aqueous solution,[38] but a substantial proportion also arises by dimerization of an intermediate, most probably HNO, whose nitrogen atoms come from the nitric acid. In non-aqueous solvents, the stability of nitramide decreases from acetonitrile to ethyl acetate and is least in hydroxylic solvents such as iso-propanol; aqueous solutions can be stabilized by the addition of sodium nitrate.[39]

Methods for preparing solutions of iodine azide in organic solvents have been described together with i.r. and Raman spectra of the compound in solid dichloromethane.[40] U.v. spectra of the halogen azides correspond well with those of other covalent azides and are in agreement with C_s symmetry.[41] Chemical shifts and coupling constants have been obtained from ^{15}N n.m.r. spectra of HN_3 and ClN_3.[42] The reactivity of IN_3 towards tin(II) chloride,[43] a number of metal carbonyls,[44] and the Group 3 iodides[45] has been investigated. With $SnCl_2$, the product with either chlorine, bromine or iodine azide is the unstable oxidation product $SnCl_2(N_3)_2$, although with IN_3 in the presence of tetramethylammonium chloride there is ligand exchange and the complex anion $[SnCl_4IN_3]^{2-}$ can be isolated.[43] Complete displacement of carbon monoxide occurs with $Mn_2(CO)_{10}$, $Co_2(CO)_8$ and $Ni(CO)_4$ leading in each case to liberation of iodine and formation of the metal(II) azide, while with $Fe(CO)_5$ or $Mo(CO)_6$ the products are respectively $Fe(CO)_2IN_3$ and the highly explosive $Mo(CO)_2(N_3)_2$.[44] Cyanates such as $[Re(CO)_4NCO]_2$ and $Os(CO)_2NCO$ have also been isolated. Structures with bridging azide groups are suggested for the mixed iodide azides, MI_2N_3, obtained with either AlI_3 or GaI_3 in benzene solution.[45]

A neutron diffraction study of NH_4N_3 shows an N-N distance of 1.186Å and the importance of hydrogen bonds in stabilizing the structure.[46]

5.1.4 Bonds to Halogens

E.s.r. evidence has been presented for the formation of the $NF_3^{\cdot +}$ radical both by photolysis of NF_3-F_2-AsF_5 mixtures[47] and γ-irradiation of NF_4^+ salts.[48] Such a species has been posulated previously as an intermediate in the formation of NF_4AsF_6.

The fundamental vibrational modes for the gauche and trans isomers of N_2F_4, which constitute the equilibrium mixture, are very close making assignment of i.r. bands extremely difficult,[49] but from measurements on solutions in liquid argon or nitrogen an unambiguous assignment for each isomer is now possible. Although it is possible to obtain $N_2F_3^+SbF_6^-$ and the arsenic analogue by treating N_2F_4 with the appropriate pentahalide in anhydrous hydrogen fluoride, weaker Lewis acids such as BF_3 or SnF_4 do not react similarly.[50] Salts of these compounds can however be obtained by the metathesis in HF shown in equation(5) for the tin

$$2N_2F_3SbF_6 + Cs_2SnF_6 \longrightarrow N_2F_3SnF_5 + 2CsSbF_6 + N_2F_4 \quad \ldots (5)$$

compound. Evidence supporting the stabilization of the novel perfluorohydrazinium cation, $N_2F_5^+$, has been reexamined with the conclusion that the compound isolated was in fact $(NO)_2SiF_6$.[51]

Nitrosyl and nitryl fluorides react with chromyl fluoride yielding respectively $NOCrO_2F_3$ and $NO_2CrO_2F_3$;[52] the anion contains cis dioxo groups and cis fluorine bridges. Matrix techniques have enabled isolation of nitrosyl iodide at 9K from nitrogen(II) oxide and iodine atoms; the product shows i.r. bands at 1809, 470 and 216 cm^{-1}.[53]

5.1.5 Bonds to Oxygen

The N_2O_4, N_2O_3 and N_2O_2 molecules which are all characterized by long N-N bonds, planarity, and diamagnetism, have been treated by a localized molecular orbital method.[54] The results, which agree well with those from the more laborious ab initio calculations point to high p-orbital character in the N-N σ-bond, the absence of a π-component, and weakening of the N-N bond by oxygen lone pair delocalization which is antibonding. N-N bonding is also considered as part of a more general theoretical treatment of A-A bond strengths in A_2B_{2n} species.[55]

Catalysis of reaction(6) by a mixture of $PdCl_2$, copper(II)

$$CO + 2NO \longrightarrow CO_2 + N_2O \qquad \ldots (6)$$

chloride and 2MHCl leads to greater conversion to N_2O than previously observed with the homogeneous catalyst $RhCl_3$ and there is no induction period.[56] With $PdCl_2$ alone the rate is reduced due to deposition of metallic palladium but in the presence of acidic copper chloride this is avoided by oxidation of the metal and formation of the $CuCl_2^-$ anion.

The reddish solids obtained when nitrogen(II) oxide and Lewis acids, such as the boron halides, tin(II) chloride or titanium(IV) chloride, hydrogen chloride or sulphur dioxide react at 77K, contain from i.r. and Raman spectroscopic measurements the asymmetric dimer O:N·O:N.[57] Force constant calculations showed that in this molecule both N–O groups retain strong multiple bond character and are joined by a weak N–O single bond. A novel iron-nitrosyl cation, $Fe_2(NO)_6^{2+}$, can be isolated as the hexafluorophosphate salt from a reaction between $Fe(CO)_2(NO)_2$ and $NOPF_6$, but more interestingly the same compound results when $NOPF_6$ reacts with iron powder in nitromethane.[58] There is no evidence for bridging NO groups and the compound is diamagnetic thus leading to the formulation $[(NO)_3Fe{=}Fe(NO)_3]^{2+}$. Nitrosyl complexes are formed with Co^{2+} ions in zeolites on treatment with nitrogen(II) oxide, but there is apparently little electron transfer between the metal and NO and complex formation appears to be related to the cation position in the oxide lattice of the zeolite.[59] Among papers concerned with the environmentally important catalytic reduction of nitrogen(II) oxide is a report that NO can be reduced in aqueous solution to approximately equal amounts of nitrogen and nitrogen(I) oxide by $[Coen_2(NO_2)_2]^+$ in the presence of primary amines.[60] The di(cyclopentadienyl) titanium complex $(cp_2TiCl)_2$, also reduces nitrogen(II) oxide in this case rapidly and quantitatively to nitrogen(I) oxide but further reduction to nitrogen is very slow.[61]

A number of 1:1 adducts with congruent melting points have been identified from phase studies between N_2O_3 and aromatic compounds such as toluene, m-xylene, mesitylene and anisole, although with benzene only the possibility of an incongruently melting compound was observed.[62] The compounds are considered similar to the N_2O_4 adducts with donation of electron density from the aromatic to the nitrogen oxide.

The pressure and temperature dependencies of linkage isomerization in the complexes $[M(NH_3)_5ONO]^{2+}$ where M=Co,Rh or Ir, have been determined in aqueous solution,[63] the volume profile indicating that the mechanism is intramolecular in agreement with previous work. In the case of the nickel complex, $[Nien_2(NO_2)_2]$, bands at ca.500 and 800nm characteristic of the nitro-form are replaced on heating to ca.124°C by bands due to isomeric nitrito-form which is less stable at room temperature.[64] However as the nitro form has the smaller volume, this should be pressure stable and indeed no isomerization occurs on heating under a pressure of 16kbars. Finally complex anions containing both the nitro and nitrito forms, i.e. $[Cu(NO_2)_4(ONO)_2]^{4-}$ and $[Ni(NO_2)_3(ONO)_3]^{4-}$, have been observed by electronic and i.r. spectroscopy on solidified melts from reactions of respectively copper sulphate and nickel chloride in the $LiNO_2$-KNO_2 eutectic at 120°C.[65]

Complex formation between nitric acid and Ph_3PO, Ph_3AsO, and a number of other phosphine and arsine oxides involves essentially hydrogen bonding with phosphorus compounds, but proton transfer reactions giving $R_3AsOH^+ \ldots NO_3^-$ are important with the more basic oxide.[66] An alternative preparative route to the trimethylsilyl and -germyl nitrates is outlined in equation (7), using the

$$(Me_3MN:)_2C + 2HNO_3 \longrightarrow 2Me_3MONO_2 + \tfrac{1}{2}(H_2NCN)_2 \quad \ldots(7)$$

appropriate carbodiimide at 0°C.[67] I.r. data point to the presence of unidentate nitrate groups.

The coordinated nitrate groups in $Sn(NO_3)_4$ oxidize triphenylphosphine in carbon tetrachloride solution giving $[Sn(NO_3)_2(Ph_2PO_2)]$, which has properties appropriate to a phosphinate bridged polymer with unidentate nitrate groups.[68] With nitric oxide the product is also a polymer formulated as $[OSn(NO_3)_2]_n$ while the nitrosonium compound, $(NO_2)_2[Sn(O_2CCF_3)_6].CF_3CO_2H$, is the product with trifluoroacetic acid. Bidentate nitrate groups are observed in the crystal structures of $Tl(NO_3)_3.3H_2O$,[69] $Ph_2Sn(NO_3)_2.Ph_3PO$,[70] $Ph_2Sn(NO_3)_2.Ph_3AsO$,[71] and $[Ce(NO_3)_4(H_2O)(4,4'\text{-bipyridyl})]^-$[72] leading to coordination numbers of 9 for thallium, 7 for tin and 11 for cerium. X-ray crystallography also shows that the N_2O_4 solvates obtained when $ScCl_3$ and yttrium metal react with N_2O_4 in ethyl acetate should be formulated as the nitrosonium salts $(NO)_2[M(NO_3)_5]$.[73] Although they have the same stoichiometry, the yttrium anion contains five symmetrically bidentate nitrate groups whereas with scandium four groups are bidentate and one is unidentate.

A reexamination of the $M(NO_3)_4$-Me_3PO system for M=Th or U shows that in addition to the already known compounds $M(NO_3)_4 \cdot 5Me_3PO$, two new neutral species, $Th(NO_3)_4 \cdot 2.67Me_3PO$ and $U(NO_3)_4 \cdot 3.33Me_3PO$, can be obtained.[74] Two ionic compounds have also been isolated which are formulated, following crystal structure determinations, as $[Th(NO_3)_3(Me_3PO)_4]_2[Th(NO_3)_6]$ and $Ph_4P[Th(NO_3)_5(Me_3PO)_2]$.

5.2 PHOSPHORUS

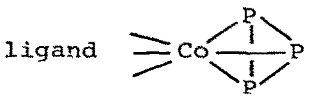
5.2.1 Phosphorus and Phosphides

Volatilization of red phosphorus as P_4 is catalysed by aluminium chloride according to new mass spectrometric data.[75] Methods for the direct formation of phosphorus-carbon bonds by the alkylation or arylation of elemental phosphorus with nucleophiles and under oxidizing conditions have been reviewed,[76] and white phosphorus has been shown to react readily with alkoxides[77] and alkanethiolates[78] following equation (8). The carbon tetrachloride serves as a

$$P_4 + \underset{X=O\text{ or }S}{6RX^-} + 6CCl_4 \rightarrow 4P(XR)_3 + 6CHCl_3 + 6Cl^- \quad \ldots(8)$$

source of positive chlorine and the rate determining step is considered to be the initial cleavage of a P-P bond.

Cobalt and nickel compounds containing cyclo-triphosphorus as a ligand are obtained when an excess of white phosphorus reacts in butanol with hydrated $Co(BF_4)_2$ or $Ni(BF_4)_2$ in the presence of the ligand 1,1,1-tris(diphenylphosphinomethyl)methane, $MeC(CH_2PPh_2)_3$.[79] The products formulated as $Co(P_3)L$ and $[LNi(P_3)NiL](BF_4)_2$ have the structures shown in (11) and (12) respectively with mean values for the Co-P and Ni-P distances of 2.30 and 2.35Å.



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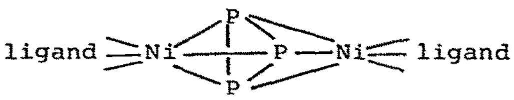

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New iron,[80] ruthenium,[81] and osmium[81] phosphides, MP_4 have been prepared from the elements in the presence of iodine. The compounds represent a new structure type in which the metal atom is surrounded octahedrally by phosphorus atoms while the phosphorus atoms are in tetrahedral coordination by metal and other phosphorus atoms. The iron structure and that for the heavier analogues differ, however, in the ways in which the MP_6 octahedra share corners and edges, reflecting the different steric and bonding requirements of the metals. Physical properties have been reported for single crystals of CuP_2, NiP_2 and RhP_3 obtained from reactions between the elements in a tin flux at temperatures up to 1150°C,[82] and from single crystal data the high temperature modification, β-Ta_3P, has the β-V_3S structure.[83] Twelve-membered Cu_6P_6 rings in which each copper atom is linearly coordinated by two phosphorus atoms and each phosphorus atom is in trigonal pyramidal coordination to three copper atoms are present in a Cu_3P_2 network present in the new ternary, $K_3Cu_3P_2$.[84] A second new copper ternary, CaCuP, crystallizes in the hexagonal system and most probably has a modified Ni_2In-type structure.[85] Different structures have been found for $BaZn_2P_2$ and its arsenic analogue, both compounds obtained by heating the elements to 1000°C.[86] While the phosphorus compound consists of layers of edge shared ZnP_4 tetrahedra (Zn-P, 2.486Å), in the arsenic derivative there is a three dimensional network of edge and vertex shared zinc-arsenic tetrahedra (Zn-As, 2.522-2.591Å) with the barium atoms accommodated in the holes in this network. Among other ternary compounds prepared and investigated are: NaMnX where X=P-Bi with the Cu_2Sb structure,[87] $CaMn_2X_2$ and $SrMn_2X_2$ where X=P or As with $CaAl_2Si_2$ structures,[88] KZnX where X=P or Sb with an Ni_2In structure,[89] ZrCoP, NbCoP, NbNiP and TaFeP with anti-$PbCl_2$ structures,[90] and $Ln_6Ni_6P_{17}$ where Ln=La, Ce or Pr which have structures closely related to $Cu_{12}Sb_4S_{13}$.[91]

The structure of $Au_7P_{10}I$, prepared from red phosphorus and gold using chemical transport with iodine, contains 12-membered phosphorus rings condensed into sheets (mean P-P, 2.23Å).[92]

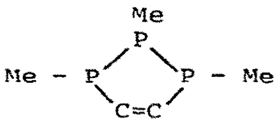
5.2.2 Compounds with P-P Bonds

I.r. and Raman spectra of the diphosphine MePHPHMe in the liquid phase are consistent with the presence of both the *trans* and *gauche* forms but in the solid state there is no evidence for the *gauche* rotamer.[93] Vibrational data have also been analysed for Ph_2PPPh_2 and its deutero analogue, PhXPPXPh where X=Br or I, and I_2PPI_2 and normal coordinate analyses carried out to assess the effect of substituent variation on the force constant for P-P stretching.[94]

An analogy has been drawn between tetraalkyl disilanes and the corresponding diphosphines to show that steric factors operating in both compound types are the same and there is thus no necessity to invoke a special electronic "gauche-effect" to rationalize conformational preferences in the diphosphines.[95] Finally, centrosymmetric trans structures are proposed for the tetra-n-propyl- and n-butyl-diphosphinedisulphides in the solid state from the absence of i.r. and Raman coincidences.[96]

The reaction of 1,2-dibromoethane and two mols of KPHPh leads, contrary to earlier reports, to 1,2-diphenyl-diphosphane, PhHPPHPh, which is stable at -30°C,[97] and this compound is also obtained by hydrolysis or alcoholysis of $(Me_3Si)PhPPPh(SiMe_3)$. The diphosphane on treatment with Ph_2PPPh_2 gives the asymmetric diphosphane $PhHPPPh_2$, but above -30°C, the diphenyldiphosphane disproportionates to give $PhPH_2$, $(PPh)_5$ and the triphosphane $H_2(PPh)_3$. The latter was identified from ^{31}P n.m.r. measurements which show the two A_2B and one ABC spin systems expected for the three possible diastereoisomers.[98]

Two new carbaphosphanes (13) and (14) are among the products from reactions between cis-1,2-dichloroethylene and $K_2(PMe)_4 \cdot 2THF$



