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Chapter 5

ELEMENTS OF GROUP 5

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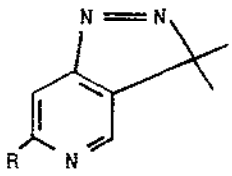
5.1 NITROGEN

5.1.1 Nitrogen-Nitrogen Bonds

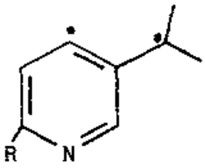
New dinitrogen cobaltates have been synthesised by treating $Co(PMe_3)_3(c-C_5H_8)$, itself obtained by reducing cobalt(II) chloride with magnesium in the presence of the appropriate ligands, with an alkali metal.[1] The compounds, which are formulated as $M[CoN_2(PMe_3)_3]$, on further reaction with Grignard reagents give $[(Et_2O)RMgN_2Co(PMe_3)_3]_2$, for R = Me, Ph, Me_2CHCH_2 and Bu^t, shown by an X-ray study on the t-butyl derivative to contain bridging diazenide units.

Nitrogen is rapidly taken up by the 14-electron ruthenium porphyrin, Ru(TMP) where TMP is the dianion of 5,10,15,20-tetramesitylporphyrin, to give the first bis(dinitrogen) species together with a small amount of the related mono(dinitrogen) compound.[2] A novel alkenyldiazenidotungsten complex, mer-$[W(acac)(NNCMeCHCOMe)(PMe_2Ph)_3]$, results in low yield when $[W(N_2)_2(PMe_2Ph)_4]$ is treated with acetylacetone in methanol at 50°C.[3] The suggested mechanism involves initial protonation of bonded N_2 by acetylacetone to give $[W(acac)(NNH)(PMe_2Ph)_3]$ followed by nucleophilic addition of the diazenido ligand to a CO group of the diketone and water elimination. It is also possible to convert the initial nitrogen complex to both hydrazido (NNH_2) and diazoalkane ($NN=CMeCH_2COMe$) containing species.

In a low pressure nitrogen plasma, a nitrogen atom is directly inserted into the S-S linkage of the bis(dithiadiazole), $(RCNSSN)_2$ to give $(RCNSNSN)_2$, where R = Ph or p-ClC_6H_4.[4]



(1, R = NCOPh)



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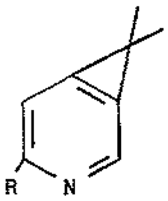
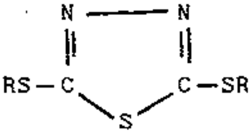


(3)

Selective excitation of the N=N π electrons in (1) leads to the intermediate diradical (2) which via subsequent ring closure gives the first known cyclo-propapyridine (3).[5] The product is stable under an argon atmosphere.

Attempts to prepare esters of 1,2-hydrazine bis(dithiocarboxylic acids) either by treating methyl iodide with $K_2[S_2CNHNHCS_2]$ or $K_2[S_2C{=}NNHC(S)SMe]$ or by reacting hydrazine with Cl(C(S)SEt led to mixtures of (4) and $(RS)_2C{:}N.N{:}C(SR)_2$.[6] Hydrazine and carbon oxysulphide react in the presence of sodium methoxide to give

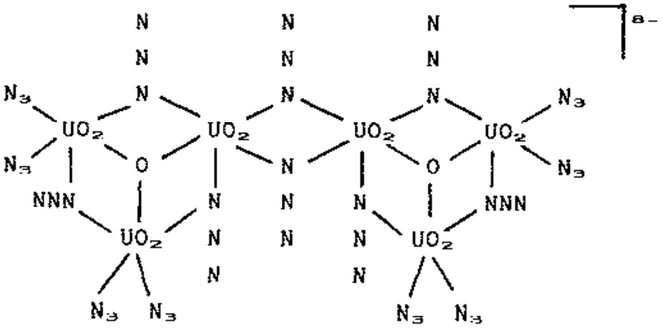

(4)

hydrazine bis(monothioformates) $Na_2[SOCNHNHCOS]$, which can be converted by methyl iodide to S,S'-dimethyl esters.[7] These in turn give dithio-thiadiazoles (4, R = Me) with Lawesson's reagent.

Non-planar, solid state structures are reported for potassium [1,2-hydrazine bis(thiocarboxylate)] and its S,S'- and O,O'-methyl esters.[8] Treatment of the potassium salt with methyl iodide gives the S-bonded ester while the O-bonded isomer results when potassium methylxanthate reacts with O-methyl thiocarbazate. In each compound the N-N bond distance is 138.5pm and although the individual R.CX.NH groups are planar, the dihedral angles relating the two halves of the molecules are, respectively, 78.8, 77.5 and 104.5°. Reaction of hydrazine with $Bu^t{}_2SiClOLi$ leads to $Bu^t{}_2Si(OLi)NHNHSi(OLi)Bu^t{}_2$ but the product from methylhydrazine is $MeNHNHSi(OH)Bu^t{}_2$.[9]

In the 1:1 DMF adduct of calcium azide, obtained in aqueous solution, calcium is coordinated by four nitrogen atoms from azide groups at ca. 240pm and two oxygens from ligand molecules;[10] a similar coordination pattern is also found in $Zn(N_3)_2.2.5H_2O$, previously described as a trihydrate.[11] The nitrogen atoms are shared as common edges and connected to give strings along the b axis. The azide group is asymmetric (N-N, 116 and 120pm) with Zn-N-N angles varying between 126.9 and 130.4. A chain polymeric structure is also present in $Et_4N[UO_2(N_3)_3]$, where two of the azide groups are shared between neighbouring metal atoms giving pentagonal bipyramidal geometry.[12] The related $(Me_4N)_4[(UO_2)_3$-

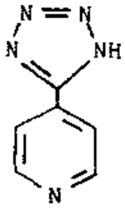
$(N_3)_8O].H_2O$ contains hexanuclear $[(UO_2)_6(N_3)_{16}O_2]^{8-}$ anions (5).



(5)

5.1.2 Bonds to Carbon

Triplet phenyl nitrene is the predominant product when phenyl azide is photodecomposed at 77K.[13] Phenyl nitrene is also observed in both pyrolysis of PhN_3 at 500°C and in photolysis of matrix isolated PhN_3, but perhaps more surprising is the observation of the nitrene spectrum when the carbene precursors (6) and and (7) are decomposed.[14] This verifies the possiblity of a previously postulated carbene-nitrene rearrangement. Related experiments with p-tolyl and naphthyl azides are also reported. In a low pressure flow system CF_3N_3 decomposes to products whose nature depends largely on the wall material of the reactor.[15] For example, with molybdenum at >1120K, FCN is the exclusive product but possible intermediates such as $F_2C{:}NF$ and $F_3CN{:}NCF_3$ were not detected.



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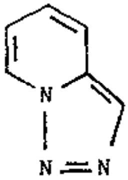
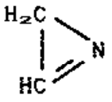


(7)

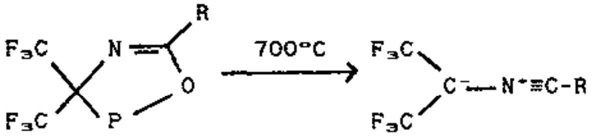
Hydrogen chloride is eliminated when 1-azido-2-chloroethane is treated with potassium t-butoxide in a low pressure flow system at 350K giving highly explosive vinyl azide.[16] Pyrolysis then yields 2H-azirine (8), which can be isolated at below 240K. On the other hand, hydrogen chloride and nitrogen are lost simultaneously when the initial compound is pyrolysed directly at 710K but the product is acetonitrile, an isomer of (8).



(8)

Conversion of organic halides to azides at room temperature in organic solvents can be facilitated by using an "azidising" polymer, such as that obtained by treating Amberlite IR400 with sodium azide.[17] The products can also be worked up without applying heat; among those obtained by this method is $CH_2(N_3)_2$ from dichloromethane.

A thermally generated nitrile ylide (9) has been observed for the first time (equation 1),[18] and methylnitrile ylide $MeC{\equiv}N^+{-}CH_2^-$ can be obtained either photochemically from CH_2N_2 and acetonitrile or by desilylating $Me(PhS)C{:}NCH_2SiMe_3$.[19]



(9) ...(1)

Molybdenum nitrido azide complexes, containing in addition 3,5-dimethyl-1-pyrazolylhydroborate as a ligand, have been isolated by treating $MoCl_4(EtCN)_2$ with Me_3SiN_3 and $Na[HB(3,5\text{-}Me_2pyz)_3]$.[20] The compounds are the di- and monoazides, $MoN(N_3)_2[HB(3,5\text{-}Me_2pyz)_3]$ and $MoN(N_3)Cl[HB(3,5\text{-}Me_2pyz)_3]$, which form mixed crystals with equivalent positions occupied by a 4:1 ratio of the di- and monoazides.

Fluoromethylamines, Me_2NCH_2F, Me_2NCHF_2 and Me_2NCF_3, have been quaternised to the appropriate substituted tetraalkylammonium salts and characterised by n.m.r. and vibrational spectroscopy.[21] In addition, a normal coordinate analysis was reported for $[Me_3NCF_3]^+$ and X-ray structures for $[Me_3NCF_3]I$ and $[Me_3NCHF_2]I$.

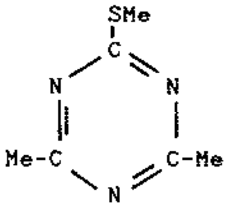
Treatment of N-bis(dichloromethyl)aniline with silicon disulphide gives the thioformyl derivative $PhN(CHS)_2$, characterised by n.m.r. and i.r. spectroscopy and an X-ray structure.[22] The latter shows that the planes through the phenyl and $N(CHS)_2$ groups are almost orthoganol (87.7°).[23] The oxygen analogue, $PhN(CHO)_2$ has a similar structure but here the dihedral angle is 70.1°;[24] with both $N(CHO)_3$ and $N(CHCl_2)_3$ the molecular symmetry is C_{3h}.[25]

N,N'-diphenylformamidine, PhNHCH:PPh, in the presence of alkali metal hydroxides, reacts with carbon disulphide to produce $M[S_2CNPhCH{:}NPh]$, solvated with acetonitrile, water, DME, acetone, etc.[25] Their thermal decomposition has been investigated [27] together with an X-ray structure for the dioxan adduct of the potassium salt.[28] Here there is an E,E conformation for the planar S_2CNCN unit and potassium is in distorted trigonal pyramidal coordination to one oxygen, one nitrogen and three sulphur atoms. Reaction with alkyl halides converts the potassium salt to esters, RSCS.NPh.CH:NPh for R = Me, Et, benzyl, etc., and the phenyl ester can be obtained by an alternative synthetic route by treating N,N'-diphenylformamidine with phenyl chlorodithioformate.[29]

Carbon disulphide reacts at -15°C with acetamidine, $MeC({:}NH)(NH_2)$ to give a salt, $[MeC(NH_2)2][S_2CN{:}CMe.NH_2]$, which can be converted to other salts by metal hydroxides [30,31] and by HCl at 0°C to the free acid.[32] This exists as the zwitterion, $H_2N^+{:}CMe.NH.CS_2^-$ and decomposes in aqueous solution to H_2S, SCN^- and CN^-. A crystal structure determination shows two different conformations for the carbamic acid with planar molecules interlinked by S...H-N hydrogen bonds ranging in distance between 296.8 and 337.0pm.[33]

Reaction of acetimidoyl dithiocarbamates with methyl iodide gives the previously unknown ester, $MeSC(S).N{:}CMe.NH_2$, in addition to dimethyl trithiocarbonate, S-methyl dithiocarbamate and the triazine derivative (<u>10</u>).[34]

Substituted oxazoles (<u>11</u>) are the product obtained from hexafluoroacetone and N,N-dialkylcyanoformamidines, $HN{:}C(NR_2)CN$; the latter can be prepared from cyanogen and a secondary amine.[35]



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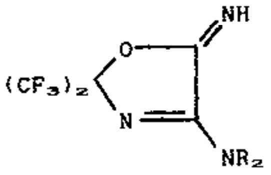
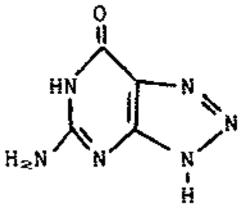


(11)

8-Azaguanine (12, LH_2) and 8-azahypoxanthine (13, $L'H_2$) form methylmercury compounds in aqueous solutions at varying pH's



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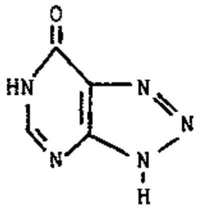
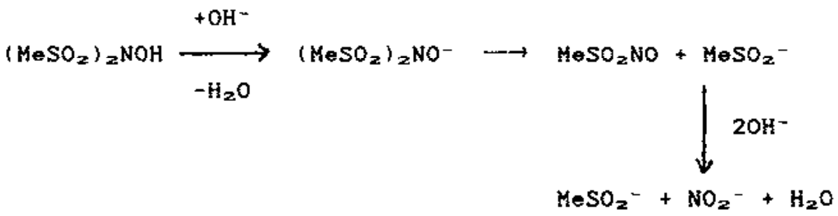


(13)

formulated as MeHgLH, $[(MeHg)_2L].H_2O$, and $(MeHg)_2L'$.[36] An X-ray structure for the latter shows bonding with the N1 and N9 atoms; in $[Zn(H_2O)(L'H)_2]$ the N9 position is also the coordination site.