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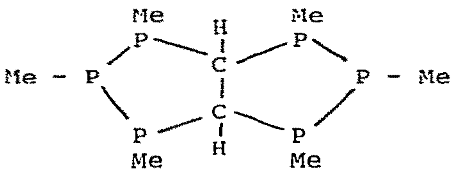
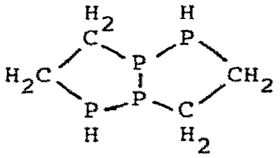


(14)

in benzene;[99] a full X-ray structure of (14) shows that the P_3C_2 ring has a skew chair conformation with the exocyclic methyl groups in axial positions giving an all-trans arrangement.[100] Mean P-C and P-P distances are 1.859 and 2.209Å respectively. Reaction of 1,2-bis(phosphino)ethane, $H_2PCH_2CH_2PH_2$, and either bromine or a phosphorus(III) halide such as $PhPCl_2$ leads to a new bicyclic secondary phosphane (15),[101] while hydrogen is eliminated when alkylene bis(phosphines), e.g. $H_2P(CH_2)_nPH_2$ or $RHP(CH_2)_nPH_2$, react with lithium alkyls.[102] The course of the reaction varies with the value of n, with compound (16) being obtained when n=3. The latter can be converted to a number of other derivatives, including the unusually stable bicyclic species(17).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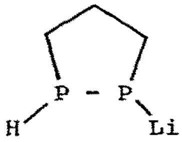
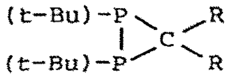
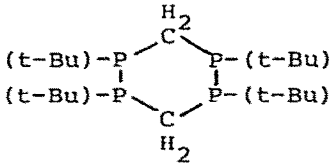
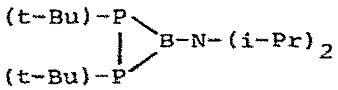

(16)


(17)

The linear diphosphane $K_2(P_2t\text{-}Bu_2)$ and either dichloromethane or 2,2-dichloropropane undergo [2+1] cyclo-condensation to give the novel three membered heterocycles (18);[103] the compound with


(18)
R=H or Me


(19)


(20)

R=H readily dimerizes to the dicarbatetraphosphane (19). In all these compounds n.m.r. spectroscopy points to an all-*trans* configuration for the t-butyl groups. A boron analogue of (18), i.e. compound (20) is the product of an analogous cyclo-condensation with $(i\text{-}Pr)_2NBCl_2$.[104]

Contrary to the general behaviour of cyclotriphosphanes, the new compound $(i\text{-}C_3F_7P)_3$ obtained when mercury abstracts iodine from $i\text{-}C_3F_7PI_2$ does not rearrange on long standing at room temperature.[105] Products with a spread of chain lengths, i.e. $K_2(t\text{-}BuP)_n$ where n=2,3 or 4, result when potassium in either THF or dioxan reacts with the cyclo-tetraphosphane $(t\text{-}BuP)_4$.[106] The product with n=2 being least soluble is readily isolated and can be converted by water and trimethylchlorosilane into the diphosphanes H(t-Bu)PP(t-Bu)H and $Me_3Si(t\text{-}Bu)PP(t\text{-}Bu)SiMe_3$ respectively.

Cyclopentaphosphanes in solution are readily characterized by ^{31}P n.m.r. spectroscopy and it has now been shown possible for unambiguous characterization in the vapour state.[107] The technique is He(I) p.e.s. when five clearly resolved, equal intensity, bands are observed that are associated with ionization from the phosphorus lone pair molecular orbitals. Data for a number of tri- and tetraphosphanes are also given. ^{31}P n.m.r. spectroscopy in solution has not given clear information on tetraphosphanes but analysis of the proton and fluorine decoupled spectra for $(RP)_4$, where $R=CF_3$, Et, i-Pr, t-Bu etc., in nematic phases confirms unambiguously the tetrameric structure and yields information on ring puckering etc.[108]

5.3.3 Bonds to Carbon or Silicon

A new method has been developed for the preparation of compounds containing phosphorus to carbon multiple bonds.[109] As an example two mols of HF are eliminated when trifluoromethylphosphine is passed over solid potassium hydroxide to give C-fluorophosphaethyne $FC{\equiv}P$. With either an increase in the phosphine flow rate or a reduction in the amount of potassium hydroxide, the reaction can be controlled to give $F_2C{=}PH$. Photoelectron and microwave spectra are also reported. A further, particularly stable compound containing a double bond can be obtained following the reactions in equation (9).[110] Elimination of hydrogen chloride occurs in

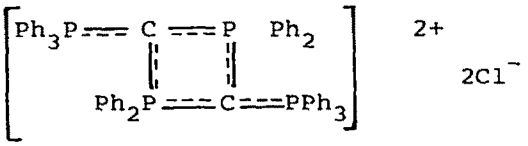
$$\underset{\text{R=mesityl}}{RPCl_2} \xrightarrow{LiCHPh_2} RPClCHPh_2 \xrightarrow{-HCl} RP = CPh_2 \qquad \ldots (9)$$

the presence of 1,5-diazabicyclo[5.4.0] undec-5-ene, and the product can be distilled under reduced pressure without decomposition. Bis[bis(trimethylsilyl)phosphano]ethane (<u>21</u>) reacts with pivaloyl chloride as shown in equation (10) to give (<u>22</u>), containing Me_3Si groups bonded to oxygen in addition to P-C double bonds.[111] A

$$\underset{(\underline{21})}{CH_2[P(SiMe_3)_2]_2} + t\text{-}BuCOCl \rightarrow \underset{(\underline{22})}{CH_2[P{=}C(OSiMe_3)t\text{-}Bu]} + 2Me_3SiCl \quad \ldots (10)$$

full X-ray structure is available showing a P-C distance of 1.69Å.

Continuing investigations into the reactivity of carbon tetrachloride now show that chloromethine bridged salts, $[R_3P{:}CCl.PR_3]Cl$, result with triethyl- and tributyl-phosphines,[112] and it has been possible to dechlorinate the analogous phenyl substituted salt $[Ph_3P{:}CCl.PPh_2Cl]Cl$ using tris(dimethylamino)phosphine to the carbodiphosphorane, $Ph_3P{:}C{:}PPh_2Cl$, as an isolable intermediate.[113] The final product is the dimeric diphosphacyclobutadiene derivative(<u>23</u>).



(<u>23</u>)

Vinyl and ethinyl phosphorus(III) compounds such as $CH_2{:}CHPX_2$, $CH_2{:}CHP(O)X_2$, or $HC\vdots CPF_4$ have been synthesized, and values of J(CP) from ^{13}C n.m.r. measurements correlated with the s character of the C-P bond.[114] Trifluorovinyl lithium and halogenated phosphanes react to give members of the series $Ph_{3-n}P(CF{:}CF_2)_n$,[115] and from a detailed vibrational assignment for trivinylphosphine it is concluded that the rules for C_3 molecular symmetry are followed.[116]

Metal carbonyls and 1,2-bis(dimethoxylphosphino)ethane(L) react photochemically to give compounds in the series $M(CO)_2L_2$ and $M(CO)_4L$ where M=Cr,Mo or W,[117] and a number of complexes have been formed between tri(t-butyl)phosphine and metal salts.[118,119] Two series of compounds are obtained with silver salts, i.e. $(t\text{-}Bu_3P)_2AgX$ and $(t\text{-}Bu_3P)AgX$, the former when $X{=}ClO_4$, BF_4, PF_6 or NO_3 are formulated as containing linear $[t\text{-}Bu_3P\text{-}Ag\text{-}Pt\text{-}Bu_3]^+$ cations while the latter for X=Cl, Br,I,CN or SCN are non-ionic.[118] The compound, $Hg(OAc)_2.t\text{-}Bu_3P$, containing bidentate acetate groups has also been prepared.[119] Silver halides react with the silyl- and germyl-phosphines, $t\text{-}Bu_2PEMe_3$, the chloride cleaving the P-E bond giving $t\text{-}Bu_2PAg$ while a tetrameric complex $(t\text{-}Bu_2PEMe_3.AgBr)_4$, possibly with a cubane structure results with silver bromide.[120]

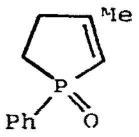
Increasing P-F and P-C bond lengths are observed from electron diffraction measurements on the compounds $t\text{-}Bu_nPF_{3-n}$ for n=1-3, and the results are compared with CNDO/2 calculations and the effects of steric strain.[121] Vibrational data for the compounds CF_3EMe_2 and $(CF_3)_2EMe$, where E=P,As, or Sb, have been assigned on the basis of C_s local symmetry and normal coordinate analyses carried out.[122]

Both sodium acetylphosphonate, $(MeCOPO_3H)^-Na^+$,[123] and the acylfluorophosphorane, $Ph_2PF_2C{:}O(Ph)$,[124] contain P-C bonds to the oxygen substituted carbon atom with lengths of <u>ca</u>.1.86Å. The latter,which has a trigonal bipyramidal structure, represents a new compound type and can be prepared from Ph_2POEt and benzoyl fluoride. Two new ligands, phenylphosphine diacetic acid,[125] and ethane-1,2-bis(phenylphosphino-acetic acid), $[CH_2P(Ph)CH_2CO_2H]_2$[126] have been prepared, the former from phenyldichlorophosphine and ethyl bromoacetate and the latter from the bis-phosphine salt, $KPhPCH_2CH_2PPhK$, and ethyl chloroacetate, and their complexing ability toward nickel(II) assessed.[127] The ligand 1,2-bis(diphenylphosphino)ethane reacts with either methyl or phenyl copper to give a compound with the formula $[Ph_2PCu(Ph_2PCH_2CH_2PPh_2)]_2.PhH$.[128]

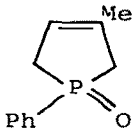
An X-ray crystal structure shows the presence of a four membered $(Ph_2P)_2Cu_2$ ring with Cu-P distances of ca.2.35Å; each copper atom is chelated by a molecule of the diphosphine ligand.

Fluxionality in five coordinate phosphorus compounds continues to be of interest and derivatives of the type $Me_2(CF_3)_2PX$[129] and $Me(CF_3)_3PX$,[130] where X=F,Cl,OMe, or SMe, have been prepared for detailed n.m.r. investigation. Trigonal bipyramidal structures are found in all cases with the axial positions being occupied by the fluorine atom and one CF_3 group for both $Me_2(CF_3)_2PF$ and $Me(CF_3)_3PF$. The pentasubstituted compound, $Me_2(CF_3)_3P$, is however non-fluxional.

Isoprene and phenyl dichlorophosphine undergo 1,4-cycloaddition to give after hydrolysis a mixture of the two isomeric 3-methyl-1-phenylphosphoiene-1-oxides, (24a) and (24b).[131] The former is in



(24a)



(24b)

the higher yield in this reaction but when phenyldibromophosphine is the starting material (24b) is produced isomerically pure.

The silylphosphines, $RP(SiMe_3)_2$ and $RPH(SiMe_3)$ where R=alkyl or aryl, have been prepared by the methods outlined in equations (11) to (14).[132] Using Me_2SiCl_2, $MeHSiCl_2$ or $t\text{-}Bu_2SiCl_2$ in place

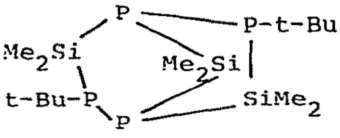
$$RPH_2 \xrightarrow{2MeLi} RPLi_2 \xrightarrow{Me_3SiCl} RP(SiMe_3)_2 + 2LiCl \quad \ldots (11)$$

$$HP(SiMe_3)_2 + RCl \longrightarrow RP(SiMe_3)_2 + HCl \quad \ldots (12)$$

$$RPHLi + Me_3SiCl \longrightarrow RPH(SiMe_3) + LiCl \quad \ldots (13)$$

$$RP(SiMe_3)_2 + MeOH \longrightarrow RPH(SiMe_3) + Me_3SiOMe \quad \ldots (14)$$

of Me_3SiCl in equation (13), the products are cyclic silyl phosphines, i.e. $(Me_2SiPMe)_3$, $(MeHSiPMe)_3$ and $(t\text{-}Bu_2SiPMe)_2$, resulting from rearrangement of initially formed silyldiphosphines such as $Me_2Si(PHMe)_2$.[133] The t-butyl analogue of this latter compound can however be isolated when t-BuPHLi and dimethyl dichlorosilane react but this reaction also gives the four membered heterocycle $(Me_2SiPt\text{-}Bu)_2$ and $(Me_2Si)_3P_4t\text{-}Bu_2$ shown by a single crystal X-ray investigation to have the norbornane structure (25).[134] Dilithiation of $Me_2Si(PHt\text{-}Bu)_2$ followed by reaction with diphenyldichlorosilane



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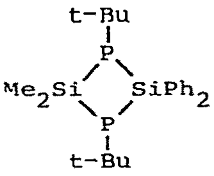

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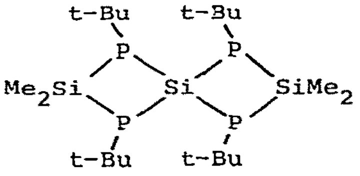
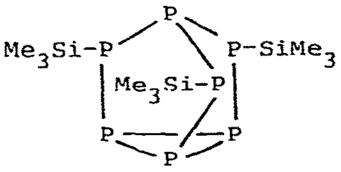


(27)

or silicon tetrachloride leads to respectively (26) and (27).[133]

White phosphorus after treatment with sodium-potassium alloy and reaction with trimethylchlorosilane is known to give $P_7(SiMe_3)_3$ (28), and a similar reaction with dimethyldichlorosilane has now been shown to give $P_4(SiMe_2)_3$ (29).[135] The structures of (28) and (29) from X-ray diffractometry are similar and related to that of P_4S_3.[136] P-P distances in the former vary between 2.214Å in the three membered ring to 2.179Å at the bridgehead atom; in



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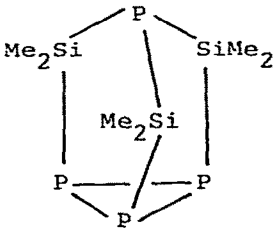
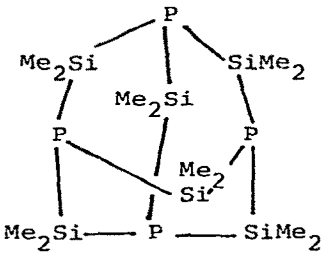


(29)

(29) the P-P distances are 2.202Å, and the P-Si distances are 2.283 and 2.247Å, the latter to the bridgehead atom. A more complex silaphosphine, $P_4(SiMe_2)_6$, which results from thermal decomposition of *inter alia* $Me_2Si(PH_2)_2$, $[(Me_3Si)_2P]_2SiMe_2$, or $(Me_3Si)_2PSiMe_2Cl$,[137] is an isotype of $P_4(GeMe_2)_6$ and has the adamantane structure (30).[138]

Among the compounds reported with bonds between phosphorus and a transition metal are (31) and (32),[139] the former resulting when tris(trimethylsilyl)phosphine reacts with $Mo(CO)_5Br$ and the latter when (31) is treated with methanol.