5.1.3 Bonds to Oxygen

Hydrolysis of a series of hydroxylamine sulphonates, i.e. $(MeSO_2)_2NOH$, $(MeSO_2)_2NOMe$, $MeSO_2NH.OSO_2Me$, $MeSO_2.NMe.OSO_2Me$ and $(MeSO_2)_2N.OSO_2Me$, has been investigated over the complete pH range



$$\begin{array}{l} (MeSO_2)_2NOH \xrightarrow[-H_2O]{+OH^-} (MeSO_2)_2NO^- \longrightarrow MeSO_2NO + MeSO_2^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \big\downarrow 2OH^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad MeSO_2^- + NO_2^- + H_2O \end{array} \quad ...(2)$$

and for the first compound, the steps outlined in equation (2) are followed.[37]

A reexamination of the of the chemistry of tetramethylammonium superoxide shows the reported dimer to be a peroxide addition compound with acetonitrile, MeC(OO) :NH, which on hydrolysis gives the acetamide adduct, $[MeC(O)^{-}(OH)NH_2]$.[38] The original preparation also produces some Me_4NOH and Me_4NOOH, and it is suggested it be replaced by the reaction of potassium superoxide with $Me_4NOH.H_2O$.

Reduction of both N_2O and NO to nitrogen by carbon monoxide at 100°C in the presence of $Rh_2(CO)_4Cl_2$ has been investigated with the following being important steps.[39]

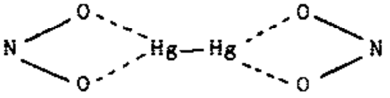
$$2NO + CO \longrightarrow N_2O + CO_2 \qquad ...(3)$$

$$N_2O + CO \longrightarrow N_2 + CO_2 \qquad ...(4)$$

$$2NO + 2CO \longrightarrow N_2 + 2CO_2 \qquad ...(5)$$

Cocondensation of iron and nitric oxide has led to matrix isolation of the binary nitrosyls, $Fe(NO)_x$ for X = 1-4, characterised for x = 1 and 2 by Mossbauer spectroscopy.[40] In addition, i.r. data for n = 4 point to the presence of three linear and one bent NO group with pseudo-tetrahedral symmetry about iron.

N-nitrosohydroxylamine-N-sulphate is the product observed in a kinetic study of the reaction of dissolved NO with sulphite and hydrogen sulphite over the pH range 4-10.[41] Reduction of NO with hydroxylamine and the substituted hydroxylamines, MeNHOH, NH_2OMe and MeNHOMe, requires abstraction of an N-bound hydrogen by NO to form HNO.[42] Trace amounts of oxygen catalyse the hydroxylamine reaction but with N,N-dialkyl hydroxylamines reduction involves abstraction at the α-carbon atom. This reaction is inhibited by O-methylation since a reactive anion cannot be formed.[43]



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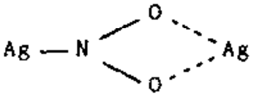


(<u>15</u>)

The mercury(I) nitrite structure contains the almost planar molecular unit (14) with mercury distances to mercury and oxygen of 252.0 and 224.4/257.7pm respectively.[44] In the ternary $Ag_2Li(NO_2)_3$ the basic unit (15) is also almost planar and the short Ag...N contact (224.1pm) suggests some degree of covalent interaction.

Some insight into the mechanism of the reduction of NO_2 to ammonia has been gained by an investigation of the electrochemical oxidation of $[(terpy)(bipy)M(NH_3)]^{2+}$ and reduction of $[(terpy)(bipy)M(NO_2)]^{+}$ (M = Ru or Os).[45] The critical step is interconversion to the nitrosyl form which can undergo a series of one electron reductions.

The complex reaction of sodium nitrite and sulphur in DMF, DMSO and HMPA has been investigated by the whole range of spectroscopic methods supplemented by gas analysis and chromatography.[46] Inter alia, the reaction leads to nitrous and nitric oxides, thiosulphate, polysulphide, polythionates and nitrate with the first step being the formation of perthionitrates, NaS_xNO_2. These can then either decompose to N_2O and thiosulphate or react with nitrite yielding nitrate and perthionitrite, NaS_2NO. Colour changes during the reaction from blue-green to orange-red are due to the formation of blue S_3^- and red $ONSS^-$.

A new synthetic route to N_2O_5 involves reaction of nitryl fluoride and lithium nitrate, the product is very pure and detailed Raman spectra are reported.[47]

Catalytic reduction of nitrate to ammonia has been observed for the first time using a modified glassy carbon electrode in water in the presence of $[Bu_4N]_3[Mo_2Fe_6S_8(SPh)_9]$.[48]

Structures of three basic mercury(I) nitrates, all hydrolysis products of mercury(I) nitrate dihydrate, i.e. $[(Hg_2)_2O(NO_3)]NO_3.-HNO_3$, $[(Hg_2)_5(OH)_4(NO_3)_2](NO_3)_4$ and $[Hg_2(OHg)_2](NO_3)_2$, show the mercurioxonium ion as a common feature of all three structures.[49] In the first it is an infinite chain species with the solvate nitric acid molecule hydrogen bonded to one of the nitrate ions. The second compound contains a finite four oxonium chain while the last contains an infinite folded layer with both Hg(I) and Hg(II) atoms.

Three bidentate nitrate groups and four water molecules give the europium atom in $[Eu(NO_3)_3(H_2O)_4].H_2O$ ten-fold, bicapped square antiprismatic, coordination.[50] Distances to the oxygen atoms of the coordinated nitrate groups are 252/263, 250/255, and 247/258pm.

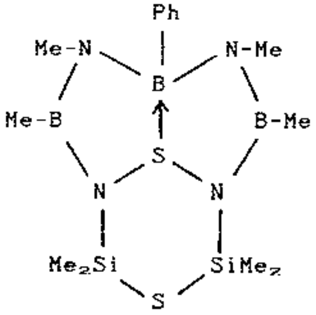
5.1.4 Bonds to Halogens

I.r. spectra are now available for Me_2NCl and the recently prepared salts $[Me_2NClH]X$ (X = CF_3SO_3, SO_3F and BCl_4 and boron trihalide addition compounds.[51] In addition there is an X-ray study for $Me_2NCl.BCl_3$ (N-B 167pm). According to n.m.r. evidence, reorganisation between $Me_2NCl.BF_3$ and $Me_2NCl.BCl_3$ in liquid sulphur dioxide at -50°C leads to both BF_2Cl and $BFCl_2$ adducts of dimethylchloramine.[52]

Tertiary phosphines are oxidised by nitrogen trichloride to R_3PCl_2 (R = Me, Et, Bu or Ph) with elimination of nitrogen. Phosphorus trichloride is similarly oxidised to PCl_5 but with chloramine. PCl_3 gives a mixture of trimeric and tetrameric cyclochlorophosphazenes.[53]

5.1.5 Bonds to Other Non-metals

Although compounds containing such bonds are discussed in detail in Chapters 3-6, a number are noted here. An interesting tricyclic product (16) is obtained in place of the expected compound when (17) and $PhB(NHMe)_2$ are refluxed in carbon tetrachloride; the product is stabilised by coordination between sulphur and boron.[54]



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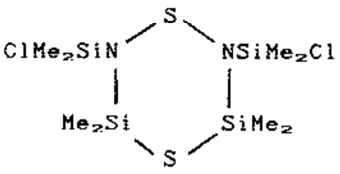


(17)

Two groups[55,56] have reported the preparation of products containing a silicon-nitrogen double bond using the reactions outlined in equations (6) and (7). The t-butyl substituent

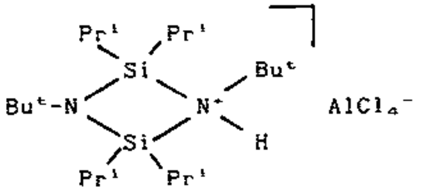
$Bu^t_2SiClN_3 + NaSiBu^t_3 \longrightarrow NaCl + N_2 + Bu^t_2Si{=}N{-}SiBu^t_3$ ...(6)

$Pr^i_2SiCl.NLiR \xrightarrow{heat} LiCl + Pr^i_2Si{=}N{-}R$ ...(7)
$(R = 2,4,6\text{-}C_6H_2Bu^t_3)$

compound has silicon-nitrogen bond distances of 156.8 and 169.5pm and reacts with THF to give a 1:1 addition compound in which bonding is exclusively via the unsaturated silicon atom (Si-O 188.8/186.6pm in the two independent molecules present). The second compound was isolated as orange crystals melting without decomposition at 97-99°C, its ^{29}Si resonance at δ 60.3 implies unsaturation. A theoretical treatment of the model compound, $H_2Si{:}NH$, points to an angle of 126.6° at the nitrogen atom but a low barrier (6.0 $kcal.mol^{-1}$) to linearisation.[57] Eletronegativity effects of attached groups will also affect the nitrogen angle.

Continuing work on silylamines has shown a monomeric, gas phase structure for $SiH_2Cl(NMe_2)$ with parameters (Si-N 168.9pm) similar to those in related compounds.[58] Dimerisation however takes place in the solid state to give a centrosymmetric structure with Si-N distances increased to 181.4/205.4pm, elongation of the Si-Cl distance is also observed.

Both mono- and diprotonated cyclosilazanes (18) and (19) have been isolated by treating $(Pr^i_2SiNBu^t)_2$ with aluminium chloride in hexane-dichloromethane solution.[59] X-ray quality crystals of



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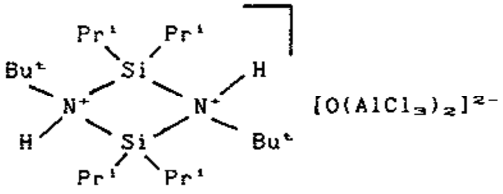
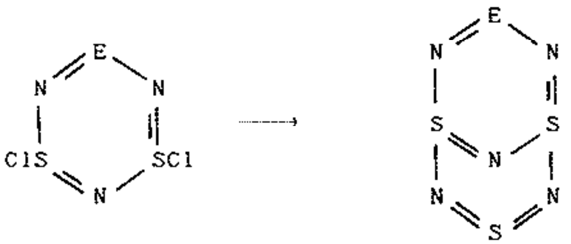


(19)

(19) could be obtained showing an increase in the Si-N separation to 179.2pm from the 174.7pm in the starting material.

Trisulphonylamines, $N(O_2SR)_2(O_2SR')$, can be prepared by cleavage of aminostannanes $Me_3SnN(SO_2R)_2$ with a sulphonyl chloride.[60]

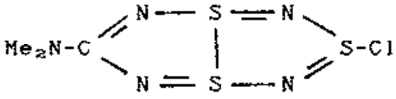
In the sulphur-nitrogen field, the interesting ring expansion in equation (8) can be achieved by treatment with either $(Me_3Si)_2NSN$



...(8)

E = Me_2NC, Et_2NC
Pr_2NC or R_2P

or Me_3SiNSO.[61] The latter reagent also yields as a minor product an eight membered ring compound (<u>20</u>) with a trans-annular S-S bond (243.2pm).



(<u>20</u>)

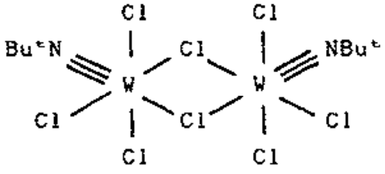
5.1.6 <u>Bonds to Metals</u>

Weak 1:1 ammonia addition compounds with lithium, sodium, potassium and cesium have been identified by matrix isolation methods.[62] I.r. band shifts are consistent with calculations of very small ammonia-metal charge transfer, with both lithium and sodium behaving as weak Lewis acids; increased interactions for K and Cs may suggest possible acid-base role reversal.

A tetrameric titanium compound containing the metal in both the +3 and +4 oxidation states is obtained by reducing $TiBr_4$ with borohydride in liquid ammonia and is formulated as $[NH_3.NH_4]_2[Ti_4Br_4(NH_2)_{12}]$.[63]

Recently reported structures for $Rb_3[La(NH_2)_6]$ and the neodymium compound are similar to those for $K_3[Cr(OH)_6]$ and K_4CdCl_6; the compounds were obtained by treating the appropriate metals with ammonia under pressure.[64] The mixed cesium-lithium compounds $CsLi(NH_2)_2$ and $CsLi_2(NH_2)_3$, obtained similarly, have structures containing infinite twisted $[Li(NH_2)_{4/2}{}^-]$ chains where the lithium atoms lie at the centre of a distorted tetrahedron of nitrogen atoms.[65]

New tungsten nitrene complexes, including (<u>21</u>)[66] and $WBr_4(NCBr_3).NCBr$,[67] have been reported, the former by treating



(<u>21</u>)

WCl_6 with an iminoborane, $Bu^tB{:}NBu^t$, and the latter from WBr_6 and BrCN. In both cases the W-N bond distance, ca. 170pm, corresponds to a triple bond. Both compounds can be converted to anionic $[WX_5(NR)]^-$ species on reaction with an appropriate phosphonium halide. An osmium nitrene, $OsF_5(NCl)$, results when the mixture from an OsF_6/Me_3SiNCO reaction is oxidised with chlorine trifluoride.[68] Crystallisation from anhydrous hydrogen fluoride gives the pure material as a white, air sensitive solid melting at 170-4°C.

Titanium-nitrogen double bonding (Ti-N ca. 182pm) with end on ligand attachement is found in both $CpTiCl_2(NCBu^nBu^t)$ and $CpTiCl_2(NPPh_3)$.[69] With $CpTiCl_2(NNPh)$ on the other hand, the ligand is side on bonded with two Ti-N separations of ca. 200pm. Side on bonding is also observed in the hydrazide complexes, $CpTiCl_2(NPhNH_2)$ and $CpTiCl_2(NHNMe_2)$.[70]

Two μ-nitrido complexes, $[Mo_2NCl_9]^{2-}$ and $[Mo_2NCl_9]^-$ with $[MePh_3P]^+$ as cation have been isolated by treating either $[MoNCl_4]^{2-}$ or $[MoNCl_4]^-$ with $MoCl_5$ in dichloromethane.[71] Related bridged nitrido complexes result from ammonolysis of $NbBr_5$, WBr_6 or TaI_5 at 350-400°C; the complexes, formulated as $[M_2NX_{10}]^{3-}$, contain a symmetrical linear nitrido bridge (Nb-N 184.5, Ta-N 184.7pm) with D_{4h} point symmetry for the molecules.[72] This contrasts with ammonolysis of WCl_6, $ReCl_5$ or $MoCl_5$, which gives $(NH_4)_2MCl_6$, with the metal in the +4 oxidation state.

The nature of metal ligand interactions in the dicyanamide complexes $M[N(CN)_2]_2L_2$ [73] and $M[N(CN)_2]_4$ [74] (M = Pd or Pt and L = Ph_3P, py, etc.) in relation to i.r. and n.m.r. data has been discussed. A gold-nitrogen cluster containing four metal and twelve nitrogen atoms has been isolated from a reaction between gold(I) iodide and $Na(PhN_3Ph)$ in liquid ammonia.[75] The four gold atoms form a rhombus where the atom separation (mean 285pm) is shorter than in the metal. The structure is completed by four bidentate diphenyl triazenido ligands alternately above and below the Au_4 ring.

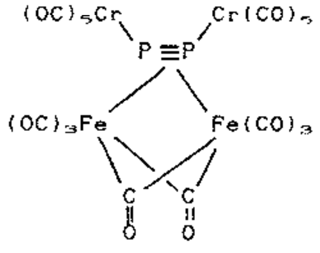
5.2 PHOSPHORUS

5.2.1 Phosphorus, Polyphosphines and Phosphides

Ab initio calculations on the trimerisation of P_2 within a D_{3h} symmetry pathway indicate that although P_6 lies 6 k.cal mol^{-1} above three P_2 fragments, decomposition to the latter has an energy barrier of 13 k.cal mol^{-1} and it may therefore be possible to detect cyclic P_6 in a low temperature inert gas matrix.[76] Further ab initio calculations are available for P_4, cyclo-P_3H_3 and tetraphospha-bicyclo butane.[77] Theoretical studies point to a 36 k.cal mol^{-1} barrier to rotation in HP=PH compared with values 63.5 and 47 k.cal mol^{-1} for HN=NH and HP=NH respectively.[78] The barrier to rotation can be taken as a measure of π bond strength and the data show that the bond between two phosphorus atoms is stronger than that between two silicons (22 k.cal mol^{-1}). Further the diphosphene trans-HP=PH is calculated to be ca. 27 k.cal mol^{-1} more stable than the isomeric H_2PP form.

Coordination of a $P\equiv P$ unit, both side and end-on, occurs in the cluster (23) which results when $Fe_2(CO)_9$ reacts with $(OC)_5CrPBr_3$.[79]

Cis-trans isomerisation of $Bu^t_3C_6H_2P=PC_6H_2Bu^t_3$ has been reviewed and reaction with oxygen at 80°C over three days shown to give a mixture of (24), (25) and (26).[80] Magnesium dehalogenation of



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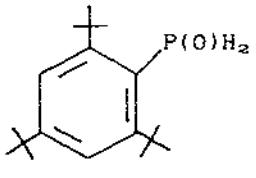

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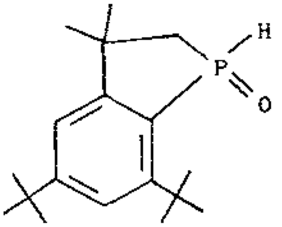
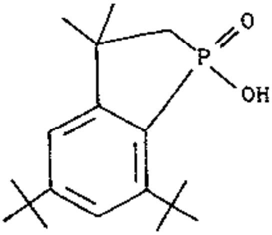


(<u>25</u>)

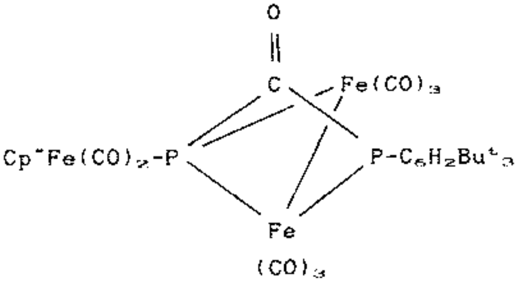


(<u>26</u>)

(menthyl)PBr$_2$M(CO)$_5$, for M = Cr or W, leads to complexes containing both substituted diphosphenes, (OC)$_5$M.(menthyl)P=P(menthyl).M(CO)$_5$, and phosphinidines (menthyl)P[M(CO)$_5$]$_2$.[81] Structures for the two chromium compounds were determined showing double bond character (P-P 204.0pm) and non-involvement of the π-bond of the diphosphene in complex formation.

Complexes containing the η^2-bonded silylated diphosphene (Me$_3$Si)P=P(SiMe$_3$) are products obtained by treating NiCl$_2$[R$_2$PCH$_2$CH$_2$PR$_2$], where R = Et, Hex^c or Ph, with LiP(SiMe$_3$)$_2$.[82] Mono- and di-substituted compounds, i.e. NiCl[R$_2$PCH$_2$CH$_2$PR$_2$][P(SiMe$_3$)$_2$] and Ni[R$_2$PCH$_2$CH$_2$PR$_2$][P(SiMe$_3$)$_2$]$_2$ are low temperature stable intermediates. Complexes containing the related PhP=PPh can be obtained from the original nickel chloride complex and PhP(SiMe$_3$)$_2$ while Ni[R$_2$PCH$_2$CH$_2$PR$_2$][P$_2$Bu^t$_2$] can be prepared using [P(SiMe$_3$)Bu^t]$_2$ as starting material.

Cleavage of the double bond of a coordinated diphosphene has been observed for the first time when Cp"Fe(CO)$_2$P=PC$_6$H$_2$Bu^t$_3$ was treated with an excess of Fe$_2$(CO)$_9$.[83] The products were (<u>27</u>), in which the phosphorus atoms are linked by a carbonyl bridge, and a small amount of the diphosphene complex (<u>28</u>). X-ray structures were carried out for both compounds. Treatment of Cp"Mn(CO)(NO)-P(SiMe$_3$)$_2$ with Bu^t$_3$C$_6$H$_2$PCl$_2$ gives the diphosphenyl complex, Cp"Mn(CO)(NO)P=P-C$_6$H$_2$Bu^t$_3$, [84], while an excess of nickel carbonyl converts Cp"M(CO)$_2$-P=P-C$_6$H$_2$Bu^t$_3$, for M = Fe or Ru to the adducts (<u>29</u>).[85]



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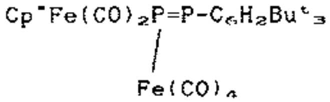
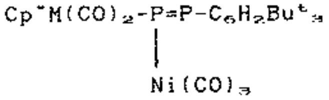


$$Cp^{*}Fe(CO)_2P{=}P{-}C_6H_2Bu^t_3 \quad (\text{P}{-}Fe(CO)_4)$$

(28)



$$Cp^{*}M(CO)_2{-}P{=}P{-}C_6H_2Bu^t_3 \quad (\text{P}{-}Ni(CO)_3)$$

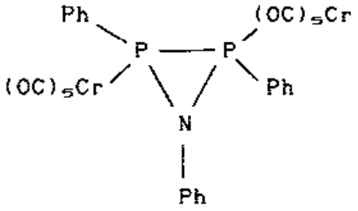
(29)

The general reactivity of two diphosphenes, $P_2[C(SiMe_3)_3]_2$ and $P_2[C_6H_2Bu^t_3]_2$, towards electrophiles and nucleophiles has been investigated.[86] With hydrogen chloride, the former gives $(Me_3Si)_3C{-}PH{-}PCl{-}C(SiMe_3)_3$ and $PHCl[C(SiMe_3)_3]$, depending on the amount used, while with $HBF_4.Et_2O$, the product is $[PH_3(C(SiMe_3)_3)][BF_4]$. On the other hand, P=P bond cleavage occurs with the tri-t-butylphenyl analogue even when using only one equivalent of hydrogen chloride. Both mono and di-cations, $[RP{=}PRAg]^+$ and $[AgRP{=}PRAg]^{2+}$ ($R = C_6H_2Bu^t_3$), result from reaction with $Ag[SO_3CF_3]$ and the anion [RP-PRMe]- is produced on treatment with methyllithium. Quenching with methanol then gives the diphosphine RHP-PMeR; similar reactions occur with BuLi and Bu^tLi.

Electrochemical reduction leads to radical anions $[R_2P_2]^{\cdot -}$ for R = $(Me_3Si)_3C$ [87,88] and $C_6H_2Bu^t_3$ [87] which are sufficiently stable to be investigated by e.s.r. spectroscopy; the related arsenic species can also be obtained.[87] Treatment of $[(Me_3Si)_3C]_2P_2$ with sodium in naphthalene apparently gives the same species.[88]

[2+1] Cycloadditions between the chromium carbonyl complexes of phenyl and anisyl diphosphenes, $[RP{=}PR][Cr(CO)_5]$, and respectively phenylazide and sulphur lead to the heterocycles (30) and

(31).[89] ^{31}P n.m.r. shifts for a range of Group 6 metal



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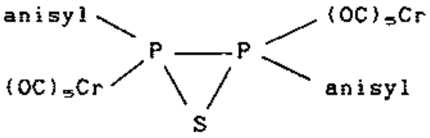
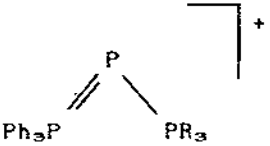


(31)

complexes with diphosphenes, phospha-ethenes and phospha-allenes have been interpreted in terms of their structures in solution. [90]

Addition of aluminium chloride to a dichloromethane solution of the triphosphenium tetrachloroaluminate (32) gives initially a chloromethylation product (33), but further reaction with the starting material leads to a 1,2-diphosphoniodiphosphirane dication (34).[91] For the second stage of the reaction to proceed, it



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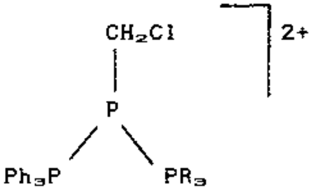

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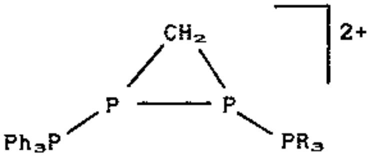


(34)

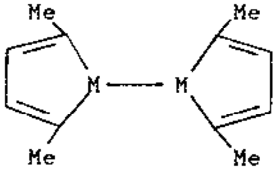
is essential that one of the phosphorus atoms carries an amino-substituent and compounds have been isolated for R = NMe_2 or piperidino and R_3 = Bu^t(piperidino)$_2$. An X-ray structure is available for the latter.

A new review summarises work in the polyphosphine area since the 1982 review.[92] and the chemistry of transition metal complexes containing P, P_2, P_3 and P_4 units has also been surveyed.[93]

Solutions of alkali metals from lithium to cesium in liquid ammonia react with phosphine to give MPH_2 but the lithium salt is unstable at room temperature and evolves phosphine.[94] Both KPH_2 and $RbPH_2$ have three different crystalline forms between 110 and 400K, with a NaCl type high temperature form. Between the same limits $CsPH_2$ shows only the CsCl type structure.