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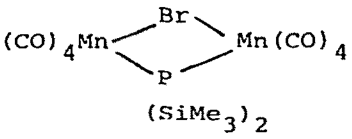

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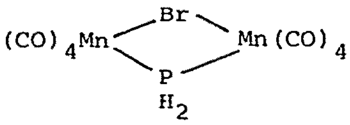


(32)

5.2.4 Bonds to Halogens

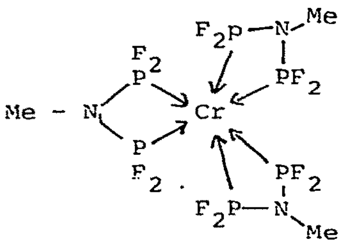
Phosphorus trifluoride reactions with H_2S or SO_2 to give respectively OPF_3 and SPF_3 are greatly influenced by the applied pressure, supporting a mechanism in which the rate determining step involves bond formation rather than decomposition of the sulphur reactant.[140] PF_3 can also be oxidized by sulphenyl fluorides such as CF_3SF or CF_2ClSF when the products are the corresponding mercaptotetrafluorophosphoranes, $RSPF_4$.[141]

Table 1. Reactions with Me_2NPF_2(L) and $MeN(PF_2)_2$(L')

Reactant	Products	Reference
Fe (vapour)	FeL_5, FeL'_4	142
Cr (vapour)	CrL_6, CrL_4L', $CrL_2L'_2$	143
Co (vapour)	$Co_2L_2L'_3$	144
$M(CO)_6{}^a$	ML'_3	145
$Fe(CO)_5$	$Fe(CO)L'_2$, $Fe_2(CO)_5L'_2$	145
$Ni(CO)_4$	$Ni_2(CO)_2L'_3$, $Ni_2(CO)_3L'_2$	145
$Co_2(CO)_8$	$Co_2(CO)_2L'_3$, $Co_2L'_5$	146
$Co_4(CO)_{12}$	$Co_4(CO)_{12-2n}L'_n{}^b$	146
$cpMn(CO)_3$	$cpMn(CO)L'$, $cpMnL'_2$	147
$[cpFe(CO)_2]_2$	$(cpFeCO)_2L'$, $(cpFeL')_2$	148

^{a}M = Cr,Mo or W ^{b}n = 2-5

In a series of papers, King and his coworkers have defined the ligand properties of the, respectively, mono- and bi-dentate aminophosphine ligands, Me_2NPF_2 ($\equiv$L) and $MeN(PF_2)_2$ ($\equiv$L'), toward metallic vapours, metal carbonyls and cyclopentadienyl metal carbonyls. The results, which are summarized in Table 1, include a number of full crystal structure determinations. The aminodiphosphine, L', can bridge as well as show bidentate characteristics as seen in the structures of the chromium and cobalt compounds shown diagrammatically in (33)[145] and (34)[144] while in the iron compound, $[cpFe(PF_2)_2NMe]_2$, one molecule of the ligand is cleaved to $NMePF_2$ and PF_2 fragments which, together with a complete ligand molecule, form a triple bridge between the two cpFe groups.[148] The carbon monoxide molecules in the product $Co_2(CO)_2L'_3$ obtained from $Co_2(CO)_8$ can be replaced on treatment with an excess of bromine giving $Co_2Br_4L'_3$, an X-ray structure showing surprisingly that the original Co-Co bond was preserved.[149]



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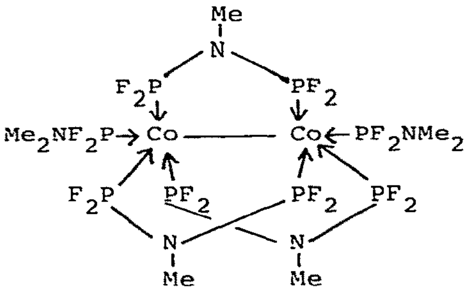
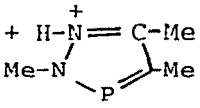


(34)

Methylhydrazones of primary alkyl ketones react with phosphorus trichloride according to equation (15) to give the diazaphospholium

$Me_2C{:}NNHMe + PCl_3 \longrightarrow 2HCl +$



Cl^- ... (15)

(35)

salt (35), which from X-ray data contains a planar five membered ring system.[150] This form is apparently stabilized with respect to that containing a P-Cl covalent bond by the possibility for π-electron delocalization. Monomeric compounds of the type $PCl_2(N{:}CR_2)$, $P(N{:}CR_2)_3$, $Ph_2P(N{:}CR_2)$ and $POCl_n(N{:}CR_2)_{3-n}$ where n=0-2, some of which are intensely coloured, are the products from reactions of phosphorus halides with amino-lithium reagents Li(N:CR$_2$) where R=Ph,t-Bu, etc.[151] An X-ray structure for P(N:CPh$_2$)$_3$ shows pyramidal coordination at phosphorus with P-N-C bond angles of 123°.

Multinuclear n.m.r. spectroscopy has been used to show that in scrambling reactions between PCl$_3$, POCl$_3$ or PSCl$_3$ and B(NEt$_2$)$_3$, the mixed compounds are formed in higher yields than expected on the basis of a random distribution.[152] The preferential affinity for chlorine of phosphorus over boron in the PCl$_3$ system and the reverse situation for the phosphoryl and thiophosphoryl system is discussed in terms of the Lewis acidity of boron and the effective electronegativity of the phosphorus moieties.

Analysis of vibrational data for (PF$_2$)$_2$O point to the presence of a single conformer with symmetry lower than C_{2v} in the solid state while at least two conformers are present in the liquid and gas phases, the more predominant form having C_1 symmetry.[153]

Ab initio calculations have been used to investigate a number of isomeric forms of trifluorophosphorane, PF$_3$H$_2$, and the calculated geometries are consistent with the well-known structural trend for long axial bonds.[154] According to further calculations intramolecular exchanges appear to occur through a series of Berry pseudorotation steps.

A number of main group fluorides including PF$_5$, AsF$_5$ and SbF$_5$ react with trifluoroacetate,[155] fluorosulphate,[156] and methanesulphonate[156] ions to give 1:1 octahedral complex ions. The compound PF$_4$ (acac), which can be isolated when PF$_5$ and acetylacetone react at low temperatures, contains two very similar basically octahedral molecules in the asymmetric unit.[157]

At room temperature, phosphorus pentachloride and chromyl chloride react in either POCl$_3$ or CCl$_4$ solution to give a novel complex formulated as (PCl$_4$) (CrOCl$_4$).[158] I.r. data suggest a monomeric anion, isostructural with VOCl$_4$.$^-$ Investigation of the acceptor properties of PhPCl$_4$ and PhPCl$_3$$^+$ shows formation of PhPCl$_5$$^-$ ions with the former in the presence of large stabilizing cations, while molecular 1:1 complexes are formed with unhindered pyridines.[159] With ligands such as 2,2'-bipyridyl or 1,10-phenanthroline (L), the products are ionic six-coordinate complexes (PhPCl$_3$L)Cl. Pyridine on the other hand with PhPCl$_3$$^+$, as either the hexachloro-phosphate or -antimonate, displaces the group 5 pentahalide to give the pyridine adduct of $PhPCl_4$, but stable ionic complexes $(PhPCl_3L)(MCl_6)$ result with the bidentate ligands (L).

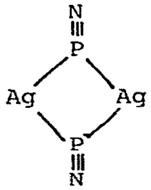
The preparation and possible stereochemistry of pentafluorophenyl phosphoranes in the series $(C_6F_5)_nPX_{5-n}$ where n=1 or 2 and X=F or Cl has been reported, together with reactions with Me_3SiOEt and $(Me_3Si)_2NMe$ giving products such as $(C_6F_5)_2POF$ and $[(C_6F_5)_2PFNMe]_2$.[160]

According to ^{31}P n.m.r. studies, phosphoryl halides are protonated at the oxygen atom in highly acidic solvents such as 100% sulphuric acid, oleum, HSO_3F and HSO_3Cl,[161] but whereas solutions of phosphoryl chloride are stable in the first two media, the corresponding bromide is solvolysed giving intermediates such as $PBr_2(OH)_2^+$. With phosphorus pentachloride, the initial products are PCl_4^+ and/or $PCl_3(OH)^+$ but further solvolysis occurs.

The product from a reaction between $POCl_3$ and o-toluidine has been shown by X-ray crystallography to be an oxygen-bridged compound $[(MeC_6H_4NH)_2P(O)]_2O$ rather than the expected trisubstituted derivative $(MeC_6H_4NH)_3PO$.[162] The substituted phosphoryl and thiophosphoryl chlorides Me_2POCl and Me_2PSCl are solvolysed at low temperatures by methylamine and molecular weight data for the products, $Me_2PONHMe$ and $Me_2PSNHMe$, point to association in solution.[163]

5.2.5 Bonds to Nitrogen

Matrix isolation techniques have led to isolation of a number of metal-phosphorus nitride species by cocondensation of metal vapours with gaseous PN generated by heating P_3N_5 to 900°C.[164] Products with the formula $M(PN)_2$ are obtained with copper, silver and gold while nickel gives $Ni(PN)_4$; at present it is not known whether coordination occurs via phosphorus or nitrogen but the bridged structure (35) is suggested for the silver compound.



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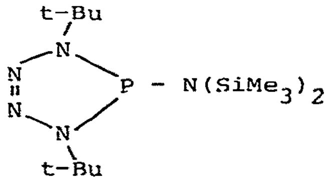
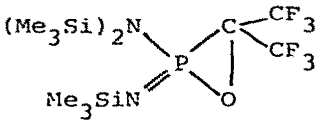


(36)

The 1:1 addition compound between t-butyl azide and the two-coordinated phosphorus(III) species, $(Me_3Si)_2NP:Nt\text{-}Bu$, from X-ray measurements has the tetraazaphospholidine structure (36)containing an almost planar five-membered ring, rather than the imino-bridged trizaphosphetidine alternative. The analogous two-coordinate monophosphazene, $t\text{-}Bu(Me_3Si)NP:Nt\text{-}Bu$ (L), on reaction with Zeise's salt gives the neutral, trans complex $PtCl_2L_2$ in which the ligands are bonded through the phosphorus atoms.[166] On treatment with water or methanol addition takes place across the P-N double bond. The versatility of these monophosphazenes is further demonstrated by the possibility of cycloaddition reactions between $(Me_3Si)_2NP:NSiM_3$ and both hexafluoroacetone and perfluorobiacetyl giving respectively (37) and (38).[167]



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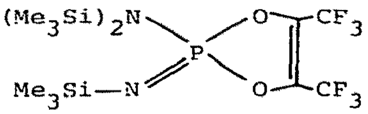


(38)

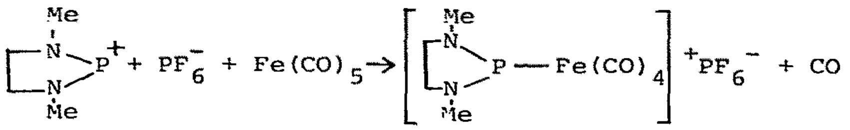
Reactions of substituted dialkylsulphurdiimides, $R_2S(:NSiMe_3)_2$, with diphenylchlorophosphine and dialkylchlorophosphines follow different routes as shown in equations (16) and (17).[168]

$$R^1_2S(:NSiMe_3)_2 + 2Ph_2PCl \longrightarrow R^1_2S(:NPPh_2)_2 + 2Me_3SiCl \quad \ldots (16)$$

$$R^1_2S(:NSiMe_3)_2 + 2R^2_2PCl \longrightarrow [R_2S(:NSiMe_3)(:NPR_2.PR_2)]^+Cl^- + Me_3SiCl \quad \ldots (17)$$

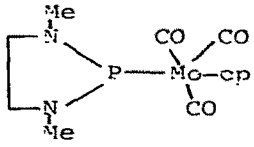
R^1, R^2 = Me or Et

The first X-ray data are now available for the two-coordinate phosphorus(III) cation, $(i\text{-}Pr_2N)_2P^+$, obtained when aluminium trichloride reacts with $(i\text{-}Pr_2N)_2PCl$.[169] P-N bond lengths are 1.61Å while the N-P-N angle at 114.8° is in agreement with trigonal planar hybridization at phosphorus. The geometry about the amine nitrogen atoms is close to planarity as might be expected for optimization of the conjugation of the nitrogen lone pairs and the empty phosphorus 3p orbital. The presence within such cationic species of a free electron pair and a positive charge should make them effective π-type Lewis acids as well as weak σ-type Lewis bases. That this is the case is demonstrated by the displacement of carbon monoxide by the cyclic cationic aminophosphine (39) shown in equation (18).[170] Reactions with strongly

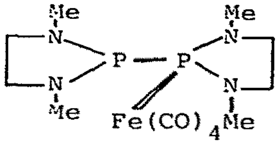


(39) ... (18)

nucleophilic transition metal reagents, including Na[Mocp(CO)$_3$] and Na_2[Fe(CO)$_4$], have also been described when products with structures (40) and (41) proposed on the basis of i.r. and n.m.r. data are obtained.[171]



(40)



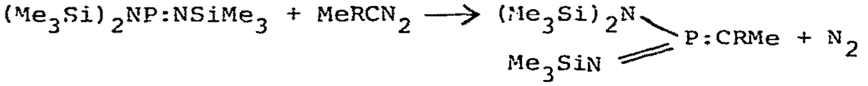
(41)

Crystal structures have been determined for tri(morpholino)phosphine and its piperidine analogue to investigate the relative orientations of the lone pairs on nitrogen atoms attached to a phosphorus(III) atom.[172] Both compounds show two small (*ca*. 98°) and one larger (*ca*. 110°) N-P-N bond angles and two short (*ca*. 1.69Å) and one long (*ca*. 1.73Å) P-N bond distance. The nitrogen atom associated with the long P-N bond is essentially sp^3 hybridized and the lone pair is *anti* to the phosphorus lone pair while there is sp^2 hybridization at the remaining nitrogen atoms and here the lone pairs are at *ca*. 90° to each other and to the phosphorus lone pair.

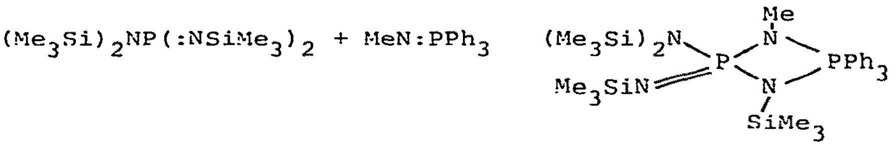
Square pyramidal and square planar nickel(II) complexes can be prepared with the bidentate ligand $PhN(PPh_2)_2$,[173] and a number of complexes have been reported for optically active ligands of the type $(Ph_2P)NCHRCO_2Me$, derived from Ph_2PCl and the appropriate L-α-aminoacid esters.[174]

In continuation of structural investigations of derivatives of the cage compound, $P_4(NMe)_6$, data are now reported for two fully oxidized forms $O_4P_4(NMe)_6$ and $S_4P_4(NMe)_6$[175] and for two polymorphs of the monothio compound $SP_4(NMe)_6$.[176] Although there were problems due to disorder, the phosphorus(V) species have structures with close to T_d symmetry and it is interesting that there is only a small effect on P-N bond distances when either oxygen or sulphur are added to the P_4X_6 core.[175] In the monothio compound, P-N distances range between 1.63 and 1.73Å with the shortest bond associated with the oxidized phosphorus atom.[176]

The successful isolation of a series of three-coordinate phosphorus(V) compounds which also contain a P-C double bond has been announced.[177] Such compounds, which have often been postulated as reaction intermediates, result from the reaction shown in equation (19) between α-alkyl diazoethanes and the two-coordinate monophosphazene discussed above. Amino-diimino phosphoranes and iminophosphoranes undergo addition as shown in equation (20) yielding a series of new diazadiphosphetidines,[178] while with methanol, as indicated in equation (21), aminoiminothiophosphoranes (42) yield bis(amino)thiophosphoric acids by addition across the P:NBu double bond.[179] Compounds (42) with R=t-Bu also reacts with, inter alia, $GeCl_4$, $SnCl_4$, PCl_3, $AsCl_3$ and $SOCl_2$ to give new four membered ring compounds such as (43), (44) and (45) as cis-trans isomer mixtures.