P-P bond formation is promoted when phosphonous or phosphinous chlorides are treated with the mild, homogeneous reducing agent 1,3,1',3'-tetraethyl-bis(2,2'-imidazolidene).[95] Good yields of R_4P_2 can be obtained from R_2PCl for R = Bu^t, Hex^c, Ph or mesityl while with $Bu^t{}_3C_6H_2PCl_2$, the products are either $Bu^t{}_3C_6H_2PCl$-$PCl(C_6H_2Bu^t{}_3)$ or $Bu^t{}_3C_6H_2P{=}PC_6H_2Bu^t{}_3$, depending on the reaction stoichiometry.

Two papers [96,97] report the results on exchange in the Me_4M_2-$Me_4M'_2$ and M_4M_2-$Me_2M^2{}_2$ systems, where M and M' are Group 5 elements and M^2 is a Group 6 element. Mixtures of Me_4P_2 and Me_4As_2, for example, exchange rapidly (equilibrium constant 0.26) to give Me_2PAsMe_2 either as neat liquids or in benzene solution, and exchange similarly occurs with Me_4Sb_2-Me_4Bi_2 and Me_4Sb_2-Me_4As_2 mixtures. No exchange however was detectable in the Me_4P_2-Me_4Sb_2 and Me_4P_2-Me_4Bi_2 systems in 6 days at 25°C. Mixtures of (35, M = As and Sb) also exchanged and crystals of (36), which is thermochromic, could be isolated by fractional crystallisation.



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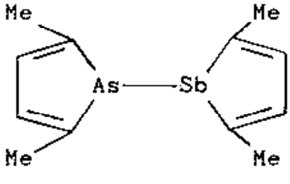
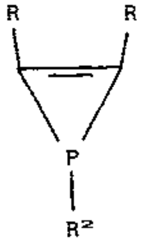


(36)

In systems involving Group 6 methyls, $Me_2M_2^2$ where M^2 = S, Se or Te, exchange with Me_4M_2, where M = P, As, Sb or Bi, gave the corresponding mixed products $Me_2M\text{-}M^2Me$, which were characterised by n.m.r., Raman and mass spectrometry.

Treatment of the phosphete (37) with a dichlorophosphine, R^2PCl_2, leads to the phosphetium salt (38) which can be reduced with Bu_3P to give the diphosphate (39).[98]



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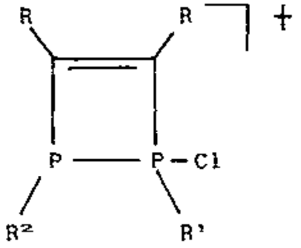

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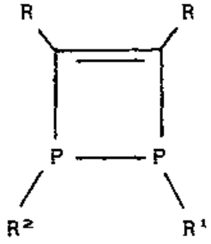
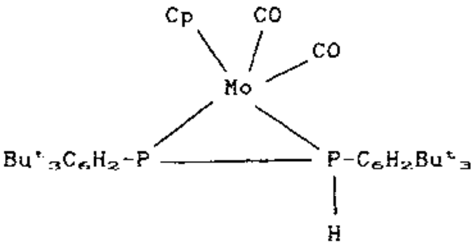


(39)

Products, including RHP-PHR, RHP-PClR, RP=PR and $RP[Mo(CO)_2Cp]_2$, $(R=Bu^t{}_3C_6H_2)$ are obtained when $Bu^t{}_3C_6H_2PCl_2$ reacts at room temperature with $K[CpMo(CO)_3]$; at higher rection temperatures, however, one of the products is a novel complex (40) containing a P_2Mo ring, which shows slight multiple bond character in the P-P system.[99]

Bond cleavage by either potassium in THF or potassium naphthalide in the three membered heterocycles (41), (42) and (43) has been studied. At low temperatures, the first compound gives the dipotassium salt, $KBu^tP.B(NPr^i{}_2).PBu^tK$, which can be converted to the trimethylsilyl compound $(Me_3Si)Bu^tP.B(NPr^i{}_2).PBu^t(SiMe_3)$ with Me_3SiCl.[100] Above -78°C the potassium salt rearranges to the asymmetric analogue $KBu^tP.PBu^t.BHNPr^i{}_2$. P-P bond cleavage is also observed with (42), giving $KBu^tP.CMe_2.PBu^tK$ which decomposes above -78°C to $KPHBu^t$, but with (43) there is preferential P-N cleavage to give $KBu^tP.PBu^t.NHPr^i$.[101] These differences in metallation with P-C, P-N and P-B systems are fully discussed.



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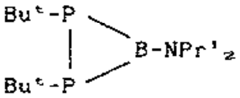

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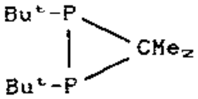

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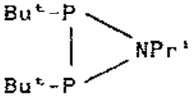
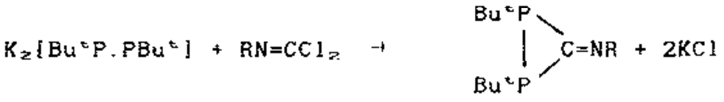


(43)

A new three membered P_2C heterocycle (44) is formed as shown in equation (9), where R = 2-$Bu^tC_6H_4$, 2,4-$Bu^t{}_2C_6H_3$, 2-MeC_6H_4 or mesityl.[102]



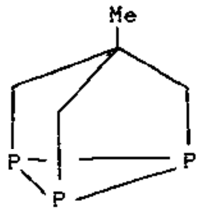
(44) ...(9)

In addition to other products, the reaction of white phosphorus with sodium in liquid ammonia gives the diaminotriphosphine, $H_2N.PH.PH.PH.NH_2$, and although the compound is stable only in liquid ammonia solution, its structure can be investigated by ^{31}P n.m.r. spectroscopy at -65°C.[103]

The substituted triphosphines, $(Bu^tP)_2PMMe_3$ where M = Si or Sn, are obtained when either $(Bu^tP)_{3or4}$ is metallated with potassium and subsequently treated with Me_3MCl.[104] The tin compound reacts further with $RPCl_2$ where R = Cl or Bu^t to give the tetraphosphines $(Bu^tP)_2P.PClR$, each containing a P_3 ring system.

The cyclotriphosphine (45) on treatment in a sealed tube at ca.

200°C with sulphur or selenium in 1:3, 1:5 and 1:6 ratios gives respectively (46, 47 and 48, with X = S or Se).[105] Although compound (48, X = Se) was detected by n.m.r. spectroscopy, the major product in the 1:6 ratio experiments was, in fact, (47, X = Se).



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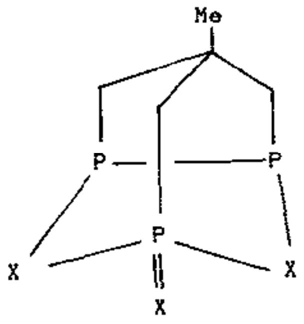

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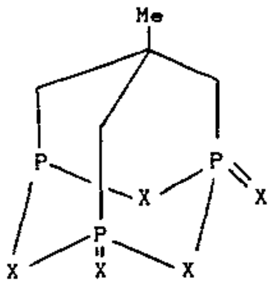

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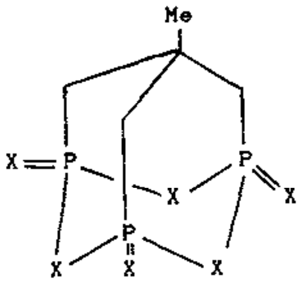
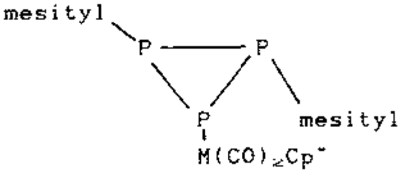


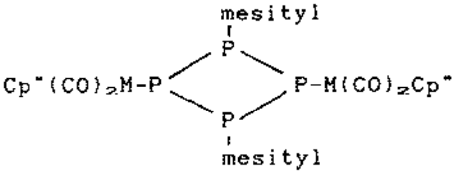
(48)

Substituted cyclotriphosphines (49) are the major products of reaction between (mesityl)PCl_2 and $Cp^{*}M(CO)_2P(SiMe_3)_2$, for M = Fe or Ru but tetaphosphines (50) are by-products and the structure of (50, M = Ru) has been determined by X-ray diffraction.[106]

A number of papers [107-111] deal with investigations of phosphine mixtures by ^{31}P n.m.r. selective population transfer

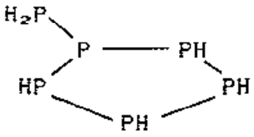


(<u>49</u>)



(<u>50</u>)

experiments. For example, d-, l- and meso-forms of n-P_4H_6 and the isomeric $P(PH_2)_3$ have been identified in mixtures containing 26-48% P_4H_6 and their n.m.r. parameters defined.[107] Mixtures containing 10-15% P_5H_7 obtained by thermolysis of P_2H_4 similarly show three forms of n-P_5H_7 and the iso-form $P(PH_2)_2(P_2H_3)$.[108] P_6H_6 is formed not as a six-membered ring species but as the phosphino-cyclopentaphosphine (<u>51</u>), [109] while for the P_6H_8 stoichiometry there is evidence for three distinct forms of $P(PH_2)(P_2H_3)_2$, two of $P(PH_2)_2(P_3H_4)$ together with the highly symmetrical 2,3-diphosphinotetraphosphine, $H_2P.P(PH_2).P(PH_2)$.[110] In the P_7H_9 system, one isomeric form of 2,3-diphosphinopentaphosphine, $H_2P.P(PH_2).P(PH_2).P_2H_3$, has now been identified.[111]



(<u>51</u>)

A 3:1 molar ratio of $MeP(SiMe_3)_2$ and PCl_3 reacts at -78°C to give the iso-triphosphine $P[P(SiMe_3)Me]_3$, via $Cl_2P.P(SiMe_3)Me$ and $ClP[P(SiMe_3)Me]_2$ as intermediates.[112] The product has almost C_3 symmetry with P-P and P-Si distances of respectively 220.1 and 225.2pm.

Alkyl lithiums (RLi) react with the cyclo-tetraphosphines, $P_4Bu^t{}_3SiMe_3$ and trans-$P_4Bu^t{}_2(SiMe_3)_2$, to give monolithiation with loss of one Me_3Si group; but with the related tetraphosphines, $P_4(SiMe_3)_4$, $P_4Bu^t(SiMe_3)_3$ and cis-$P_4Bu^t{}_2(SiMe_3)_2$, there is P-P cleavage to give n-tetraphosphides, $LiP_4Bu^t{}_{4-n}(SiMe_3)_nR$ (n =

2-4).[113] Even at low temperatures in THF solution, the compounds rearrange via a 1,3-Li/$SiMe_3$ shift to give secondary phosphines, e.g. $LiP[P(SiMe_3)R][P(SiMe_3)P(SiMe_3)_2]$, and on warming to room temperature silyl phosphines such as $LiP(SiMe_3)_2$, $P(SiMe_3)_3$ or $RP(SiMe_3)_2$ are eliminated. In this way, $P_4(SiMe_3)_4$ can be converted into Li_3P_7.

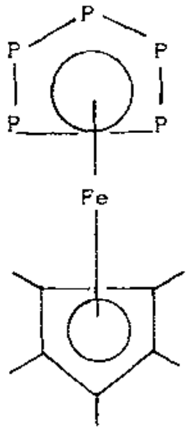
Cyclic voltametry and differential pulse polarography provide data on the electrochemical conversion of $RPCl_2$ to cyclophosphines, showing formation of tetramers for R = Bu^t or 2-BrC_6H_4 and pentamers for R = Ph or 4-BrC_6H_4.[114] Small amounts of other ring sizes are usually also obtained.

White phosphorus is cleaved by sodium in diglyme to give mixtures of salts of the P_5^-, P_4CH^-, $P_3CH_2^-$ anions, all considered to have mesomerically stabilised monocyclic structures.[115] LiP_5 can be obtained in a pure state by treating P_4 with $LiPH_2$.