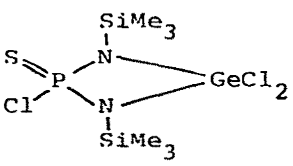
$$(Me_3Si)_2NP{:}NSiMe_3 + MeRCN_2 \longrightarrow (Me_3Si)_2N(Me_3SiN{=})P{:}CRMe + N_2 \quad \ldots \; (19)$$



$(Me_3Si)_2NP(:NSiMe_3)_2$ + MeN:PPh$_3$ ... (20)

$$(Me_3Si)RNP(:S)(:Nt\text{-}Bu) + MeOH \longrightarrow (Me_3Si)RNP(:S)(OMe)NHt\text{-}Bu \quad \ldots \; (21)$$

(42) R=Me_3Si or t-Bu



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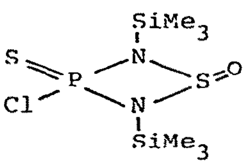

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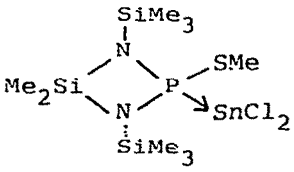


(45)

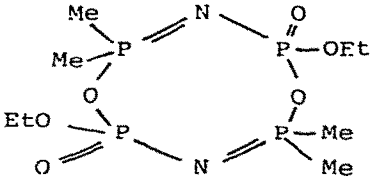
Trimethylchlorosilane is displaced when cyanogen chloride and silylated iminophosphoranes, $R_3P{:}NSiMe_3$, react to produce the cyanoimino derivatives $R_3P{:}NCN$.[180] Both 1:1 and 2:1 reactions have been observed between phosphoryl chloride and lithium bis(trimethylsilyl)amide, the former giving an N-silylphosphinimine, $Me_3SiN{:}PCl_2OSiMe_3$, rather than the isomeric substituted phosphine oxide $(Me_3Si)_2NP(O)Cl_2$.[181] The product from the 2:1 reaction is formulated as $(Me_3Si)_2NPCl(OSiMe_3)(:NSiMe_3)$.[182]

New halogeno-azides in the series $PX_n(N_3)_{3-n}$, $PSX_n(N_3)_{3-n}$, and $POX_n(N_3)_{3-n}$, where X=Cl or Br and n=1-3, can be obtained using sodium azide and the appropriate phosphorus halide in acetonitrile solution,[183] and identified by ^{31}P n.m.r. and solution i.r. spectroscopy. An excess of sodium azide leads to complete halogen displacement but $P(N_3)_3$ decomposes slowly in solution at room temperature to give a product probably analogous to the tetramer $P_5N_8Cl_9$. Azidobis(dimethylamino)phosphate and trimethyloxonium hexachloroantimonate react as shown in equation (22), the product

$$OP(N_3)(NMe_2)_2 + Me_3O^+SbCl_6^- \longrightarrow [(Me_2N)_2P(OMe)N_3]^+SbCl_6^- + Me_2O \quad \ldots(22)$$

decomposing on heating to give the $SbCl_5$ adduct of $OP(N_3)(NMe_2)_2$ by loss of methyl chloride.[184]

A new eight membered P-N-O heterocycle (46) is the product when diethylphosphoric amide$(EtO)_2P(O)NH_2$, reacts with dimethylchlorophosphinate in the presence of a tertiary base.[185] No vibrational



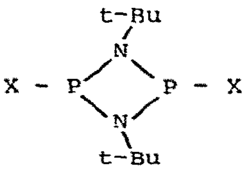
(46)

band, assignable to N-H stretching, can be found in the i.r. spectrum of imidobis(diphenylphosphinesulphide), $(Ph_2PS)_2NH$, at room temperature but a weak band at 3250 cm^{-1} appears on cooling the sample to -180°C.[186] On coordination to divalent transition metals this compound loses a proton giving products with the formula $M[(Ph_2PS)_2N]_2$.

Benzylmethylamino-fluorophosphoranes, $PhCH_2(Me)NPF_{4-n}R_n$ where R=Me or Ph and n=0-2, have been prepared,[187] and the thermal decomposition of both $Ph_2P(S)NHCH_2Ph$ and $Ph_2P(S)NHMe$ investigated.[188] The former yields hexaphenylcyclotriphosphazene while the linear triphosphazene $Ph_2P(NHMe){:}NPPh_2{:}NP(S)Ph_2$ is obtained, along with $Ph_2P(S)NMe_2$ and $Ph_2P(S)SMe$, is obtained with the latter.

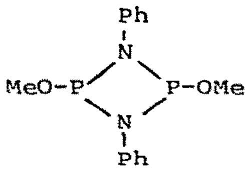
Non-equivalence of the i-propyl groups, previously suggested by n.m.r. data for N,N-di(i-propyl)-P-phenyl-phosphoramidic chloride $PhP(O)Cl(Ni\text{-}Pr_2)$, has now been confirmed by a full X-ray structure determination.[189] The P-N bond distance, 1.614Å, implies a substantial π-component which is said to be consistent with an n-σ* type interaction, i.e. the alternative to (p-d)π bonding.

<u>P-N Ring Compounds.</u> In addition to showing very different ^{31}P n.m.r. shifts, geometrical isomers of the cyclodiphosph(III)azanes (<u>47</u>) differ markedly in physical properties and in their reactivity with for example sulphur,selenium and methyl iodide.[190] Isomer identification in these systems has been aided by a demonstration from X-ray crystallography that the isomer of (<u>47</u>) $X{=}NC_5H_{10}$ with a small ^{31}P chemical shift has the <u>cis</u> configuration. Structure determination on two further diphosphazanes, (<u>48</u>) and (<u>49</u>), showed both compounds to have the alternative <u>trans</u> arrangement of substituents at the phosphorus atoms.[191] Detailed ^{31}P,[192] ^{1}H,[193] and ^{13}C[193] n.m.r. data for these and other phosphorous(III)-nitrogen compounds are now available showing, for example, that geometrical isomers have opposite signs for $^2J(PNP)$,[192] while for compounds with a methyl group <u>cis</u> to a phosphorus lone pair both J(PHCH) and J(PNC) are relatively large and positive.[193]

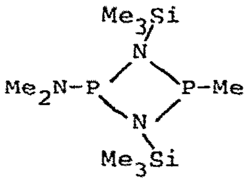


X=NMe$_2$ or OMe

(<u>47</u>)

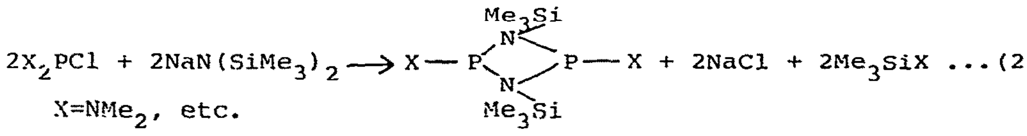


(<u>48</u>)



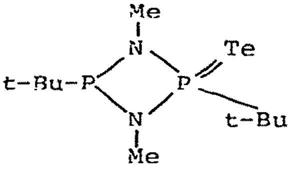
(<u>49</u>)

Cyclophosphazanes carrying a secondary amine group at phosphorus have been obtained by the reaction in equation (23) and while the products are almost exclusively in the <u>cis</u> form, on heating <u>cis-trans</u> mixtures are obtained.[194] A crystal structure determination for



...(23)

the phosphorus(III)-phosphorus(V) species (50) indicates a *cis* structure with a non-planar ring and P-N bond lengths of 1.683 and 1.750Å.[195]



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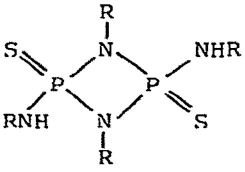

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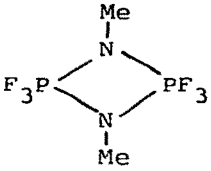
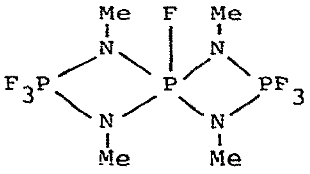


(52)

Thermolysis of trialkylphosphorothioic amides, $P(S)(NHR)_3$ where R=Me, Et, n-Pr, i-Pr, n-Bu, t-Bu, etc., in the range 190-240°C causes loss of two mols of amine with the formation of the cyclodiphosphazanes (51).[196] N.m.r. analysis points to the compounds having *trans* arrangements of the phosphorus substituents.

The product from a reaction between heptamethyldisilazane and the diphosphazane (52) can be separated into $(MeN)_6P_4F_8$ and two isomeric forms of the compound $(MeN)_4P_3F_7$.[197] One of these, with a tricyclic structure is already known but for the second isomer and the tetra-phosphorus compound spiro structures (53) and (54) are suggested.



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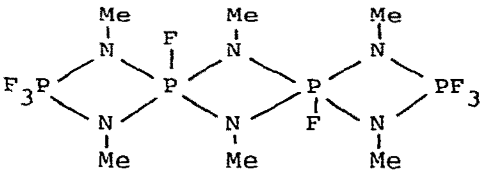
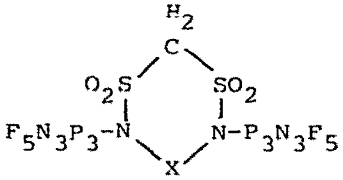
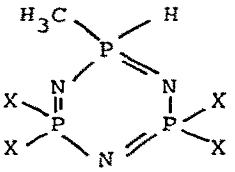


(54)

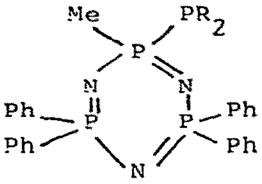
Similarities between O_2SF_2 and the N_2PF_2 unit from the cyclophosphazenes has been exploited in an application of the Xα method to show that there is substantial π-bonding with 3d orbital participation in each case.[198]

Hexafluorophosphazene reacts with 1- or 2-propenyl lithium[199] or cyclohexyl lithium[200] to give in each case the monosubstitution product. A geminally disubstituted compound can be obtained with 1-propenyl lithium but with the 2-propenyl analogue there is ring degradation. The fluorophosphazene also reacts with $N(SnMe_3)_3$ and $ClSO_2CH_2SO_2Cl$ to give $[P_3N_3F_5N(SnMe_3)SO_2]_2CH_2$ which can be cyclized on treatment with SCl_2 or $MePCl_2$ to (55 a and b) respectively.[201]


(55) a X=S
b X=PMe


(56) a X=Cl
b X=Ph

High yields of a new hydrido-cyclophosphazene (56a) have been reported from an unusual reaction between $P_3N_3Cl_6$ and methyl magnesium chloride, in the presence of $(n\text{-}Bu_3PCuI)_4$.[202] The compound is obtained only after addition of 2-propanol and it is suggested that an intermediate in which two phosphazene groups are attached to a copper atom is important. A second hydrido-compound (56b) reacts with diorganochlorophosphines to give after dehydrochlorination the P-P bonded species (57) while with methyldichlorophosphine, the bridged compound (58) is the product.[203]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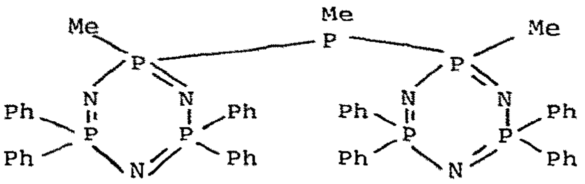

(58)

Amination of $P_3N_3Cl_6$ is kinetically controlled and with four mols of an amine the products are mixtures containing mainly the trans non-geminal isomer. In acetonitrile solution there is evidence for thermodynamic control and by carrying out reactions in this solvent at lower temperatures it has been possible to raise substantially the yield of the less favoured cis isomer.[204]

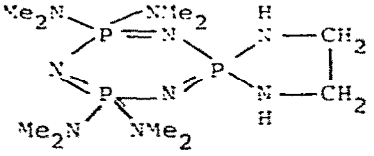
Potassium fluorosulphite in acetonitrile reacts with a number of non-geminal bis(dialkylamino)chlorotriphosphazenes to give pairs of isomeric cis and trans difluorides.[205] As found previously for the dimethylamine derivative attack occurs at the PCl_2 centre and the amine configuration of the starting material is retained. Data for bis(alkylamino)derivatives are also given. All three possible isomeric forms for $P_3N_3Cl_4(NHi\text{-}Pr)_2$ have now been isolated from reactions with four mols of i-propylamine and although the relative proportions of the gem-, cis- and trans-isomers vary with the solvent, the latter is always obtained in the largest amount.[206]

Mass spectrometric data for the phenylated cyclophosphazenes, $P_3N_3Ph_nCl_{6-n}$ where n=2,3,4,6, and the isomeric tetramers $P_4N_4Ph_4Cl_4$ enable species containing geminal and non-geminal phenyl groups to be differentiated.[207]

N-methylaniline reacts by a predominantly non-geminal path with $P_4N_4Cl_8$ to give the partial substitution products, $P_4N_4Cl_{8-n}(NMePh)_n$ where n=1,2(2 isomers), 3,4(5 isomers) and 6, but isomer yields are strongly solvent dependent.[208] 2,4- and 2,6-Aminotetraphosphazenes $P_4N_4Cl_6(NR^1R^2)_2$ give ^{31}P n.m.r. spectra which can be analysed as respectively AA'BB' and A_2B_2 spin systems.[209]

The higher cyclochlorophosphazene oligomers cannot be separated by vacuum fractional distillation as ring interconversions are induced giving substantial amounts of both the trimer and tetramer.[210] Similarly ring size changes are observed when mixtures containing $(PNCl_2)_{3-7}$ are treated with both butylamine and sodium phenoxide.

Among structural investigations in this area is a study of the spirocyclic phosphazene (59) which contains a non-planar P_3N_3 ring and a PN_2C_2 ring in the envelope conformation.[211] The angles

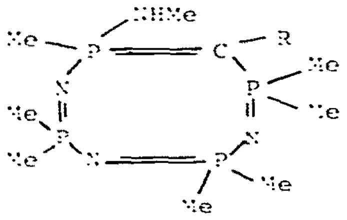


(59)

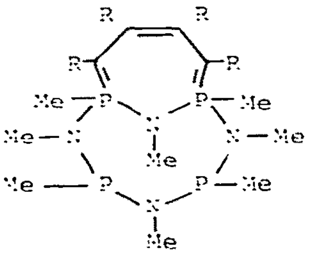
at the spiro-phosphorus atom in the five- and six-membered rings are 95.6 and 115.0° respectively, while the P-N distances are respectively 1.68 and 1.59Å. Orientation of the side chain in

$P_4N_4Cl_7(NPPh_3)$ differs from that in the corresponding trimer and probably represents a new type arising from specific steric factors.[212] The relationship between substituent orientation and ring conformation has been strengthened by data on a third isomeric form of the compound $P_4N_4Cl_4(NMe_2)_4$. Crystallographic investigation of the cis-trans-cis-trans isomer shows a structure similar to that of the corresponding tetrafluoride and, as expected, a ring conformation intermediate between the saddle and the tub.[213] A saddle ring conformation with equal P-N ring bond lengths (1.575Å) but exocyclic P-N distances of 1.679 and 1.656 is reported for the cyclotetraphosphazene fully substituted by pyrrolidine groups.[214]

Introduction of a carbon atom into the P_4N_4 ring system appears to cause no great conformational change nor are bond lengths greatly affected according to a structure determination on the azaphosphorine (60a) and its C-benzoyl derivative (60b).[215] The ring system of each compound is in the tub conformation and bond lengths in (60a) are P-N(endo) 1.609, P-C(endo) 1.717, P-C(exo) 1.815Å. Reaction of two mols of methyl acetylenedicarboxylate and the cyclic tetramer $(MePNMe)_4$ gives the bicyclic 1,2,7-azadiphosphepine (61).[216]



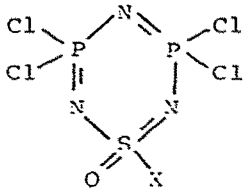
(60) a R=H
b R=COPh



(61) $R=CO_2Me$

The octafluoride, $P_4N_4F_8$, is the only tetrameric compound for which a planar ring system has been found and in view of this the structure of the pentameric fluoride is of some interest. This compound can be obtained in three monoclinic modifications, two of which have been investigated by low temperature X-ray diffractometry.[217] In neither form is the ring planar; the first contains a boat shaped ring with a pseudo-two-fold rotation axis passing through a phosphorus and a nitrogen atom, while the ring conformation in the second form is reminiscent of that found in $P_5N_5Br_{10}$. Mean P-N distances and P-N-P angles are 1.549Å and 137.4° for the first form and 1.546Å and 140.6° for the second.

Isothiocyanato derivatives of the mixed ring compound (62, X=F or Ph) have been isolated, the monosubstituted product being a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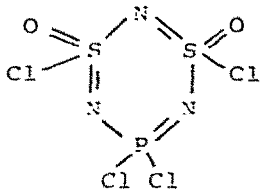
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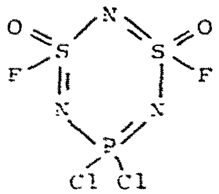
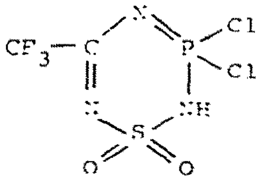

(64)

mixture of the expected geometrical isomers and the disubstitution product being the geminal isomer.[218] With dimethylamine, the cis-form of compound (63) gives a series of substitution products $PN_3S_2O_2Cl_{4-n}(NMe_2)_n$ with n=1 (four isomers), 2(three isomers), 3(two isomers), and 4(two isomers), which have been separated and assigned tentative structures on the basis of ^1H n.m.r. spectroscopy.[219] Reactions with piperidine in acetonitrile have also been investigated.[220] With the fluorine analogue (64), aminolysis takes place only at the phosphorus centre and the structures of the isomers obtained are discussed on the basis of ^{31}P n.m.r. spectra.[221]

Derivatives of a new six membered ring system can be prepared by a reaction between the trichloro-phosphazo derivative $CF_3CCl_2N:PCl_3$ and sulphamide as a mixture of the tautomers (65) and (66),[222] which on treatment with phosphorus pentachloride can be converted into (67, X=Cl). Reaction with antimony trifluoride gives initially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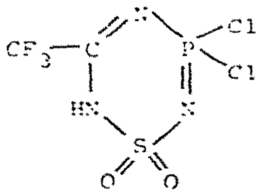
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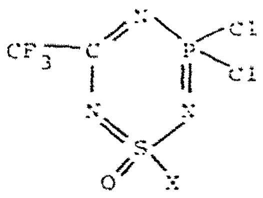
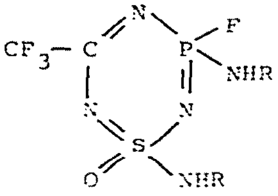

(67)

the S-monofluoride (67,X=F) but in the presence of aluminium trichloride further reaction leads to the P-difluoride.[223]

Reactions of (67, X=F) with primary and secondary amines have also been reported,[224] one of the products with the former is the rearrangement compound (68). A second new type of heterocycle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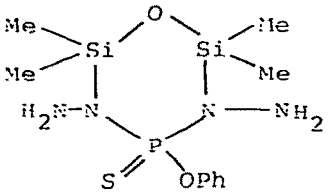

(69)

(69) results when phenoxythiophosphoryl dihydrazide and dimethyldichlorosilane are hydrolysed in tetrahydrofuran in the presence of triethylamine.[225]

5.2.6 Bonds to Oxygen

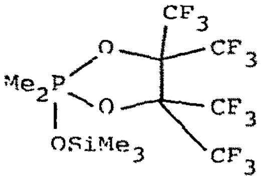
Anhydrous cobalt(II) and nickel(II) hypophosphites can be prepared either by treating the metal benzoate with the anhydrous acid or by dehydrating the hexahydrates with 2,2-dimethoxypropane.[226] Magnetic measurements are typical of high spin octahedral stereochemistry in each case but i.r. spectroscopy indicates that probably both chelating and bridging H_2PO_2 groups are present.

Structures are reported for both $Na_2HPO_3.5H_2O$[227] and $Cd(H_2PO_3)_2.H_2O$.[228] The phosphite ion in the former lies on a mirror plane with values of 1.525 and 1.522Å for the independent P-O bonds, the P-H distance is 1.39Å. Coordination about cadmium in the second compound is distorted octahedral but pairs of octahedra share an edge giving Cd_2O_{10} units. Two H_2PO_3 groups are joined by a medium strength hydrogen bond so that the anion can be considered as one $H_4P_2O_6{}^{2-}$ species. Solubility studies have been reported for the $MHPO_3$-H_3PO_3-H_2O systems where M=Fe(II) and Cr(II),[229] and it has been shown that the Group 2 orthophosphites, $M(H_2PO_3)_2$ can be dehydrated to give the corresponding diphosphites $MH_2P_2O_5$.[230]

A new mixed phosphinous-phosphinic acid anhydride has been isolated using the method shown in equation (24),[231] and good yields of the trimethylsilylester of dimethylphosphinous acid,

$$(CF_3)_2POP(CF_3)_2 + (CF_3)_2P(O)Cl \longrightarrow (CF_3)_2POP(O)(CF_3)_2 + (CF_3)_2PCl \quad \ldots (24)$$

$Me_2POSiMe_3$, have been reported from the treatment of dimethylphosphinous acid and Me_3SiNMe_2.[232] The compound is oxidized by sulphur and gives $Me_2P(OSiMe_3)(:NSiMe_3)$ when treated with trimethylsilyl azide. Thermolysis at 80°C leads to the diphosphane monoxide, $Me_2P(O)PMe_2$, while with hexafluoroacetone the dioxaphospholane (70) can be isolated. Similar 1,3,2-dioxaphospholanes



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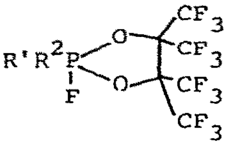

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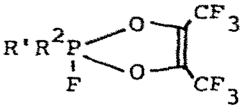
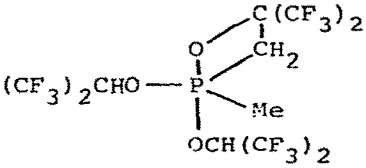


(72)

(71) or 1,3,2-dioxaphospholenes (72) result when fluorophosphines or fluorophosphites react with respectively hexafluoroacetone or hexafluorobiacetyl.[233] With phosphine and methyl phosphine, there is confirmation that hexafluoroacetone gives the insertion products $H_2PC(CF_3)_2OH$ and $MeHPC(CF_3)_2OH$, and in addition two di-insertion compounds $HP[C(CF_3)_2OH]_2$ and $MeP[C(CF_3)_2OH]_2$ have been isolated.[234] A similar product cannot be isolated using Me_2PH and here the reaction gives a mixture of Me_2PPMe_2, $Me_2P(O)OCH(CF_3)_2$, and the fluxional phosphorane $Me_2PF[OCH(CF_3)_2]_2$.

A series of hexafluoro-iso-propoxy derivatives of phosphorus(III) has been obtained from reactions between inter alia PCl_3,[235] PBr_3,[235] Me_2PCl[236] or $MePCl_2$[236] and the lithium salt $LiOCH(CF_3)_2$. The two trihalides gave mixtures of all three possible products, $PX_n[OCH(CF_3)_2]_{3-n}$ where n=0-2, while the products from the methyl derivatives, e.g. $Me_2POCH(CF_3)_2$, gave 1,2-oxaphosphetanes such as (73) on further reaction with hexafluoroacetone.[236] The expected dichloro-phosphorus(V) compound, $Cl_2P[OCH(CF_3)_2]_3$, can be obtained from the phosphite and chlorine, which then can react with two mols



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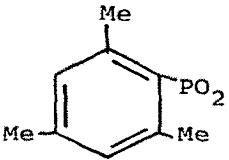
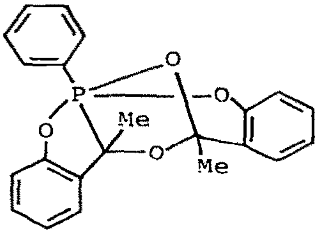


(74)

of $LiOCH(CF_3)_2$ to give the penta-alkoxide $P[OCH(CF_3)_2]_5$ as a low melting solid.[237] Other phosphorus(V) species, such as $R_nP[OCH(CF_3)_2]_{5-n}$ where R=Me or Ph and n=1 or 2, result when the appropriate phosphorus(III) alkoxide is oxidized by chlorine in the presence of $LiOCH(CF_3)_2$.[238]

Evidence for the formation of the monomeric mesitylmetaphosphonate (74) has been obtained during the pyrolysis of Diels-Alder adducts of mesityl-2,4-butadienylphostinate.[239]

In the presence of triethylamine, phenyldichlorophosphine and o-hydroxyacetophenone give a product with the expected stoichiometry $PhP(OC_6H_4COMe)_2$, but crystallographic methods show it to have an unusual tricyclic oxyphosphorane structure (75) with distorted trigonal bipyramidal coordination about phosphorus.[240]



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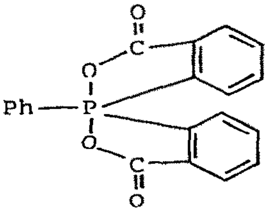

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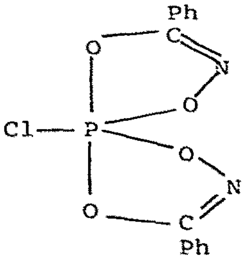
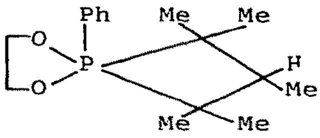


(77)

The general problem of the stereochemistry about phosphorus(V) in spirocyclic compounds has attracted wide attention this year with detailed crystallographic data showing an increasing number of structures falling on the Berry exchange coordinate between the trigonal bipyramidal arrangement and the less favoured square pyramidal structure. Two compounds (76)[241] and (77)[242], both containing chelating groups, in fact have structures close to ideal trigonal bipyramidal while with compound (78)[243] and the two catecholates $PhP(O_2C_6H_4)_2$[244a] and $t\text{-}BuP(O_2C_6H_4)_2$[244b] the structure is only slightly displaced from square pyramidal. Increasing distortion along the Berry coordinate is found for



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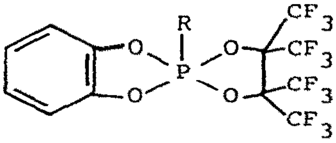
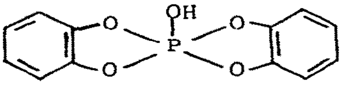


(79)

$(OCH_2CH_2NH)_2PH$ and $(OC_6H_4NH)_2PH$ obtained from tris(dimethylamino) phosphine and respectively ethanolamine and o-aminophenol,[245] and for the perfluoropinacol derivatives (79, R=t-Bu or Ph).[246]

Finally in this area, Holmes[247] has developed a model based on the pseudo-rotation hypothesis, which enables the relative stabilities of all trigonal bipyramidal and square pyramidal isomers of a given five-coordinate phosphorus compound to be estimated. The results give isomer energies in agreement with those from *ab initio* calculations and reproduce the ΔG values for intramolecular ligand exchange processes. Apicophilicity scales can be constructed and the model incorporates ring strain and other steric terms.

^{31}P n.m.r. spectra point to an equilibrium in acetonitrile solution between the phosphorane (80) and phosphate (81) forms of the product obtained when the siloxy-spirophosphorane (82) reacts with hydrogen chloride. In the solid state the phosphate structure (81) is stabilized probably because of strong intermolecular O-H...O=P hydrogen bond formation.[248] A similar problem arises with the product obtained from phosphoryl chloride and benzilic acid but here the equilibrium lies wholly towards the penta-coordinated form (83).[249] Aryl hydroxamic acids RC(O)NHOH react with phosphorus(V) halides to give products such as (84).[240] Substitution followed by intramolecular addition takes place when chlorophosphines react with benzil mono(o-hydroxyanil) as shown in equation (25) to give the bicyclic product (85).[251] The



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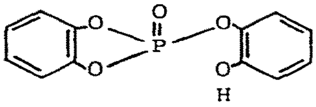

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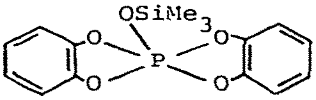

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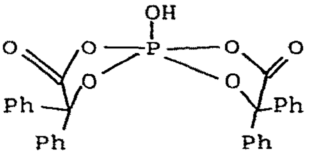

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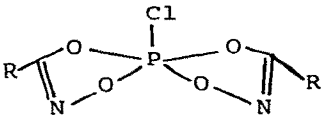
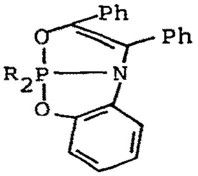


(84)

$R_2PCl + HOC_6H_4N{:}CPhCPh({:}O) \longrightarrow$



... (25)

(85)

phosphorus coordination number can be increased to six by addition of alkali metal salts in the presence of a cryptand.

The acceptor properties of phosphorus(V) chlorides substituted with catechol, i.e. $PCl_3(O_2C_6H_4)$ and $PCl(O_2C_6H_4)_2$, toward chloride ion and pyridine have been assessed by ^{31}P n.m.r. spectroscopy and the former shown to be comparable to $PhPCl_4$.[252] Both compounds give cationic species on treatment with antimony pentachloride which are highly reactive probably on account of their strained geometry. The coordination number is readily increased to six on treatment with 2,2'-bipyridyl or 1,10-phenanthroline. A similar cation, $[P(O_2C_6H_4)_2(2,2'\text{-bipy})]^+$, as the hexafluorophosphate has been examined crystallographically showing a slightly distorted octahedral arrangement with mean P-O and P-N bond lengths of 1.67 and 1.90Å respectively.[253]

Structural data are now available for two aluminium phosphates, $Al(H_2PO_4)_3$[254] and $Al(H_2PO_4)(HPO_4).H_2O$.[255] The former consists of isolated AlO_6 octahedra and corner sharing $O_2P(OH)_2$ tetrahedra stacked to form columns parallel to the c axis, while the latter consists of layers of $AlO_5(OH_2)$ octahedra sharing vertices with $PO_2(OH)_2$ and $PO_3(OH)$ tetrahedra. In $Sn(H_2PO_4)_2$ each tin(II) ion is coordinated by oxygens from four different $H_2PO_4^-$ groups with the latter linked together by strong hydrogen bonds into infinite chains,[256] and crystal data for $Hf(H_2PO_4)_3.H_2O$ point to a layer structure similar to that in the well-known α-zirconium phosphate ion exchanger.[257]

Up to five different ^{31}P n.m.r. peaks have been observed in various solutions of gallium phosphate which with the help of data from ^{71}Ga resonances can be assigned to uncomplexed phosphate, $GaH_3PO_4^{3+}$, $GaH_2PO_4^{2+}$, a polymeric gallium phosphate and a complex with the $H_5P_2O_8^-$ ion.[258]

The carbamoyl phosphate ion $(O_3PO.CONH_2)^{2-}$ obtained when potassium dihydrogen phosphate reacts with potassium cyanate gives Group 2 metal salts which decompose in aqueous suspension at room temperature and when heated above 100°C.[259]

On heating, potassium fluorophosphate $KHPO_3F$ loses hydrogen fluoride rather than water with formation of the trimetaphosphate salt.[260] Silicon,[261] tin[262] and antimony[262] difluorophosphates can be prepared from reactions between the appropriate halide and the free acid either alone or mixed with $P_2O_3F_4$. In addition to $Si(PO_2F_2)_4$ a second product, $H[Si(PO_2F_2)_5]$, results with silicon tetrachloride.[261] The tin compound, $Cl_2Sn(PO_2F_2)_2$, is formulated as a polymer with difluorophosphate bridges, while for the two antimony compounds, $Cl_4Sb(PO_2F_2)$ and $F_4Sb(PO_2F_2)$, discrete dimers are considered present on the basis of spectroscopic evidence.[262] Coordination polymers formulated as $M(PO_2Cl_2)_2.2D$, where M=Ca, Mg or Zn, have been obtained from reactions between metal oxides and $P_2O_3Cl_4$ in an oxygen donor solvent (D) such as ether, dioxan or $POCl_3$.[263]

Complex ions containing coordinated di- and tri-phosphate groups have been prepared by displacement of water from $[Co(NH_3)_5(H_2O)]^{3+}$ or $[Coen_2(H_2O)_2]^{3+}$.[264] From ^{31}P n.m.r. results the two isomeric forms which exist for the triphosphate complex of the former are formulated as $[(H_3N)_5CoOPO_3PO_3PO_3]^{2-}$ and $[(H_3N)_5CoOP(:O)(OPO_3)_2]^{2-}$ respectively.[264] A hydrated cyanamido-triphosphate, $Na_5P_3O_9NCN$, has been isolated from a reaction between trimetaphosphate and sodium cyanamide and its properties studied.[265]

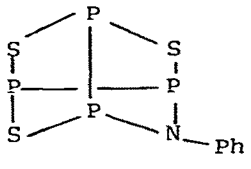
Topotactic conversions of $Pb_2P_4O_{12}.4H_2O$ to the dihydrate[266] and the latter to $Pb_2HP_3O_{10}$[267] have been investigated. A crystal structure determination for $Pb_2P_4O_{12}.2H_2O$ shows the presence of two independent centrosymmetric P_4O_{12} rings interconnected by lead atoms,[266] and for $Pb_2HP_3O_{10}$ the tripolyphosphate ion has mirror symmetry about a plane passing through the central phosphorus atom.[267]

Among papers discussing apatites are three concerned with oxygen species. One which is formulated as $Ca_{10}(PO_4)_6O\square$ is only stable between 850 and 1050°C in a vacuum or in the presence of anhydrous gases;[268] these very specific conditions for stability may account for the controversy concerning this oxyapatite. Below ca. 800°C the compound rehydrates to the stable oxy-hydroxy-apatite while above 1050°C decomposition occurs to a mixture of tri- and tetra-calcium phosphates. Oxyapatites of calcium and strontium can be converted to peroxy species by heating in the presence of oxygen,[269] and the general problem of apatitic structures containing oxygen in different oxidation states has been discussed.[270]

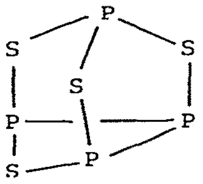
The properties of zirconium phosphate ion exchangers continue to attract attention; this work is not discussed in detail but new information is included in references 271-281. Titanium phosphate, α-Ti(HPO$_4$)$_2$.H$_2$O, is isomorphous with the better known zirconium compound but investigation of its ion exchange properties is limited by the ready hydrolysis of the phosphate groups.[282] A series of titanium-zirconium-phosphate solid solutions can be formed and these are of interest as the smaller passageways associated with the titanium compound may modify the ion selectivity. A second variation on the zirconium phosphate structure results when fluorozirconates are slowly decomposed in the presence of hydroxymethane-phosphonic acids.[283] The products with formulae such as Zr(HOCH$_2$PO$_3$)$_2$.H$_2$O have layer structures and intercalation of alkylamines has been observed.