A chromium complex, $Cp^*Cr(P_5)CrCp^*$, containing the stabilised cyclo-P_5 unit has been isolated from a reaction between $[Cp^*(CO)_2Cr]_2$ and white phosphorus in xylene at 140°C.[116] Currently, complexes containing cyclic P_6 and As_5 units are known. An X-ray structure shows the new compound contains three parallel five-membered rings. A second species (52) containing P_5 as a 6π electron donor has been obtained from a reaction between white phosphorus and $[Cp^*Fe(CO)_2]_2$ at 150°C, as air stable, sublimable green crystals, melting at 270°C.[117]

The first pure cyclopolyphosphine oxides (53)-(56) can be prepared by controlled air oxidation of $P_6Bu^t_4$ and $P_7Bu^t_5$.[118]

White phosphorus retains one of its triangular P_3 faces when it adds to $Cp_2Zr[P(SiMe_3)_2]_2$ to give the new hexaphosphine derivative (57).[119] A new structural type for the P_7R_5 composition (58), a bis(cyclotriphosphino)phosphine, results when two mols of the cyclotriphosphine (59) react with $MePCl_2$; equimolar quantities of the reactants lead to the chlorotetraphosphine (60).[120]



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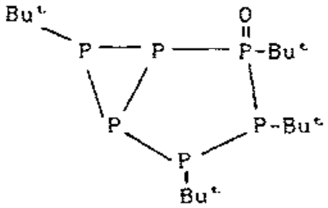

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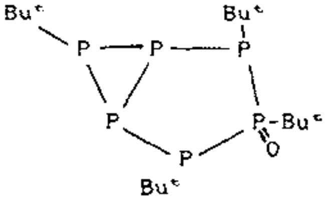

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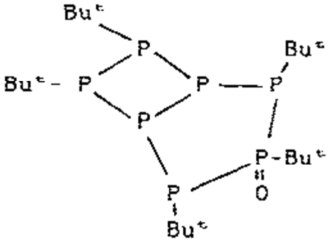

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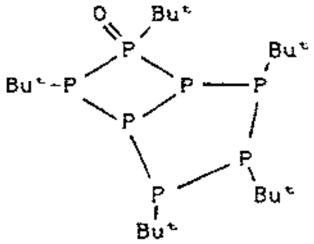

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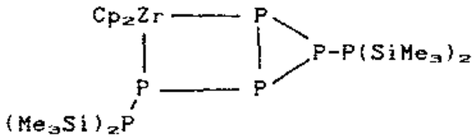

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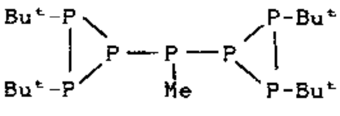

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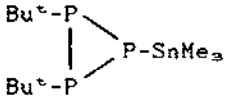

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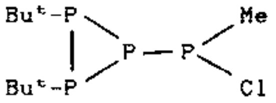
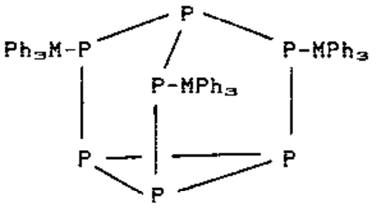


(60)

Germanium and tin derivatives of the P_7 nortricyclen cage (61, M = Ge or Sn) result when (61, M = Si) reacts with either Ph_3GeCl or Ph_3SnCl.[121] N.m.r., i.r. and single crystal X-ray structures are available for all three compounds. The related lithium salt, Li_3P_7, obtained from a high temperature reaction of the elements, crystallises in a new structure when the cage is surrounded by 12 lithium ions; the P-P distances, 224.9, 214.7 and 217.6pm for basal, basal-bridge and bridgehead distances respectively, are however typical of the heptaphosphoranortricyclen cage.[122] Valence tautomerism in $M_7{}^{3-}$ systems has been investigated by a ^{31}P n.m.r. study of the mixed $[P_{7-x}As_x]^{3-}$ species ($x \sim 3$) obtained by heating a stoichiometric mixture of Rb, P and As to 900K.[123] Six signals are observed in ethylenediamine solution and assigned to species in the series $[P_{7-x}As_x]^{3-}$ with x = 0-5.



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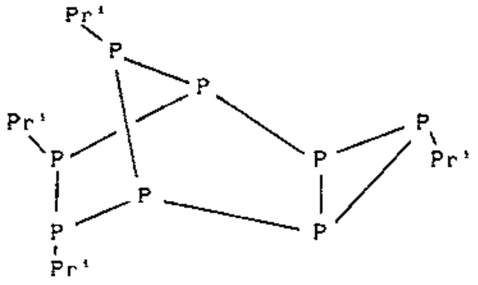
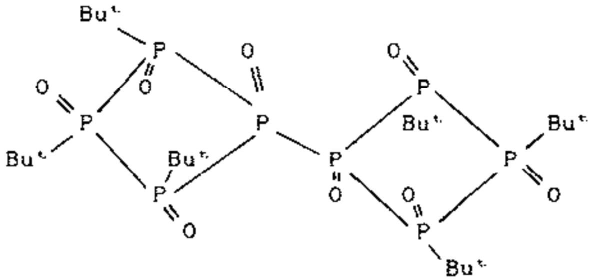


(62)

A new octaphosphine, $P_8Pr^i{}_4$ (62), with a homonorbornene constitution has been isolated by thermolysis of the product mixture obtained when mixtures of Pr^iPCl_2 and PCl_3 are treated with magnesium metal.[124] For a phosphorus(III) compound, $P_8Bu^t{}_6$ is surprisingly stable but it can be converted to an octa-oxide (63) by hydrogen peroxide, peracetic acid or cumene hydroperoxide.[125] Pure samples of P_9Et_3, can be obtained by thermolysis of either P_5Et_4-P_4 or P_7Et_5-P_8Et_6-P_5Et_5 mixtures at 200-220°C and the related t-butyl can be prepared by dehalogenation of a 1:2 mixture of Bu^tPCl_2 and PCl_3.[126] Complete analysis of the ^{31}P n.m.r. spectra show they are based on a deltacyclane type structure (64), in two configurational isomeric forms.



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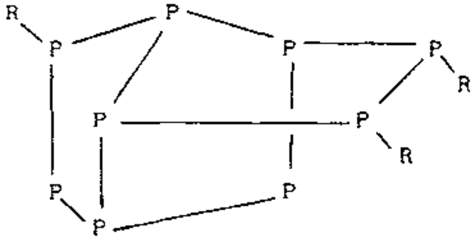
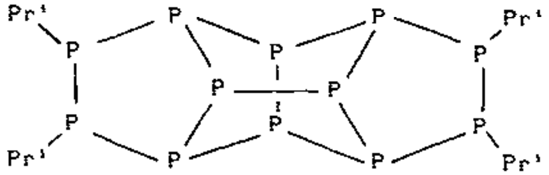


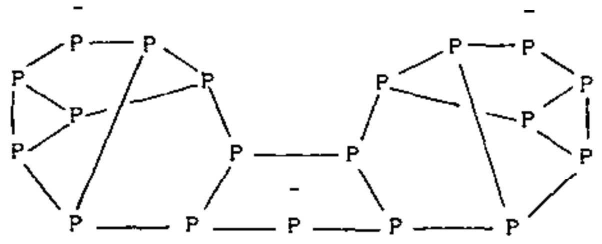
(64)

A central P_8 unit with the realgar, cradle structure is found in $P_{12}Pr^i_4$, previously obtained by dehalogenating a mixture of Pr^iPCl_2 and PCl_3 with magnesium in THF solution.[127] The full P_{12} structure shown in (65) has close to C_{2v} symmetry and contains the essential structural element of Hittorf's phosphorus. Two P_{16}^{2-} salts have recently been isolated, $Li_2P_{16}.8THF$ by disproportionation of Li_2HP_7 in THF solution,[128] and the solvated sodium salt by reaction of white phosphorus with sodium in the presence of 18-crown-6 in boiling THF.[129] P_{19}^{3-} anions with structure (66) deduced from detailed two-dimensional n.m.r.



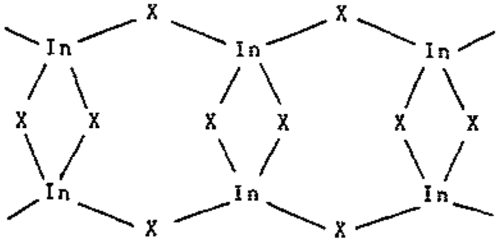
(65)

spectroscopy can be obtained in a number of ways including nucleophilic cleavage of P_4 with either $LiPH_2$ or metallic sodium or potassium, reaction of Li_3P_7 with white phosphorus, and reaction of Li_2P_{16} with $LiPH_2$.[130] The compounds are possibly intermediates



(66)

in P_{16}^{2-} formation from P_7^{3-}. Finally in this section, treatment of Na_3P_{21} with alkyl bromides or Me_3SiCl leads to partially metallated compounds, such as $NaP_{21}Me_2$, $NaP_{21}Et_2$, $NaP_{21}Pr^i{}_2$ and $NaP_{21}(SiMe_3)_2$.[131]



(67)

Strings of edge and vertex sharing InP_4 or $InAs_4$ tetrahedra (67, X = P or As), are found in the structures of the new Zintl phases $Sr_3In_2P_4$ and $Ca_3In_2As_4$, obtained by heating the elements to 250K.[132] The $Ba_3Sn_2P_4$ structure, shown in Figure 1, contains infinite chains of $(Sn_2P_4)^{6-}$ units formed by linking Sn_2P_4 groups via one double (SnP_2Sn) and two single (SnPSn) bridges to give a series of alternating four and eight membered rings.[133] Among new polyphosphides obtained during the period under review are: $TiMn_2P_{12}$,[134] $ZrNi_4P_2$ (with a $ZrFe_4Si_2$ structure),[135] $ZrNi_2P_2$ ($CeAl_2Ga_2$ structure),[135] $SrPt_4P_6$, $SrPt_4As_6$, $BaPt_4As_6$ and $BaPt_2P_3$(pyrite type structures),[136] $CaCu_4P_2$ (rutile type structure of calcium and phosphorus atoms with chains of edge sharing copper tetrahedra occupying the vacancies),[137] and $ZrCu_2P_2$ and $HfCu_2P_2$ ($CaAl_2Si_2$ structure).[138]

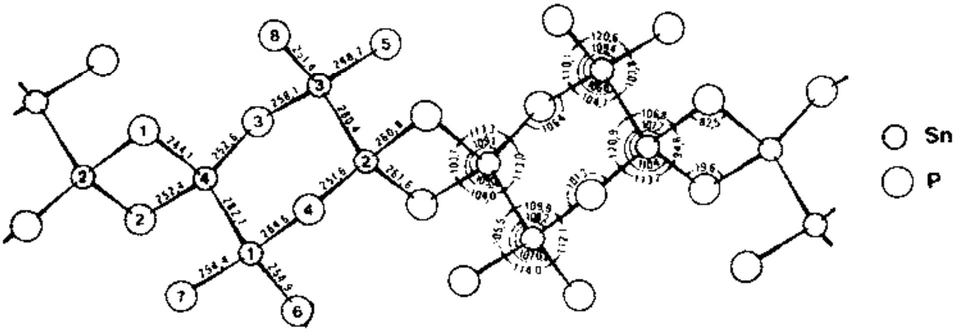
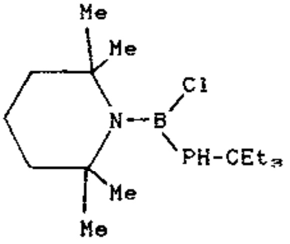


Figure 1. Structure of $Ba_3Sn_2P_4$ (Reproduced by permission from Z. Anorg. Allg. Chem., 532(1986)73).

5.2.2 Bonds to Group 3 Elements

A series of compounds containing P-B double bonds has been isolated from reactions of $RPHB(mesityl)_2$, where R = Ph, mesityl or Hex^c, with t-butyl lithium.[139] The compounds, $[Li(Et_2O)_2RPB(mesityl)_2]$ for R = mesityl or Hex^c and $[Li(12\text{-crown-}4)_2]$-$[(mesityl)PB(mesityl)_2]$ are monomers from X-ray single crystal studies with planar geometry about both phosphorus and boron and P-B separations (ca. 183pm) suggesting substantial double bond character. Dehydrohalogenation of the substituted phosphinoborine (68) on the other hand produces a cyclic dimer (69), rather than a π-bonded monomer, even though both atoms carry bulky



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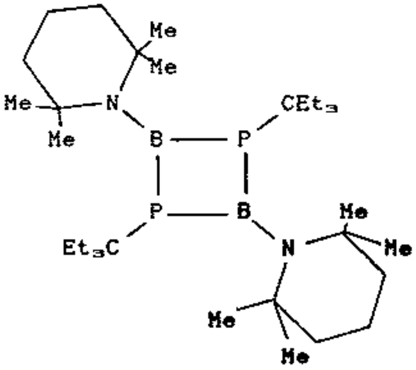
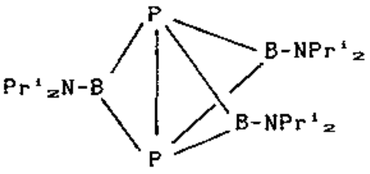


(69)

substituents.[140] On the other hand, $Ph_2PB(mesityl)_2$, is monomeric with a P-B bond length, 185.9pm, substantially shorter than the single P-B distance.[141]

Four membered P_2B_2 and As_2B_2 ring compounds, $(RMBR^1)_2$ for R = mesityl, R^1 = 2,2,6,6-tetramethylpiperidino and M = P or As, can be obtained by treating $RMLi_2$ with R^1BCl_2 but an X-ray structure for the phosphorus compound shows that the P-B bond is single (191.6pm).[142] Reaction of RPHLi with R^1BCl_2 similarly yields $RP(H)B(Cl)R^1$ which also contains a single B-N bond.