5.2.7 Bonds to Sulphur or Selenium

In agreement with ^{31}P n.m.r. spectroscopy, a highly symmetrical (D_{2d}) structure analogous to that in realgar (As$_4$S$_4$) has been obtained from X-ray data for α-P$_4$S$_4$.[284] Values for the P-S and P-P distances are 2.108 and 2.350Å respectively while S-P-S and P-S-P angles are 95.1 and 98.9° respectively. Aniline and α-P$_4$S$_3$I$_2$ react at 25°C to give in addition to α-P$_4$S$_4$, for which structural data are also presented, a second new compound, α-P$_4$S$_3$(NPh).[285] On the basis of spectroscopic data, this compound is assigned structure (<u>86</u>) in which an N-Ph group bridges the opened edge of the initial α-P$_4$S$_3$I$_2$ structure. With β-P$_4$S$_3$I$_2$, reaction with aniline gives the diazadiphosphetidine [S$_2$P$_2$(NPh)$_2$(NHPh)]$_2$, in addition to P$_4$S$_3$ and β-P$_4$S$_4$; structure (<u>87</u>) is suggested from spectroscopic data for the latter.



(<u>86</u>)

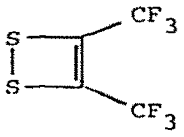


(<u>87</u>)

Hydrolysis of P$_4$O$_6$S$_4$ at 0°C in ammonium hydrogen carbonate solution yields a tetrathiocyclotetraphosphate salt, (NH$_4$)$_4$(P$_4$O$_8$S$_4$).2H$_2$O.[286]

He(I) p.e.s. for HS_2PF_2, $M(S_2PF_2)_2$ where M=Mn,Co,Ni or Zn, and $Cr(S_2PF_2)_3$ have been measured and assigned, and a series of six main bands identified which correspond to all the p-electron based σ- and π-molecular orbitals of the chelate rings.[287] Dithiophosphinate groups in $[Co(S_2PPh_2)_2.quinoline]$ span axial and equatorial positions in a basically trigonal bipyramidal structure from a recent X-ray diffraction study on this new compound.[288] The quinoline molecule lies in the equatorial plane. Lanthanoid dithiophosphinate complexes with the formulae $Ln(S_2PR_2)_3$ for $R=C_6H_{11}$ and $Ln(S_2PR_2)_4^-$ for R=Me, OEt or C_6H_{11} have been isolated.[289] Steric forces are important in determining the nature of the product with, for example, the cyclohexyl phosphinate giving anionic complexes with the lighter (larger) lanthanoids while with the smaller lanthanoids (Sm-Ln) only neutral tris complexes can be produced. Two structural types occur in solution for compounds with the formulae $Ph_4As\,[Ln(S_2P(OEt)_2)_4]$ from ^1H and ^{31}P n.m.r. spectra, again associated with lanthanoid size.[290]

Phosphorus(V) compounds containing a five-membered ring with two sulphur atoms bonded to phosphorus are often the products when the thiete (88) reacts with trivalent phosphorus compounds such as $PhPH_2$, $PhPCl_2$, $(MeO)_3P$.[291] The pyridinium fluorodithiophosphoric betaine (89) with hydrazine and phenyl hydrazine gives respectively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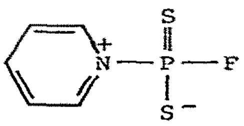

(89)

(pyH)$(FPS_2NHNHPS_2F)$ and (pyH)$(PhNHNHPS_2F)$, while with hydrogen sulphide the product is the pentathiodiphosphate, (pyH)(FPS_2SPS_2F).[292] Di-Grignard reagents react with thiophosphonic anhydrides as shown in equation (26), and the resulting acids can be readily converted to the corresponding salts, esters, amides and chlorides.[293]

$$(R^1PS_2)_2 + XMg{-}R^2{-}MgX \longrightarrow HS(S)P(R^1){-}R^2{-}P(R^1)(S)SH \quad \ldots \quad (26)$$

R^1 = Me, Ph or $4\text{-}MeOC_6H_4$

$R^2 = (CH_2)_{4,5,6,8,10}$

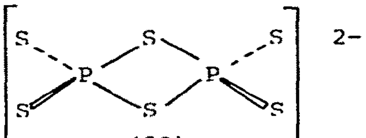
New mixed valence thiophosphorus compounds containing chiral centres can be obtained from reactions such as (27) and (28).[294]

$$X_2PS_2H + CF_3(F)PNMe_2 \longrightarrow X_2P(S)SP(CF_3)F + Me_2NH \qquad \ldots \text{ (27)}$$
X=F or CF_3

$$CF_3(F)P(S)SH + X_2PNMe_2 \longrightarrow CF_3(F)P(S)PX_2 + Me_2NH \qquad \ldots \text{ (28)}$$
X=F or CF_3

N.m.r. characterization is reported while magnetic non-equivalence is noted, particularly at the phosphorus(III) centres, as a consequence of the chirality.

The products obtained from heating mixtures of silver and phosphorus in the presence of either sulphur or selenium have been shown to be $Ag_2P_2S_6$[295] and $Ag_4P_2Se_6$[296] respectively. The former is a hexathiodimetaphosphate (89) with terminal and bridging P-S distances of 1.99 and 2.12Å respectively,[295] while the latter consists of P-P bonded anions (90) in which the mean P-Se and P-P distances are 2.19 and 2.30Å respectively.[296] An X-ray structure shows, however, that both anion types are present in crystals of $Zn_4(P_2S_6)_3$.[297] Other compounds containing anions with this stoichiometry including $Ag_4P_2S_6$, $Tl_4P_2Se_6$, $In_4(P_2S_6)_3$ and $In_4(P_2Se_6)_3$ have been prepared from mixtures of phosphorus, sulphur and the appropriate metal sulphide or selenide.[298] X-ray data point to a defect $Fe_2P_2S_6$ structure for $In_4(P_2S_6)_3$, while in $InPS_4$, indium and phosphorus atoms occupy tetrahedral sites in a cubic close packed array of sulphur atoms.[299]



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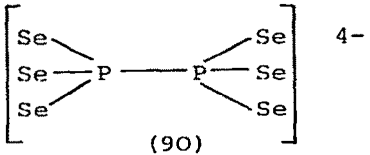
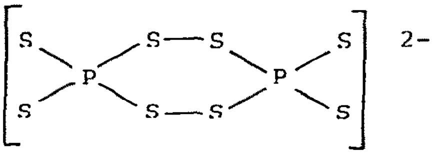


(90)

A sulphur-rich derivative, $Hg_2P_2S_7$, has now been prepared from a stoichiometric mixture of mercury(II) sulphide, red phosphorus and sulphur and shown by X-ray crystallography to contain the thiodiphosphate $(S_3PSPS_3)^{2-}$ anion.[300] The P-S bridge bonds 2.108Å, are a little longer than the terminal distances (mean, 2.029Å); the angle at the bridging sulphur is 108.6° and the PS_3 groups are almost eclipsed.

A compound with the formula $(py_2H)_2(P_2S_8)$ results when P_4S_{10} and pyridine react, probably in the presence of a trace of moisture.[301] The anion shown in (91) contains a six-membered ring system in



(91)

the chair conformation with two different exocyclic P-S distances, 1.946 and 1.966Å; the P-S distance in the ring is 2.130Å.

Attempts to obtain crystals of Cu_7PS_6 by halogen transport led to Cu_6PS_5Br, for which a crystal structure was obtained.[302]

5.3 ARSENIC

5.3.1 Arsenides

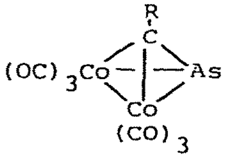
Structures have been determined for a number of lanthanoid arsenides; that for $NdAs_2$ represents a new structure type and contains almost planar As_4 zig-zag chains.[303] These are centrosymmetric with terminal and bridging As-As distances of 2.477 and 2.497Å respectively and As-As-As angles of 104.3°. The basic structural unit in both the high and low temperature forms of Eu_5As_3[304] and in Eu_5As_4[305] is an $AsEu_6$ trigonal prismatic unit. The triarsenides crystallize with respectively a disordered variant of the Ca_5Pb_3 structure and the Mn_5Si_3 structure, while Eu_5As_4 is found with a more symmetrical version of the Sm_5Ge_4 structure. The ternary arsenides $CaMn_2As_2$, $SrMn_2As_2$ and $BaMn_2As_2$ have been prepared from the elements;[306] structure determinations show arsenic to be in seven-fold coordination in the calcium and strontium compounds but in nine-fold coordination by four Mn(2.560Å), four Ba(3.484Å) and one As atom (3.745Å) in the barium analogue.

Cobalt and nickel complexes containing cyclo-triphosphorus as a ligand have been mentioned earlier,[79] and parallel experiments in the presence of yellow arsenic lead to complexes with the formula $[(ligand)M(\mu\text{-}As_3)M(ligand)]X_2$ for M=Co or Ni and $X=BF_4$ or BPh_4.[307] A triple decker structure analogous to that shown in (12) is confirmed from X-ray diffraction for these products.

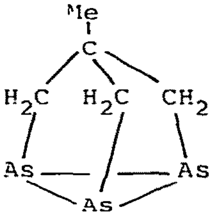
Experiments with S_2Cl_2 and substituted Group 5 chlorides have now been extended to show that with $MeAsCl_2$ and $MeSbCl_2$ the products are homoatomic species such as $(MeAs)_x$ and $(MeSb)_x$ rather than the alternative heteroatom catenates.[308]

5.3.2 Bonds to Carbon

A new type of hybrid main group-transition metal cluster compound shown in (92) contains a coordinated arsa-acetylene RC≡As.[309] These compounds are obtained from $Co_2(CO)_8$ and $RCCl_2AsCl_2$ and although it was thought they might serve as a source of the unknown arsa-acetylene, thermolysis at 200°C gave only Co_2As.


R=Me or Ph

(92)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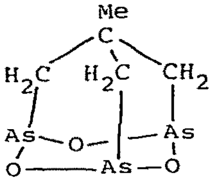
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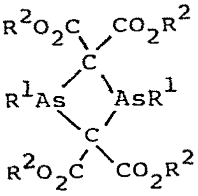

(95)

Structural data for the cyclotriarsane (93) first prepared in 1974, show that the molecule possesses a plane of symmetry but the overall symmetry is close to C_{3v};[310] As-As distances are 2.422 and 2.405Å, with As-As-As angles of 59.7 and 60.5° and As-As-C angles close to 90°. A new polyfunctional halogenoarsine, $MeC(CH_2AsI_2)_3$, has been obtained by selective cleavage of the Ph-As bonds in $MeC(CH_2AsPh_2)_3$ by hydrogen iodide,[311] and this iodide can, on treatment with sodium in tetrahydrofuran, be converted into the cyclotriarsinetrioxide, $MeC(CH_2AsO)_3$ with the structure shown in (94).[312]

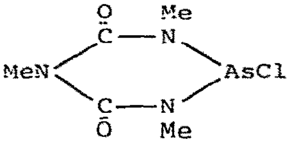
Changes in i.r. and Raman spectra in the As-C stretching region for triethylarsine have been interpreted as showing the presence of chiefly two conformers in the liquid state but only one, which may be the all *trans* or all *gauche*, in the solid.[313] Data for the analogous antimony compound are also given. Malonic esters and alkyldichloroarsines react to give the 1,3-diarsacyclobutanes (95) via the intermediates $R^1AsCl[CH(CO_2R^2)_2]$, $R^1As[CH(CO_2R^2)_2]_2$, and $(R^1AsCl)_2C(CO_2R^2)_2$ which can be isolated.[314] If arsenic trichloride is a reactant, the product is an analogue of (95) with

R^1=Cl. Both neutral and cationic complexes of silver perchlorate and $(C_6F_5)_3As$, i.e. $(C_6F_5)_3As.AgOClO_3$ and $[Ag(As(C_6F_5)_3)_3]_2ClO_4$, can be isolated from benzene solutions.[315] The arsine is readily oxidized to the dichloride, which on reaction with silver salts gives monosubstitution products $(C_6F_5)_3AsClX$ where X=NO_3, ClO_4 or O_2CCH_3.

Elemental fluorine diluted with argon cleanly oxidizes <u>inter alia</u> Ph_3As,Ph_2AsMe and the antimony analogues, in $CFCl_3$ solution to the corresponding difluorides,[316] while triaryl arsines and stibines react rapidly with both ICl and IBr in acetonitrile to give the appropriate mixed halide.[317] Similar oxidations occur with ICN and BrCN but with triphenyl bismuth both ICl and ICN cause phenyl group cleavage and the isolated products are Ph_2BiCl and Ph_2BiCN respectively. A convenient preparative route to Ph_3AsF_2 is the reaction between Ph_3AsO and 40% HF solution.[318] The course of the reaction is surprising as with HCl or HBr the arsine oxide gives the hydroxyhalide, $Ph_3AsO.HX$.

5.3.3 Bonds to Halogens

Arsenic trichloride and the substituted biuret $MeN[C(O)NMeSiMe_3]_2$ react to give a new heterocycle (96), while a four-membered As-N-C compound (97) is the product when the silylated urea, $(Me_3SiMeN)_2CO$,



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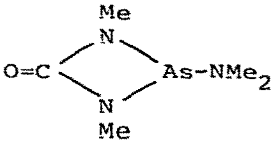

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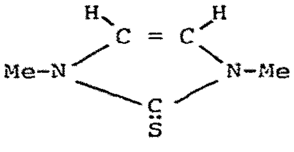


(98)

reacts with tris(dimethylamino)arsine.[319] Arsenic trichloride and aryl substituted chloroarsines on the other hand give moisture sensitive 1:1 complexes with tetramethylthiourea and 1,3-dimethyl-2(3H)-imidazolethione (98) which are thermally stable but dissociate in solution.[320] A crystal structure of the $AsCl_3$ adduct with (98) shows pseudotrigonal bipyramidal geometry about arsenic with the sulphur atom of the ligand occupying an equatorial position.[321] Weak intermolecular As...Cl interactions lead to dimeric units in the solid state.

Simple 1:1 addition compounds, $MX_3.NH_3$ where M=As,Sb or Bi and X=Br or I, can be obtained either from the components in benzene or ether solution or by heating a mixture of the oxide with ammonium chloride.[322] Although they are insoluble in common solvents, i.r. data are consistent with the presence of terminal halogen atoms and monomeric structures are suggested.

Intercalation of arsenic(V) fluoride has been reexamined using highly oriented pyrolytic graphite showing from X-ray and gravimetric methods formation of the compounds $C_{8n}AsF_5$, where n (the stage of intercalation) is 1,2 or 3.[323] X-ray crystallography confirms that coordination in the AsF_5 adduct with N-methyl-S,S-difluorosulphoximine, $MeNSOF_2$, involves the nitrogen, rather than the oxygen atom of the ligand (As-N, 1.99Å).[324]

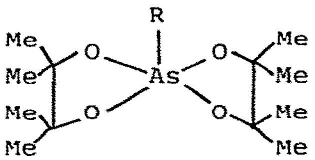
The oxide chloride $AsOCl_3$ can be obtained as a low temperature stable entity by ozonolysis of arsenic trichloride in a solvent such as $CFCl_3$.[325] A band at 987 cm^{-1} is assigned to stretching of the As=O double bond and the data can be interpreted on the basis of a pyramidal structure. Warming to room temperature causes decomposition and the formation of a polymer $(As_2O_3Cl_4)_n$ with loss of chlorine and $AsCl_3$. Attempts to prepare the fluorine and bromine analogues were not successful.