An unusual trigonal bipyramidal P_2B_3 cage compound (70) has been isolated when $(Pr^i{}_2N)BCl.P(SiMe_3)_2$ and $(Pr^i{}_2N)BCl_2$ are heated in the absence of solvent to 160°C; the phosphorus atoms occupy apical positions with P-B distances of 196.9pm.[143]



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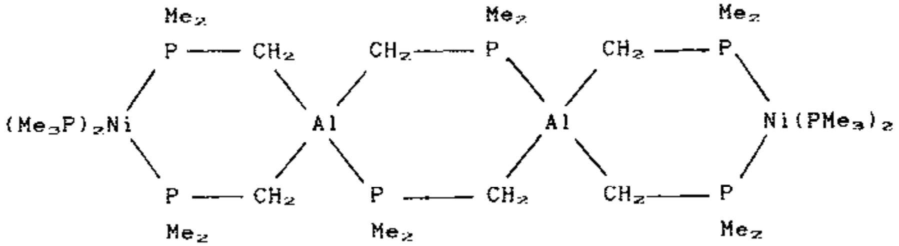


(71)

Electron diffraction data for the trimer $(Me_2PAlMe_2)_3$ have been refined on the basis of a chair (C_{3v}) model showing Al-P distances of 243.4pm with Al-P-Al and P-Al-P angles of 131.7 and 96.4°, respectively.[144] A related compound $(MePhPAlMe_2)_3$ results when benzene is eliminated from MePhPH and Me_2AlH mixtures, and spectral data suggest the product is an isomer mixture due to different orientations of exocyclic groups and different ring conformations.[145]

The major product of the reaction between $Al(CH_2PMe_2)_3$, PMe_3 and $Ni(COD)_2$ in pentane at low temperatures is a yellow, thermochromic cyclic dimer, formulated as (71).[146]

New gallium phosphides formulated as $Ga(PRX)_3$, where R = Bu^t or $Bu^t{}_3C_6H_2$ and X = Bu^t or H, have been prepared by treating $GaCl_3$ with either three mols of $Bu^t{}_2PLi$ or $Bu^t{}_3C_6H_2P(H)Li$ in toluene or THF at -78°C.[147] Reactions of $GaCl_3$ with one mol of $Bu^t{}_2PLi$ and two mols of RLi (R = Me or Bu^n), on the other hand, give dimers $(R_2GaPBu^t{}_2)_2$.

5.2.3 Bonds to Group 4 Elements

As in previous reviews, bonds to phosphorus(III) are treated before phosphorus(V) compounds and in each section multiply bonded species are considered first.

Bonds between Carbon and Phosphorus(III). A new approach to phospha-alkyne synthesis uses the reaction between acid chlorides and $P(SiMe_3)_3$ (equation 10), in which acylphosphines are probably intermediates.[148] Loss of $(Me_3Si)_2O$ occurs at 120-160°C in the

$$RCOCl + P(SiMe_3)_3 \rightarrow [(Me_3Si)_2P{-}C(O)R] + Me_3SiCl \qquad ...(10)$$

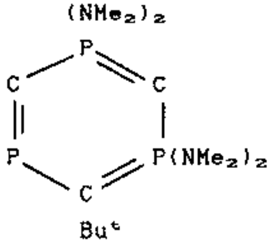
$$[(Me_3Si)_2P{-}C(O)R] \rightarrow Me_3SiP{=}CR(OSiMe_3)$$

$$P{\equiv}CR \xleftarrow{-(Me_3Si)_2O} Me_3SiP{=}CR(OSiMe_3)$$

R = Pr^i, CH_2Bu^t, etc.

presence of sodium hydroxide as catalyst to give the appropriate phospha-alkyne which can be characterised by cycloaddition reactions with CH_2N_2, MeN_3, etc.

The synthesis of the first triphosphabenzene (72) is reported as the sole product of the reaction of $P{\equiv}CBu^t$ and the diphosphete (73).[149] The compound is air and moisture sensitive and



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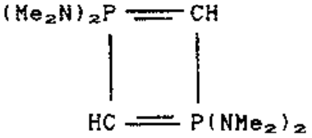

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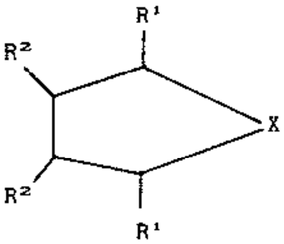

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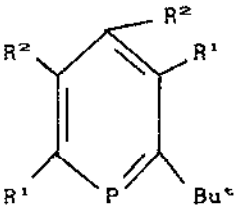
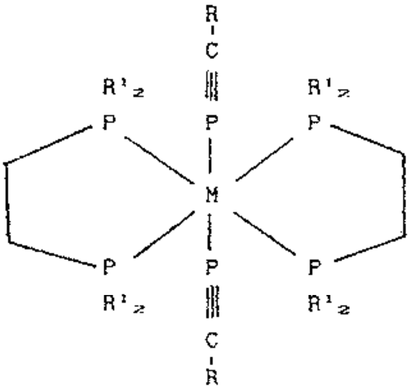


(75)

contains an almost planar ring with five short P-C bonds (mean 170.2pm) and one long bond (175.8pm). The phospha-alkyne also undergoes Diels-Alder reactions with cyclic 1,3-dienes (74),

R^1/R^2 = H, Me, Ph: X = O, P(S)Ph, etc.) to give unstable adducts which decompose to λ^3-phosphinines (75).[150]

η^1-Bonding by both $P\equiv CBu^t$ and $P\equiv C$(adamantyl) has now been observed in a series of compounds formulated as shown in (76, R^1 = Et, Ph or 4-MeC_6H_4: M = Mo or W).[151] The structure has been confirmed for the adamantyl derivatives (76, R^1 = Et and M = Mo) by X-ray studies, which show short Mo-P and P-C distances, 230.5 and 152pm respectively. μ^3-μ^2 behaviour on the other hand is found in the complex anions $[M_3H(CO)_9(P\equiv CBu^t)]^-$ isolated from reaction of $P\equiv CBu^t$ with $[M_3H(CO)_{11}]^-$ where M = Fe or Ru.[152]



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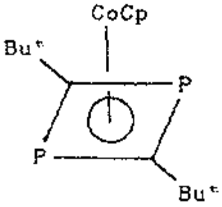

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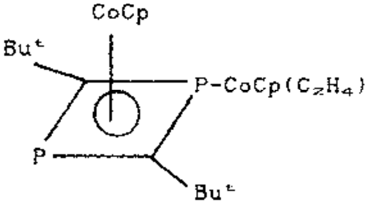

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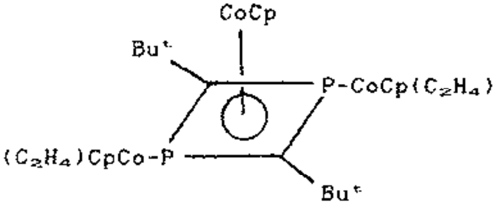
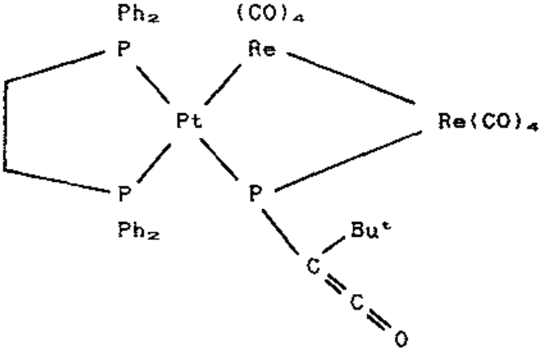


(79)

$P\equiv CBu^t$ dimerises on reaction with $CpCo(C_2H_4)_2$ to give successively the complexes (77)-(79), [153] and a second group of workers have widened the scope of the reaction by using a range of ethylene complexes, $[M(C_5R_5)(C_2H_4)_2]$ where R = H, M = Co or Rh and R = Me, M = Co, Rh or Ir.[154] The products are confirmed as complexes, $(C_5R_5)M(PCBu^tPCBu^t)$, of the previously unknown 1,3-diphosphacyclo-butadiene by an X-ray study of the product with R = Me and M = Co. The P_2C_2 ring is essentially planar with equivalent P-C bond lengths.

A phosphinidine complex (80) is obtained in the reaction between $[ReH_2(CO)_8]$ and $[Pt(dppe)(P{\equiv}CBu^t)]$ as a consequence of carbon monoxide attack on the coordinated phospha-alkyne.[155]



(80)

Two groups, [156,157] have reported ab initio calculations for CH_3P. In the first, local minima corresponding to CH_3P, CH_2PH and $CHPH_2$ were identified but singlet phospha-ethene was the global minimum, lying some 43 kcal.mol^{-1} below singlet methylphosphinidine. The calculations also support the proposition that R_2PCR species are key intermediates in the photolysis of phosphinodiazomethanes; they have singlet ground states and are best considered as λ^3-phosphinocarbenes rather than λ^5-phospha-acetylenes. In the second, calculations for HPX_2 where X = CH_2, NH or O are also given together with a comparison with the two-coordinate analogues HPX. Among the conclusions is the fact that d orbital participation is small but becomes increasingly significant as the electronegativity of X increases.

Further calculations [158] have attacked the problems of addition and insertion reactions of phosphinidine (PH) with ethylene and the electronic characteristics of the isomeric vinyl phosphine (HP=CHMe), the phosphirane $\overline{H_2C\text{-}CH_2\text{-}PH}$ and the phospha-alkenes HP=CHMe and $MeP{=}CH_2$. The latter is calculated as being the most stable isomer with vinyl phosphine the least stable. Valence isomerism in phospha-alkenes has been reviewed, [159] as has the problem of cycloadditions with compounds containing λ^3-σ^2 bonds between phosphorus or arsenic and carbon.[160]

Almost quantitative yields of the phospha-alkene, $(\mathrm{Pr}^i_2\mathrm{N})\mathrm{P{=}C}(\mathrm{NPr}^i_2)[\mathrm{P}(\mathrm{NPr}^i_2)_2]$, can be obtained by photolysis of the bis(phosphino)diazomethane, $(\mathrm{Pr}^i_2\mathrm{N})_2\mathrm{P.C}(\mathrm{N}_2)\mathrm{.P}(\mathrm{NPr}^i_2)_2$; the reaction is considered to proceed via the phosphinocarbene intermediate $(\mathrm{Pr}^i_2\mathrm{N})_2\mathrm{P}^+{=}\mathrm{C}^-\mathrm{-P}(\mathrm{NPr}^i_2)_2$.[161] 2-Phosphapropene, $\mathrm{MeP{=}CH_2}$ has been identified in the gas phase by photoelectron spectroscopy and mass spectrometry as a pyrolysis product of $\mathrm{Me_2PCl}$.[162] The new perfluorinated phospha-alkene, $\mathrm{C_2F_5P{=}C(CF_3)F}$, results by $\mathrm{Me_3SnF}$ elimination when $\mathrm{Me_3SnP(C_2F_5)_2}$ is heated at 300°C and 10^{-3} torr; with dienes it reacts to give [2+4] cycloaddition products and addition of protonic species HX, for X = OMe, Br or $\mathrm{NMe_2}$, to the double bonds yields chiral phosphines $\mathrm{C_2F_5P(X)CF(CF_3)H}$.[163] Direct condensation between $\mathrm{Bu^t_3C_6H_2PH_2}$ and substituted benzaldehydes, $4\text{-}\mathrm{RC_6H_4CHO}$ where R = H, OMe or $\mathrm{NMe_2}$, in the presence of catalytic p-toluenesulphonic acid, also leads to phospha-alkenes.[164]

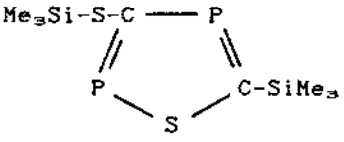
The E and Z isomers of $\mathrm{Bu^t_3C_6H_2P{=}C(SiMe_3)R}$ and $\mathrm{Bu^t_3C_6H_2P{=}CHR}$, for R = Ph, $\mathrm{SiMe_3}$ and Br, have been separated by fractional crystallisation and HPLC.[165] Structures have been determined for both isomeric forms of $\mathrm{Bu^t_3C_6H_2P{=}CHPh}$, which show major differences in the P-C-C and C-P-C angles and in the dihedral angle between the P=C double bond and the phenyl ring.

Orthorhombic $\mathrm{Me_3C_6H_2P{=}CPh_2}$ at -125°C has molecular parameters almost identical with those for the monoclinic form investigated earlier.[166] Electron diffraction measurements for $\mathrm{CF_3P{=}CF_2}$ give 169.0 and 190.1pm for the P=C and P-C bonds respectively with a C-P=C angle of 108.8°.[167] The cyclic dimer $\mathrm{(CF_3PCF_2)_2}$ in the gas phase has a puckered ring system with C-P-C and P-C-P angles of 77.6 and 95.6° respectively; here the mean C-P distance is 189.8pm.