5.3.4 Bonds to Oxygen

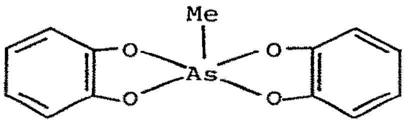
Exchange of oxygen between the $AsO(OH)_2^-$ ion and solvent water follows a combined first order path, for which $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ are 25kJmol^{-1} and -120JK^{-1}mol^{-1}, and a pathway second order in arsenite ($\Delta H_2^{\ddagger}$, 33 kJmol^{-1}; $\Delta S_2^{\ddagger}$, -102 JK^{-1}mol^{-1}) from line broadening ^{17}O n.m.r. measurements.[326] The first order oxygen exchange is thought to correspond to a nucleophilic displacement by water on arsenite while the second order path is associated with the process in equation (30).

$$2AsO(OH)_2^- \longrightarrow H_2O + As_2O_3(OH)_2^{2-} \qquad ...(30)$$

X-ray crystallographic data for the three five-coordinate spirocyclic arsenic compounds shown in (99)[327] and (100),[328] show that the same problems concerning the ground state structure, i.e. whether this is trigonal bipyramidal or square pyramidal, as were encountered with similar phosphorus compounds are important here. The two structures represented by (99) have intermediate



(99) R=Ph or OH



(100)

structures (the phenyl derivative is closer to a trigonal bipyramid while the hydroxide is closer to a rectangular pyramid) and, in agreement with conclusions from phosphorus chemistry, the structures lie on the Berry pathway for ligand displacement between the idealized end forms.[327] The structure of (100) shows *trans* basal angles of 143.1 and 158.6° and As–O distances falling between 1.793 and 1.833Å and is best described in terms of a rectangular pyramid.[328]

Although earlier ^{1}H n.m.r. spectra showed only one signal which did not change on cooling for the methoxy protons in $(MeO)_3Me_2As$, a reexamination by both ^{1}H and ^{13}C variable temperature n.m.r. spectroscopy shows two methoxy signals at lower temperatures.[329] These data are consistent with an intramolecular exchange process with an energy of activation of *ca.* 14 $kcalmol^{-1}$.

On heating under a high oxygen pressure, arsenic(III) oxide is converted to the pentoxide which crystallizes in the space group $P2_12_12_1$.[330] The compound contains a new type of framework structure based on corner sharing AsO_4 tetrahedra and AsO_6 octahedra. Mean distances to the tetrahedrally and octahedrally coordinated arsenic atoms are 1.676 and 1.818Å respectively while angles at the bridging oxygen atoms range between 122.2 and 136.1°. Two series of arsenates, M_3AsO_4 and $MAsO_3$, characterised by X-ray methods can be prepared by solid state reactions between the pentoxide and the superoxides KO_2, RbO_2 or CsO_2.[331] It was further shown that the tribasic arsenates combine with As_2O_5 to give products with the formula $M_3As_3O_9$, thought to contain the cyclic trimeta-arsenate ion. The compound $NaHAs_2O_6$, obtained when a mixture of $H_5As_3O_{10}$ and NaH_2AsO_4 was heated at 260°C, contains a new two dimensional ion.[332] The formula is $(As_2O_6)_n^{2n-}$ and is formed by corner sharing between alternate AsO_4 tetrahedra and AsO_6 octahedra.

New i.r. data suggest that the compound reported as being $SnHAsO_4.H_2O$ should be formulated as the μ-oxo-ditin dihydrogen arsenate, $Sn_2O(H_2AsO_4)_2$.[333]

Structures for two mixed chromium arsenates, $K_2HAsCr_2O_{10}$[334] and $(NH_4)_2HAsCr_3O_{13}$,[335] are based on corner sharing AsO_4 and CrO_4 tetrahedral units. In the former bridging and terminal As-O distances are 1.71 and 1.66Å respectively.

5.3.5 Bonds to Sulphur or Selenium

A number of hydrated and anhydrous alkali metal thioarsenates in the series $AsO_{4-n}S_n{}^{3-}$, where n=1-4, have been prepared and full structural data obtained for K_3AsS_4, $Na_3AsO_3S.7H_2O$, and $Na_3AsO_2S_2.11H_2O$.[336] Data have also been obtained for $Na_3AsS_4.8H_2O$.[337] In all cases the anions are tetrahedral with mean As-O and As-S distances of 1.68 and 2.15Å.

Solid state reactions between Na_2S and As_2S_3 lead to the thioarsenites Na_3AsS_3 and $NaAsS_2$ for which structures are available.[338] Pyramidal $AsS_3{}^{3-}$ ions with As-S and S-As-S parameters equal to 2.25Å and 101.9° occur in the former while the "meta" compound contains infinite $(AsS_2)_n^{n-}$ chains formed by corner sharing of AsS_3 pyramids; in each compound the arsenic lone pair is stereochemically active. Complex formation between arsenic(III) and sulphide ion has also been studied spectrophotometrically in aqueous solution; constants for the important equilibria, shown in equations (31) and (32), at 22°C and unit ionic strength are evaluated as respectively 2.5×10^{134} and 1×10^{92}.[339]

$$3H_3AsO_3 + 6S^{2-} + 9H^+ \rightleftharpoons As_3S_6{}^{3-} + 9H_2O \qquad \ldots (31)$$

$$2H_3AsO_3 + 5S^{2-} + 6H^+ \rightleftharpoons As_2S_5{}^{4-} + 6H_2O \qquad \ldots (32)$$

Two new compounds, $MnAs_2Se_4$ and $Mn_3As_2Se_6$, have been identified in the $MnSe-As_2Se_3$ system.[340]

5.4 ANTIMONY

5.4.1 Antimonides

In addition to producing the known $Sn_9{}^{4-}$ polyatomic anion, treatment of a Na/Sn/Sb alloy with ethylenediamine gives a compound which from ^{119}Sn n.m.r. data is thought to contain either $SbSn_9{}^{3-}$ or $SbSn_9{}^-$.[341] A new compound from the barium-antimony system, $BaSb_3$, contains an infinite two dimensional anion built up of 14-membered rings of doubly and triply connected antimony atoms.[342] In this highly puckered structure Sb-Sb distances are ca. 2.84Å with angles of 96.6 and 113.1° at triply connected and 100.0° at the doubly connected antimony atoms. Wurtzite-type structures have been confirmed for the new compounds LiBeSb and LiZnBi.[343] The two heavier atoms in each case form a tetrahedrally coordinated three dimensional framework into which lithium atoms are incorporated, leading to a structure with increased distances between buckled sheets of the two heavier metals. The new ternary compounds MZn_2Sb_2 and MCd_2Sb_2, where M=Ca or Sr, have been prepared from the elements at ca.1000°C.[344]

5.4.2 Bonds to Carbon

Organo-antimony chemistry for 1976 has been reviewed.[345] Reaction between di(t-butyl)chlorostibine and magnesium metal in tetrahydrofuran solution gives $(t\text{-}Bu)_3Sb$, which can be distilled, to leave the cyclotetrastibine $(t\text{-}Bu)_4Sb_4$, sublimable as yellow crystals.[346] The reaction probably proceeds via $(t\text{-}Bu_2Sb)_2Mg$. As found for the lighter Group 5 elements, a number of distibines, e.g. Me_4Sb_2, Et_4Sb_2 and $CH_2(SbPh_2)_2$ have been shown to react with chromium or tungsten carbonyl derivatives yielding binuclear complexes of the form $(OC)_5MSbR_2SbR_2M(CO)_5$.[347] I.r. and Raman data for $(CF_3)_2SbX$, where X=H,Cl,Br or I, have been analysed and normal coordinate analyses carried out.[348]

Tris(pentafluorophenyl)antimony, which gives the oxide $[(C_6F_5)_2Sb]_2O$ on hydrolysis, can be oxidized to the dichloride.[349] Both chlorine atoms can then be replaced on treatment with NaOMe or the silver salts $AgNO_3$ and $AgClO_4$; on treatment with water the dichloride gives the partially hydrolysed oxygen-bridged compound $[(C_6F_5)_3SbCl]_2O$.

A series of β-diketonate derivatives, R_2SbCl_2X where $R_2=(CH_2)_4$, o,o'-$C_6H_4.C_6H_4$, etc. and X=acetylacetone or dipivaloylmethane, has been prepared and investigated by n.m.r. and dipole moment methods.[350] In these compounds the R groups are part of a heterocyclic system and are constrained to occupy *cis* positions in the coordination sphere; the two chlorine atoms are thus *trans* to each other. Comparisons are made with similar compounds in which the R groups are separate and occupy *trans* positions.

Structural data have been collected for two isomeric forms of dimethylantimony trichloride.[351] The covalent form, which is obtained when dimethylantimony chloride is oxidized with either chlorine or SO_2Cl_2, has a dimeric, double chlorine bridged structure similar to that in $(Ph_2SbCl_3)_2$ with approximately octahedral coordination about each antimony. Terminal and bridging Sb-Cl bond distances are 2.355 and 2.800Å respectively. The second form is obtained from Me_4SbCl and antimony pentachloride and consists of tetrahedral Me_4Sb cations (Sb-C, 2.115Å) and octahedral $SbCl_6$ anions (Sb-Cl, 2.382Å). Isolated ions are also present in the structure of $[Me_4Sb][GaCl_4]$.[352] Structural data for Me_3SbF_2 and Me_4SbF show isolated trigonal bipyramidal monomers for the former (Sb-C, 2.10Å; Sb-F, 2.00Å) but with the monofluoride there is strong intermolecular fluorine bridging (Sb-F, 2.37 and 2.38Å) with the formation of polymeric chains parallel to the c axis.[353] The coordination about antimony is distorted octahedral and the angle at the bridging fluorine atom is 153.1°. In contrast to the increase in antimony coordination here is the distorted trigonal bipyramidal coordination about antimony in the dimethylthiophosphinate complex $Me_4SbOP(S)Me_2$, even though the ligand is potentially bidentate.[354] The asymmetric unit contains two molecules which differ primarily in the Sb-O distances (2.532 and 2.749Å). Both these are greater than the sum of the covalent radii and indicate weak covalent Sb-O bonding. As shown further by the C-Sb-C angles (100.3-118.2°) the structure is intermediate between the typically ionic $Me_4Sb^+X^-$ structure and the five-coordinate covalent structure.

Diesters of the form $Ph_3Sb(O_2CR)_2$ are readily prepared by treating triphenylantimony oxide with the appropriate acid in methanol,[355] and gem-diolates $Ph_3SbO_2CR^1R^2$, where $R^1=R^2=CF_3$ and $R^1=H$ and $R^2=CF_3$ or CCl_3, result when Ph_3SbBr_2 and the diol react.[356] Molecular weights in benzene solution point to monomeric structures and spectroscopic data can be interpreted on the basis of trigonal bipyramidal coordination with the diol spanning axial and equatorial positions.

One methyl group is displaced from pentamethylantimony on treatment with either phosphonic and phosphinic acids to give new compounds such as $Me_4SbOP(O)(OH)Me$ and $Me_4SbOP(O)Ph_2$.[357] The mixed penta-alkyl antimony derivative, Et_3SbMe_2, results when methyl lithium reacts with Et_3SbCl_2 in ether but on treatment with compounds containing acidic hydrogen atoms methane, rather than ethane is eliminated.[358] Products of the type Et_3SbMeX, where X=OR, O_2CMe, O_2PMe_2, or O_2PF_2, are thus obtained. The methyl acetylide, $Me_3Sb(C{\vdots}CMe)_2$, which has a trigonal bipyramidal solid state structure with acetylide groups in axial positions results when Et_3SbCl_2 is treated with $LiC{\vdots}CMe$. Silylated penta-alkyl stiboranes in the series, $Me_nSb(CH_2SiMe_3)_{5-n}$ where n=0-4, can be prepared by methylation or trimethylsilylmethylation of the

$$Me_3SbBr_2 + 2LiCH_2SiMe_3 \longrightarrow Me_3Sb(CH_2SiMe_3)_2 + 2LiBr \quad \ldots (33)$$

$$(Me_3SiCH_2)_3Sb \xrightarrow{MeI} [(Me_3SiCH_2)_3SbMe]I \xrightarrow{MeLi} (Me_3SiCH_2)_3SbMe_2 \quad \ldots (34)$$

appropriate alkylantimony(V) halide as shown for two examples in equations (33) and (34).[359]

Chloro-di- and -tri-methyl derivatives of silicon, germanium and tin give compounds of the type Me_3MSbPh_2 on reaction with Ph_2SbLi, while the analogous reaction with 2,2-dichloropropane leads to $Me_2C(SbPh_2)_2$.[360] Tris(trimethylgermyl)stibine reacts with either methyl or t-butyl iodide according to equation (35),[361] but with

$$(Me_3Ge)_3Sb + RI \longrightarrow (Me_3Ge)_2SbI + Me_3GeR \quad \ldots (35)$$

the tin analogue $(Me_3Sn)_3Sb$, the butyl iodide reaction gives either $t\text{-}Bu_2(Me_3Sn)Sb$ or $(Me_3Sn)_2SbSb(SnMe_3)_2$ depending on the conditions.[362]

5.4.3 Bonds to Halogens

Anionic antimony(III) fluoride structural chemistry has been reviewed with special reference to the location of the antimony lone pair of electrons.[363] According to a reexamination of the structure, the repeating unit in $NaSbF_4$ is a modified trigonal bipyramidal unit in which the lone pair occupies an equatorial position.[364] Equatorial and axial Sb-F distances are ca.1.96 and 2.07Å respectively, but in addition there are two longer Sb...F contacts (2.66 and 2.86Å) so that the repeating unit is more accurately described as SbF_6E. In the mixed halide, $CsSbClF_3$, the coordination number of antimony is effectively eight giving a hendecahedral arrangement involving five fluorine atoms (three at

1.95 and two at 2.98Å) two chlorine atoms (at 2.97Å) and the lone pair of electrons.[365] Effective eight fold coordination for antimony is also found for the 1:1 adduct between thiourea and antimony trifluoride.[366]

Two molecular complexes between $SbCl_3$ and aromatic compounds, i.e. $2SbCl_3$.(biphenyl)[367] and $2SbCl_3.Ph_2NH$,[368] have been structurally investigated. In each case the $SbCl_3$ molecules point to the phenyl rings but are displaced away from the centres of the rings. In the biphenyl compound the Sb-ring distances (3.08 and 3.26Å) are distinctly different while values close to 3.08Å are found in the diphenylamine adduct. In both compounds coordination about antimony is increased to six (distorted octahedral) by two longer Sb...Cl contacts. The 1:1 addition compound with diphenylamine hydrochloride, on the other hand, has a structure based on a square tube in which antimony is attached to three chlorines at 2.38, two at 3.08 and the sixth atom at 3.42Å.[369] Diphenylammonium cations are incorporated into the structure through hydrogen bond formation.

Antimony(III) chloride adducts with oxygen donors, i.e. $2SbCl_3$.(1,3,5-triacetylbenzene)[370] and the 1:1 adducts with terephthaldehyde and p-diacetylbenzene,[371] have also been investigated by X-ray crystallography. Spectroscopic data are reported for a range of antimony(III) and bismuth(III) halide complexes with sulphur containing ligands, including thiomorpholin-3-one, thiomorpholin-3-thione, thiazolidine-2-thione and benzoxazole-2-thione.[372] Square pyramidal and mer-substituted octahedral structures respectively are suggested for the species containing two and three moles of the ligand, while bridged structures are most likely for the compounds with 0.5 and 1.5 moles of ligand.

The compounds $Cs_3Sb_2I_9$ and $Cs_3Bi_2I_9$ are isotypic with structures based on two octahedra sharing a face;[373] bridging and terminal distances to antimony are 3.198 and 2.870Å respectively and to bismuth 3.244 and 2.920Å.

Comparison of the ^{121}Sb Mössbauer spectra for the coloured Sb(III)-Sb(V) compound, $(pyH)_6Sb(III)Sb_3(V)Br_{24}$, of known structure and those for $M_2Sb_2Br_6$, where $M=NH_4$ or Rb, shows evidence for the loss of s-electron density for Sb(III).[374] This most probably occurs via solid state bands as has been suggested for a number of Sn(II) compounds. Mössbauer data are also now available for a number of mixed antimony fluorides including

$Sb_2F_4(SbF_6)_2$ and $Se_2Te_2(SbF_6)(Sb_3F_{14})$.[375]

Although mixtures of SbF_5 and VF_5 can be recovered unchanged by fractional distillation, a 1:1 addition compound results when either a 1:2 vanadium-antimony mixture is fluorinated at 250°C or the components with a slight excess of SbF_5 are mixed at low temperature.[376]

In the addition compound between $SbCl_5$, water and dioxan, an X-ray structure shows that the water molecule is strongly coordinated to the antimony atom and dioxan is attached via hydrogen bond formation (O...O, 2.490Å) to water; i.r. and Raman spectra are also discussed.[377] N.m.r. and vibrational spectroscopy have been used to investigate the structure and ligand exchange pattern of $SbCl_5.MeCN$.[378] There is no ionization of the complex in acetonitrile solution but on addition of nitromethane Raman bands associated with the $SbCl_6^-$ ion appear implying that ionization to $[SbCl_4(MeCN)_2]^+[SbCl_6]^-$ occurs.

Antimony pentachloride reacts with both formic acid[379] and the halogenosulphuric acids, HSO_3X where X=F or Cl.[380] With the former, $SbCl_5.2HCO_2H$, $SbCl_4O_2CH$, and $SbCl_2(O_2CH)_3$ can be isolated depending on the conditions, while monosubstitution to give $SbCl_4(SO_3X)$, probably as a doubly halogenosulphate bridged dimer, occurs with the latter.

Raman spectra that can be interpreted on the basis of weak association between a tetrahedral cation and the appropriate anion have been obtained for solid and molten samples of $[SbCl_4]^+[Sb_2Cl_2F_9]^-$, $[SbCl_4]^+[Sb_2F_{11}]^-$ and $[AsCl_4]^+ [SbF_6]^-$, while the adduct between $SbCl_4F$ and NbF_5 shows a spectrum similar to that of the reactants and a fluorine bridged polymeric structure is thought to be most likely.[381]

^1H n.m.r.[382] and vibrational[383] data have been obtained for the dimeric chloroalkoxides, $[Cl_{5-n}Sb(OMe)_n]_2$ for n=1-5. Proton resonance data distinguish between terminal and bridging methoxy groups for n=5 and the experimental spectrum for the compound where n=2 is a super-position of the spectra expected for each of the five possible isomeric forms.[382] Bands in the 540-400cm^{-1} region are assigned to vibrations of the Sb_2O_2 ring.[383]

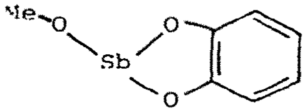
^{121}Sb Mössbauer spectra for $Me_4N[SbCl_4(N_3)_2]$ and a number of compounds containing bridging halogen or azide groups have been obtained.[384]

5.4.4 Bonds to Oxygen

From a recent X-ray investigation the compound $Sb_2O_3.2SO_3.3H_2O$, obtained when the trioxide is dissolved in sulphuric acid, should be formulated as $Sb_2(OH)_2(SO_4)_2.2H_2O$.[385] The structure of the citrate complex, $[Sb(C_6H_5O_7)_2]^{3-}$, has also been determined,[386] showing that antimony coordination is based on a trigonal bipyramid with a stereochemically active lone pair, carboxylate oxygen atoms in axial positions (Sb-O, 2.16Å), and oxygen atoms from hydroxyl groups in the two remaining equatorial positions (Sb-O, 1.99Å).

Structures for $Sb_4O_5Cl_2$[387] and Sb_5O_7I[388] contain polymeric layers with compositions of respectively $(Sb_4O_5{}^{2+})_n$ and $Sb_2(Sb_3O_7)_n^+$ with halogen atoms lying between the layers. The iodide investigated was one of the nine known polytypic modifications, specifically the non-centric form with combined ferroelastic-ferroelectric properties. The oxide-sulphide, $CaSb_{10}O_{10}S_6$ known mineralogically as sarabauite, can be obtained hydrothermally from a 1:2:3 mixture of CaO, Sb_2S_3 and Sb_2O_3,[389] has a structure based on antimony atoms coordinated to either three oxygen and/or sulphur atoms.[390]

The methoxy-1,3,2-benzodioxastibole (101) and its trithio analogue are not isomorphous but have similar structures.[391] A major feature of that for (101) is the presence of three intermolecular Sb...O interactions to different neighbours at distances of 2.36, 2.65 and 3.49Å thus increasing the effective antimony coordination number. Similar but much weaker interactions are found with the thio analogue.



(101)

Antimony(V) atoms in Sb_2O_5 are in octahedral coordination by oxygen atoms at distances between 1.91 and 2.08Å,[392] in contrast to the As_2O_5 structure[330] which includes both octahedral and tetrahedral coordination. A partially hydrated form of the oxide $Sb_2O_5.0.6H_2O$, which can be obtained when the product of $SbCl_5$ hydrolysis is dried at 550°C under an oxygen pressure, should be formulated as $Sb_5O_{12}(OH).H_2O$ according to a recent structural analysis.[393] Again the heavy atom is in six-fold coordination by oxygen and by edge and corner sharing layers of composition $Sb_5O_{13}^-$ are built up. This compound, formulated as $Sb_2O_{4.8}(OH)_{0.4}$, is probably one of the products obtained on heating a lower antimony oxide under a high oxygen pressure with water;[394] a second product is formulated as $Sb_2O_{4.4}(OH)_{1.2}$. Two crystalline forms of Sb_2O_5 have also been isolated.

^{121}Sb Mössbauer data for a series of stibonic acids $RSbO_3H_2$, (p-tolyl)$_2$SbO$_2$H and Ph_3SbO have been interpreted in favour of polymeric structures with trigonal bipyramidal coordination about antimony in all cases.[395] The axial positions are occupied by bridging oxygen atoms. A linear Sb-O-Sb bridge with the oxygen lying on an inversion centre (Sb-O, 1.943Å) has been found in the structure of μ-oxo-bis[tri(p-chlorophenyl)-1,1,1-trifluoro-2,4-pentanedionato-O,O') antimony(V)].[396]

5.4.5 Bonds to Sulphur or Selenium

$NaSbS_2$ can be obtained by heating stoichiometric mixtures of Na_2S and Sb_2S_3 in two different forms depending on the subsequent heat treatment.[397] The α-form (monoclinic, space group C2/c) results from very slow cooling, is isostructural with the potassium salt, and contains antimony in a pseudo-trigonal bipyramidal arrangement (SbS_4E). In the β-form (cubic, space group Fm3m) which is isostructural with $NaBiS_2$, antimony and sodium atoms occupy octahedral sites in a face centred array of sulphide ions. There is some ambiguity in this system however, as a second β-form (monoclinic, space group C2/m) has also been isolated and investigated crystallographically.[398] This consists of layers of condensed pseudo-octahedral SbS_5E units with Sb-S distances ranging between 2.44 and 2.92Å.

The structure of $RbSbS_2$ is similar to that for the α modification mentioned above, but the asymmetric unit contains four independent antimony atoms;[399] Sb-S(equatorial distances) are 2.26 and 2.57Å while the axial distances vary between 2.61 and 3.09Å. The rubidium and caesium salts, $M_2Sb_4S_7$, obtained from Sb_2S_3 on treatment with an aqueous solution of the appropriate sulphide and hydrosulphide at 150°, have different structures, although each contains antimony atoms in both pyramidal and pseudo trigonal bipyramidal coordination.[400]

Investigation into the phase systems between Sb_2Se_3 or Sb_2Te_3 and the Group 1 selenides or tellurides shows that the systems become more complex with increasing atomic number of the alkali metal,[401] probably on account of the increased ionic radius and larger electronegativity difference between the elements. As an example in the selenide system, lithium and sodium selenides give only $MSbSe_2$ while for rubidium and caesium ternaries with the formula MSb_3Se_5 can be isolated in addition, and finally caesium also yields $CsSb_5Se_9$. With lanthanoid selenides, X-ray diffraction and d.t.a. experiments show the formation of one ternary, $LnSbSe_3$, for Ln=La, Ce or Gd.[402]

Reactions between antimony trichloride and both substituted benzene thiols[403] and benzene-1,2-dithiol[404] have been described. Thioantimonites obtained from the former appear to give disulphides on hydrolysis but the p-tolyl derivative $Sb(SC_6H_4Me)_3$ is both thermally and photochemically stable. The initial product with benzene-dithiol is the monochloride, chloro-1,3,2-benzodithiastibole, which gives the corresponding methylthio derivative on treatment with MeSNa. A crystal structure of this compound shows mean Sb-S distances of 2.45Å, but the shortest intermolecular Sb...S contacts are 3.24 and 3.72Å, indicating that the interaction here is much weaker than in the corresponding oxygen compound. Pyramidal coordination about antimony is also found in the structure of diphenylantimony-2,6-dimethylthiophenate and from a short (3.44Å) intermolecular contact between the heavy atom and the methyl group in the 6-position, the van der Waals' radius for antimony can be calculated as ca. 1.8Å.[405]

An addition compound between 0.5mol of 4,4'-bipyridyl and antimony tris(O-ethylxanthate) has been shown by X-ray crystallography to be a lattice adduct.[406] Contrary to the situation in the free antimony xanthate, the ligands in the adduct are all crystallographically independent, although two are very similar (Sb-S 2.615, 2.892 and 2.612, 2.878Å). In the third, the Sb-S distances are 2.477 and 3.091Å.

Thioderivatives of antimony(V), e.g. $R_3Sb(S_2CNR_2)_2$, are not readily obtainable but it has now been possible to isolate a number of derivatives for R=Me, using metal dithiocarbamates. Attempts to prepare the corresponding triphenyl species were unsuccessful.[407] Analogous xanthate derivatives, $Me_3Sb(S_2COR)_2$, were also obtained. The dithiocarbamate $Me_3Sb(S_2CNMe_2)_2$, which can also be prepared by oxidation of trimethylstibine with tetramethylthiuram disulphide, has a trigonal bipyramidal structure with axial sulphur atoms (Sb-S 2.575 and 2.614Å).[408] Further weak Sb...S interaction is present from intramolecular distances of 3.274 and 3.315Å.

5.5 BISMUTH

5.5.1 Bonds to Carbon or Germanium

The organometallic chemistry of bismuth for 1976 has been reviewed.[409] Two new compounds containing Bi-Ge bonds, $(C_6F_5)_3GeBiEt_2$ and $[(C_6F_5)_3Ge]_2BiEt$, are the products when mixtures of triethylbismuth and $(C_6F_5)_3GeH$ are heated at 100 and 170°C respectively.[410] Similar reactions occur with $(C_6F_5)_2GeH_2$, ethane is lost on heating and the dimer $[(C_6F_5)_2GeBiEt]_2$, formulated as a Ge_2Bi_2 heterocycle has been isolated.

5.5.2 Bonds to Halogens

Three different crystalline modifications of a new black bismuth(I) iodide have been isolated either from reactions between the elements at 558K or by heating bismuth metal with mercury(II) iodide.[411] The α- and β-forms from recent X-ray studies contain infinite Bi_4I_4 chains in which two of the metal atoms are bonded only to three other bismuth atoms (mean Bi-Bi, 3.045Å) characteristic of Bi(O) while the other two atoms are each bonded to one bismuth and four iodine atoms (mean Bi-I, 3.137Å) and are characteristic of Bi(II) compounds. The α- and β-forms differ in the stacking of the Bi_4I_4 chains. The bromine analogue, which can be prepared from bismuth and mercury(II) bromide, has a similar structure (mean Bi-Br, 2.944Å).[412] The compound $BiBr_{1.167}$ is now also known and contains, as found for the chlorine derivative, the Bi_9^{5+} cation together with $BiBr_5^{2-}$ and $Bi_2Br_8^{2-}$ anions. Reinvestigation of the Bi-BiI_3 phase system confirms the formation of BiI and points to the existence of $Bi_{10}I_3$ with an incongruent melting point of 295°C.[413]

The addition compound between bismuth trichloride and thiosemicarbazide (tsc), like that with thiourea, has been shown to contain the metal in both cationic and anionic forms.[414] The stoichiometry is $3BiCl_3.4(tsc)$ but X-ray crystallography shows the presence of $[Bi_4Cl_{10}(tsc)_6]^{2+}$, $BiCl_6^{3-}$ and Cl^- ions. The complex cation can be considered as formed from a μ_3-chloro-tri-

[trichloro(thiosemicarbazido)bismuth]anion and a tri(thiosemicarbazido)bismuth(III) cation. The ethylenethiourea complex, $BiCl_3.2etu$, on the other hand has a chain polymeric structure with each bismuth atom in octahedral coordination to four chlorine atoms and two cis sulphur atoms from the ligands. The bismuth lone pair is not stereochemically active.

The pyridinium chlorobismuthate, previously formulated as $(pyH)_3Bi_2Cl_9$, has now been shown to have a structure containing the tetrameric $Bi_4Cl_{18}^{6-}$ anion.[415] This consists of two pairs of edge sharing $BiCl_6$ octahedra further joined by chlorine bridges; terminal Bi-Cl distances fall between 2.567 and 2.611Å and bridging distances are 2.850 and 2.941Å. As observed in previous hexahalobismuthates structures, the two independent $BiBr_6^{3-}$ ions found in the rubidium salt show slight distortions only from octahedral geometry and the lone pair is not active.[416]

Salts of the BiF_6^- ion have been obtained by heating mixtures of an alkali metal fluoride and BiF_5 to 280°C under a pressure of fluorine.[417] Evidence is presented for the formation of $H_3O^+ BiF_6^-$ when water is added to a solution of the pentafluoride in anhydrous hydrogen fluoride.

5.5.3 Bonds to Oxygen

The interrelationship between the α,β,γ and δ phases of bismuth(III) oxide have been investigated by X-ray and neutron powder diffraction,[418] and experiments in the $SrO-Bi_2O_3$ system show the formation of $SrBi_2O_4$, $Sr_3Bi_2O_6$, and $Sr_2Bi_2O_5$.[419]

A basic bismuth(III) nitrate obtained from the trinitrate in the pH range 1.2 to 2.4 is best formulated from a recent X-ray investigation as $[Bi_6O_5(OH)_3](NO_3)_5.3H_2O$.[420] Pairs of cage-like $[Bi_6O_5(OH)_3]$ groups, in which the heavy atoms occupy the corners of an octahedron and the oxygen atoms are placed above each triangular face, are linked across a centre of inversion by oxygen bridges.

Alkoxy-bismuth(III) species, such as Ph_2BiOR and the $Bi(OR)_2Me$ where R=Me,Et or i-Pr, can be obtained from the appropriate substituted bismuth bromide and sodium alkoxide.[421] The alkoxy groups can be readily displaced by thiols giving good yields of the corresponding thio derivatives.

5.5.4 Bonds to Sulphur

Redox properties, in connection with their use as positive electrodes in lithium cells, have been investigated for the Group 5 chalcogenides showing that the bismuth compounds can be reduced at room temperature to Li_3Bi with *ca*. 100% material efficiency.[422]

Investigation of the phase systems between Bi_2S_3 and both Li_2S[423] and K_2S[424] shows the formation of $LiBi_3S_5$ in addition to the known ternary $LiBiS_2$ for the former and the new compounds $K_8Bi_2S_7$, $K_2Bi_4S_7$ and KBi_3S_5 for the potassium system. A number of lead containing ternaries including $Pb_3Bi_2S_6$, $PbBi_2S_4$, $PbBi_4S_7$ and $PbBi_6S_{10}$ have also been observed.[425]

A crystal structure determination on the O-ethylxanthato-complex, $Et_4N[Bi(S_2COEt)_4]$, shows eight fold coordination by sulphur about bismuth at distances between 2.80 and 2.97Å in the form of a dodecahedron.[426] Although there are no great distortions, the three longest distances are associated with one triangular face and may represent the lone pair position.

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