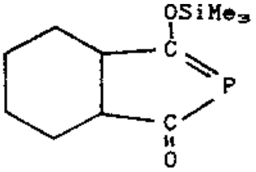
U.v. and He-I p.e.s. for $\mathrm{RP{=}C(SiMe_3)_2}$, where R = Cl, F, $\mathrm{OBu^t}$, $\mathrm{NHBu^t}$, $\mathrm{NHSiMe_3}$, $\mathrm{NEt_2}$, $\mathrm{N(SiMe_3)_2}$, Me, $\mathrm{Bu^t}$, etc., have been assigned and discussed in conjunction with MNDO calculations.[168] Ionisation potentials from π(P=C) and non-bonding phosphorus electrons agree with u.v. data. Depending on steric requirements, two conformations differing in the orientation of the amine group with respect to the molecular symmetry plane, are possible for aminophospha-alkenes. Both isomers are present in

$Pr^i{}_2NP{=}C(SiMe_3)_2$ and conformational isomerism provides an explanation for differences in n.m.r. data for species carrying NHR or NR_2 substituents.

Continuing exploitation of the relationship between C=C and P=C systems, a stable 1,2,4-thiadiphosphole (81), containing a conjugated P=C-P=C sequence of atoms, has been synthesised in a reaction between CS_2, $LiP(SiMe_3)_2$ and Me_3SiCl.[169] Acyl substituted phospha-alkenes such as (82) can be prepared by



(81)



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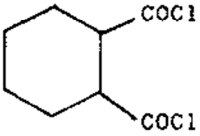

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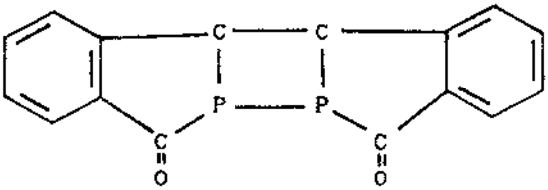

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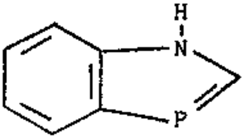


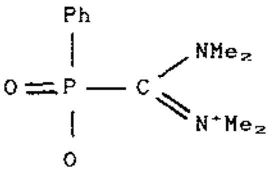
(85)

treating a 1,2-dicarbonyl dichloride such as (83) with tris(trimethylsilyl)phosphine; with phthaloyl dichloride, the product is however the [2+2] cycloaddition product (84) confirmed by an X-ray structure.[170]

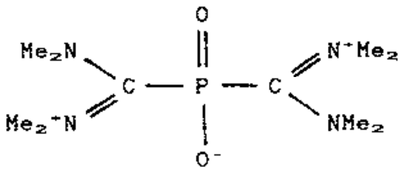
The benzazaphosphole structure (<u>85</u>) is characterised by a P=C distance of 169.5pm and a small (88.2°) C=P-C angle; the compound is isotypic with the arsenic analogue but not with the nitrogen compound because of hydrogen bonding in the latter.[171]

HX addition to the double bond in $CF_3P=CF_2$ can lead to secondary phosphines $CF_3P(H).CF_2X$ when X = OH, OR, NR_2 or PMe_2 or to the alternative $CF_3P(X).CF_2H$ products when X = Cl, Br, SMe, SeMe or $AsMe_2$.[172] Water addition is in fact pH dependent with formation of $CF_3P(OH).CF_2H$ at pH > 13 and reverse addition of alcohols has been observed in the presence of OR^-. A new heteroborane cluster has been isolated from a reaction of $ClP=C(SiMe_3)_2$ and $B_5H_8^-$.[173]

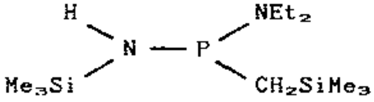
Two equivalents of ozone are taken up by the electron rich phospha-alkene, $PhP=C(NMe_2)_2$ to give (<u>86</u>), while the substituted phospha-allyl cation, $(Me_2N)_2C=P-C(NMe_2)(=N^+Me_2)$, is similarly converted to the dioxygen product (<u>87</u>).[174] A complex reaction, involving both Si-N cleavage and addition across the P=C double bond, occurs when secondary amines react with $(Me_3Si)_2NP=CHSiMe_3$.[175] With diethylamine, the products are either (<u>88</u>) or the unexpected P(III)-P(V) species (<u>89</u>) depending on the reactant ratios. With carbon tetrachloride, (<u>88</u>) is smoothly oxidised to $Me_3SiN=PCl(NEt_2)(CH_2SiMe_3)$.



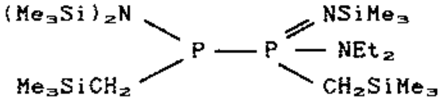
(<u>86</u>)



(<u>87</u>)

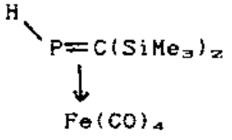


(<u>88</u>)

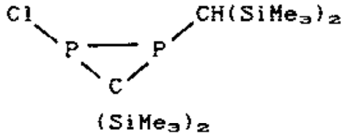


(<u>89</u>)

Three products, i.e. the complex (<u>90</u>), a functionalised diphosphirane (<u>91</u>) and a complex of the latter (<u>92</u>), are obtained when the hydride anion $[HFe(CO)_4]^-$ is added to pure $ClP{=}C(SiMe_3)_2$.[17



(90)



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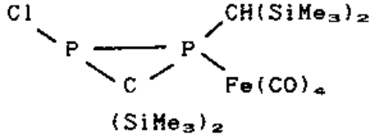
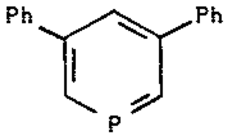


(92)

Recent work has shown that 3,5-diphenylphosphinine (93) reacts in methanol with diazomethane and $R^1R^2CN_2$ substituted species to give 1-alkyl-1-methoxy derivatives (94).[177] In aprotic solvents such as ether, however, diazomethane and (93) give a complex polycyclic species in which two phosphacyclohexene rings are bridged by a methylene group at phosphorus.



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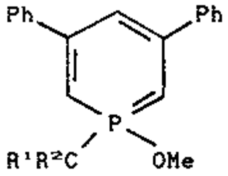


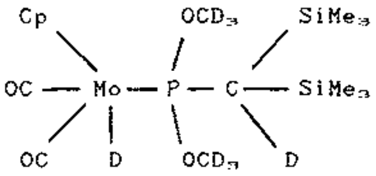
(94)

The phospha-alkene in $(bipy)Ni[P(2,6\text{-}Me_2C_6H_3){=}CPh_2].THF$ is η^2-bonded to nickel from an X-ray study showing P-C, Ni-P and Ni-C distances of 183.2, 217.7 and 198.7pm respectively, [178] but extended Huckel calculations point to η^1-bonding in $[MeP{=}CMe]Cr(CO)_5$.[179]

Phosphinidine (RP:) chemistry, stressing the involvement in low oxidation state transition metal species has been reviewed.[180]

and a short review is available on multiple bonding between transition metals and main group fragments, including the formation of open and closed phosphinidine complexes.[181]

The phosphavinylidine complex, $CpMo(CO)_2[\eta^1-P=C(SiMe_3)_2]$, containing phosphorus doubly bonded to both the metal and carbon, reacts with ethanol to give $CpMo(CO)_2\{\eta^1-P[CH(SiMe_3)_2]OEt\}$ in which the phosphido group is a three-electron donor.[182] Other electrphiles, e.g. CD_3OD, Pr^i_2NH and C_6F_5SH react similarly but whereas one mol of CD_3OD gives $CpMo(CO)_2\{=P(OCD_3)[CD(SiMe_3)_2]\}$ an excess of the reagent leads to reaction at the Mo=P bond also giving (95). With nucleophiles such as NaOMe in THF the product is (96).



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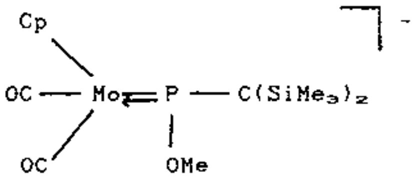


(96)

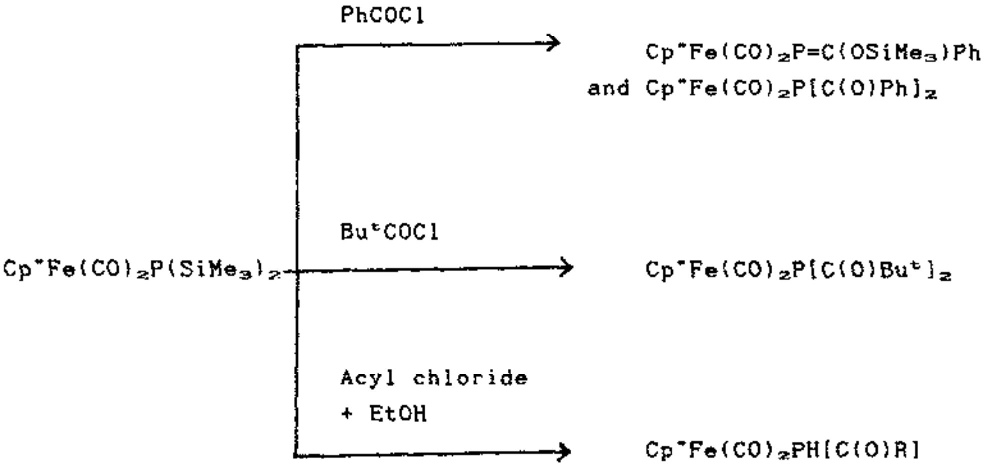
Phospha-alkenyl complexes can be obtained, for example, using acyl chlorides as shown in equation (11); the reaction probably proceeds via $CpFe(CO)_2P(SiMe_3)[C(O)R]$ as an intermediate.[183]

$$CpFe(CO)_2P(SiMe_3)_2 + RC(O)Cl \rightarrow CpFe(CO)_2P{=}C(OSiMe_3)R + Me_3SiCl \qquad ...(11)$$

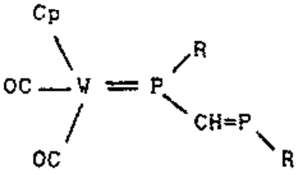
$R = Bu^t$, Ph or mesityl.

In a similar fashion, it has been possible to isolate $Cp^*Fe(CO)_2P{=}C(OSiMe_3)$(mesityl) as the sole product of the $Cp^*Fe(CO)_2P(SiMe_3)_2$ reaction with 2,4,6-trimethylbenzoyl chloride.[184] Mono and diacyl phosphido complexes, as shown in Scheme 1, can also be obtained.

A 1,3-diphospha-4-tungstobutadiene (97, $R = C_6H_2Bu^t_3$) results when $Bu^t_3C_6H_2P{=}CHPCl(C_6H_2Bu^t_3)$ is treated with $Na[CpW(CO)_3]$; its behaviour is similar to that of butadiene as on conversion to the iron carbonyl complex (98) the ligand changes conformation from trans to cis.[185]



Scheme 1



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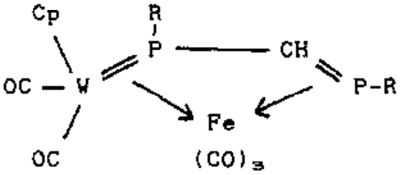
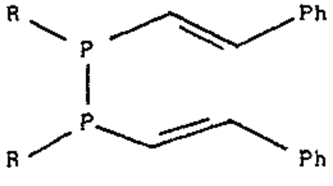


(98)

Styryl substituted diphosphines (99) can be obtained by treating RPCl(CH=CHPh), where R = $Bu^t{}_3C_6H_2$ or Bu^t, with either Bu^tLi or magnesium and the tri-t-butylphenyl substituted compound undergoes a Cope rearrangement to give the phospha-alkene (100).[186] Allyl Grignard reagents, $RCH{:}CH.CH_2MgCl$ (R = Me or Ph), react with



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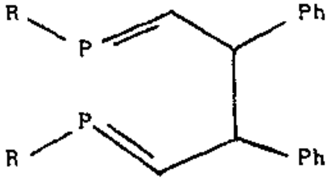

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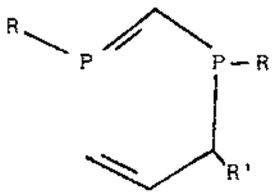

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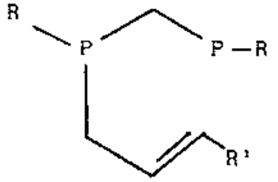
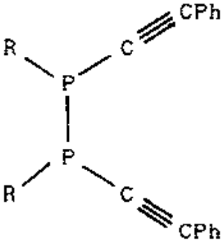


(102)

RP=CH-PClR ($R = C_6H_2Bu^t{}_3$) to give 1,3-diphosphahexadienes (101) which via a Cope rearrangement give (102), the thermodynamically stable product.[187] The diphosphahexadiyne, (103, $R = C_6H_2Bu^t{}_3$), obtained by treating RPCl(C≡CPh) with BuLi, undergoes valence isomerisation to give the cyclobutene derivative (104).[188]



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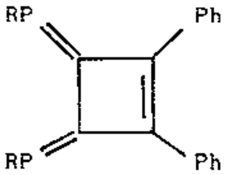


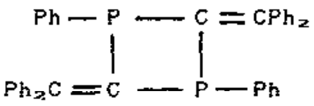
(104)

Reaction of RP:C:O ($R = C_6H_2Bu^t{}_3$) with an ylid, shown in equation (12), gives a series of new 1-phospha-allenes, but although

$$RP{:}C{:}O \quad + \quad Ph_3P{=}CR^1R^2 \quad \rightarrow \quad RP{=}C{=}CR^1R^2 \quad + \quad Ph_3PO \qquad \ldots(12)$$

R^1 = Ph, H
R^2 = Ph, CO_2Et

$(Me_3Si)_2O$ is split out when $Ph_2C{:}C{:}O$ reacts with $PhP(SiMe_3)_2$, the product is a dimer (105) rather than an allene derivative.[189] Treatment of the same phosphaketene with bis(trimethylsilyl)-diphosphines, $(Me_3Si)R'P\text{-}PR'(SiMe_3)$ where R' = $SiMe_3$, Ph or Pr^i,



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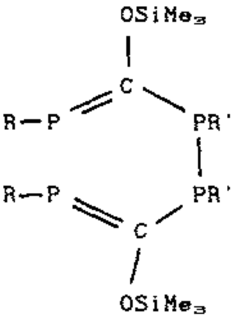


(106)

gives tetraphospha-1,5-hexadienes (106) and the structure of the phenyl compound has been determined.[190]

The 1-phospha-allene group is η^1-bonded to an $Ni(CO)_3$ group in the complex prepared by treating $Bu^t{}_3C_6H_2P{=}C{=}CPh_2$ with $Ni(CO)_4$,[191] and a μ_3-η^2-bonded $Bu^tP{=}C{=}CHPh$ ligand has been stabilised in the low yield product $[Bu^tP{=}C{=}CHPh]FeCo_2(CO)_6$ obtained from a reaction of $[PBu^t(C{\equiv}CPh)H]Fe(CO)_4$ with $Co_2(CO)_8$.[192]

Enantiomers of the axially dissymmetric phospha-allene $Bu^t{}_3C_6H_2P{=}C{=}PC_6H_2Bu^t{}_3$ have been separated for the first time by HPLC using a chiral (+)-poly(triphenylmethylmethacrylate) column; racemisation occurs on exposure to light but only very slowly in the dark.[193]

X-ray structures are available for two new nickel-1,3-diphospha-allene complexes, CpNi(RP CH PR) and $[Ni(CO)_2(RP\ \ CH\ \ PR)]_2$ ($R = C_6H_2Bu^t{}_3$) obtained by treating RP:CH.PRCl with, respectively, K[CpNi(CO)] and $Ni(CO)_4$.[194]

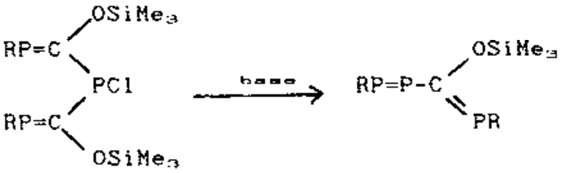
Diphospha-1-butenes can be obtained in high yield from the reaction in equation (13); the structure of the $Me_3SiC{\equiv}C$ substituted product has been determined.[195] A 1-phospha-1,2,3-butatriene has also been produced, equation (14),[196] and the first triphosphabutadiene, containing both P=P and P=C bonds in

$2ClP{=}C(SiMe_3)_2 + 2RLi \rightarrow R_2P\text{-}C(SiMe_3)_2\text{-}P{=}C(SiMe_3)_2 + 2LiCl$ ...(13)

$R = Me_3SiC{\equiv}C$, $PhC{\equiv}C$ or Ph

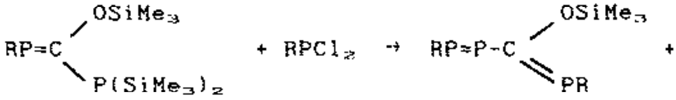
$RPCl_2 + Li(Me_3SiC{=}C{=}CR'_2) \rightarrow RP{=}C{=}C{=}CR'_2 + LiCl + Me_3SiCl$ ...(14)

$R = Bu^t{}_3C_6H_2$ $R^1 = Ph, SiMe_3$



...(15)

$R = Bu^t{}_3C_6H_2$



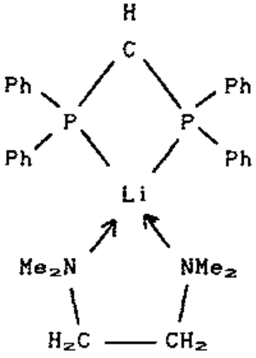
...(16)

conjugation, results from the reactions in equations (15) and (16).[197]

Two mesityl phosphines, $(mesityl)_2PH$ and $(mesityl)PH_2$ and their lithium derivatives, $[Li(OEt_2)P(mesityl)_2]_2$ and $[Li(THF)_3PH(mesityl)]$ have been synthesised.[198] The latter is a monomer with pyramidal geometry at phosphorus while the dimeric structure of the dimesityl salt is based on a planar Li_2P_2 ring. Structures have also been determined for the following lithium salts, $[Li(OEt_2)PPh_2]$, $[Li(THF)_2PPh_2]$, $[Li(THF)P(C_6H_{11})_2]$, which by contrast all have infinite chain structures based on an alternating sequence of solvated lithium ions and PR_2 groups.[199] The phosphorus atoms are in distorted tetrahedral coordination and the solid state structures are clearly different from those thought to be present in ether solutions.

$Mg(PPhH)_2$ is polymeric but the monomer, $Mg(PPhH)_2.TMEDA$ can be obtained on treatment with N-tetramethylethylenediamine as meso- and rac-forms; the structure of the latter has been determined. [200] A monomeric structure (<u>107</u>) has been found for $(Ph_2P)_2CHLi.TMEDA$ containing a slightly puckered four-membered ring with Li-P and C-P distances of 258.2 and 172.2pm, respectively. [201] A four-membered ring is also present in the tin(II) and lead(II) phosphido complexes (<u>108</u>, M = Sn or Pb) obtained by treating either $SnCl_2$ or $PbCl_2$ with three mols of $LiPBu^t{}_2$ in THF solution.[202]

The addition compounds of secondary phosphines, R_2PH where R = Pr^i or Bu^t with $CpW(CO)_3Cl$ can be dehydrohalogenated to give



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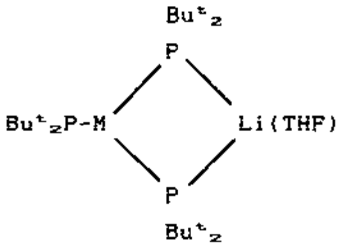
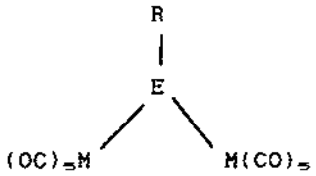
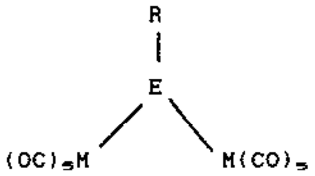


(108)

$CpW(CO)_2{=}PR_2$ using DBU, with the double bonded structure (W-P 228pm) following from an X-ray structure determination.[203] Three different types of product (109)-(111) have been obtained by treating $RECl_2$ (E = P, As or Sb) with $Na_2[M_2(CO)_{10}]$ (M = Cr, Mo or W).[204] The interrelationships between these species has been



(109)



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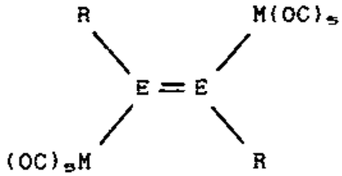

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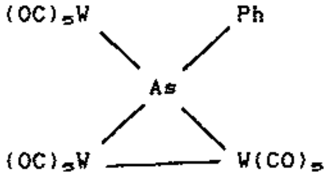

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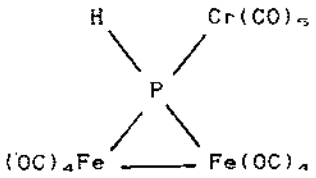

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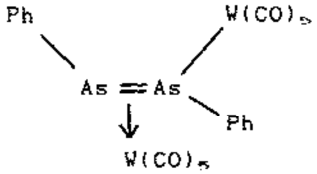

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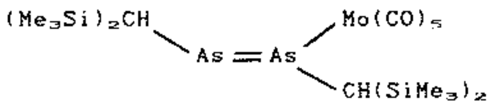

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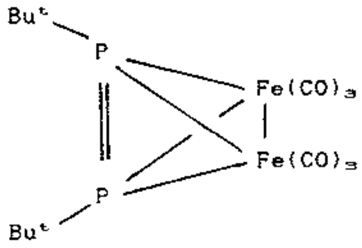

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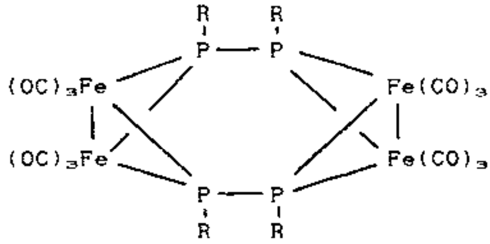

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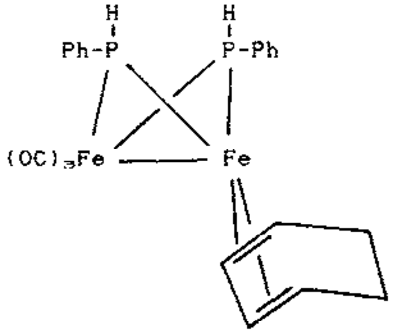


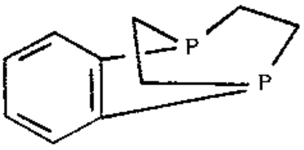
(118)

discussed in conjunction with X-ray structure determinations for (111, E = As, M = W) and (112)-(115). Oxidation of $[Fe_2(CO)_6(\mu\text{-}PBu^tH)_2]$ gives $[Fe_2(CO)_6(PBu^t)_2]$ (116), a tetrahedrane type species which contains a short P-P bond (206pm) and is probably better represented as a diphosphene complex.[205] The compound reacts with CO, C_2H_4 and C_2H_2 by insertion into the P-P bond; structures are available for the reaction products with CO and C_2H_4.

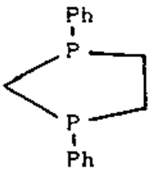
New cage compounds, $Fe_4(CO)_{12}(PR)_4$ (117) for R = Me, Ph or tolyl, are among the products of various reactions, including the oxidation of $Fe_2(CO)_6(PHR)_2$, treatment of $[Fe_2(CO)_8]^{2-}$ with $RPCl_2$

and reactions of iron carbonyl species containing P-Cl bonds with $[Fe(CO)_4]^{2-}$.[206] The structure of (<u>117</u>, R = Me) has been determined and, of the by-products, (<u>118</u>) was also investigated structurally.

Treatment of 1,2-diphosphinobenzene with successively sodium in liquid ammonia and 1,2-dichloroethane leads to the polycyclic tertiary phosphine (<u>119</u>).[207] $Cl_2P.CH_2.PCl_2$ has been converted into compounds of the type $PhXP.CH_2.PXPh$, where X = Cl, H, Et_2N



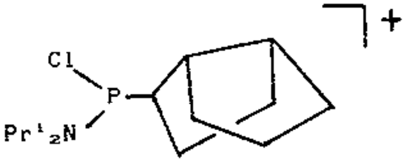
(<u>119</u>)



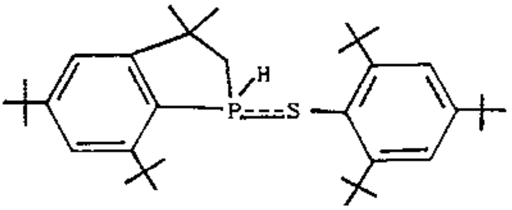
(<u>120</u>)

etc., and when $PhPLi.CH_2.PPhLi$ reacts with 1,2-dihalogenoethanes the products are the phosphorinane (<u>120</u>).[208]

The phosphetanium salt (<u>121</u>) is obtained from cyclooctadiene and the phosphenium salt, $[Pr^i_2NPCl]^+[AlCl_4]^-$,[209] and oxidative addition of a C-H bond of a t-butyl substituent gives (<u>122</u>) when $Bu^t_3C_6H_2PCl(SC_6H_2Bu^t_3)$ is treated with $AgSbF_6$.[210]



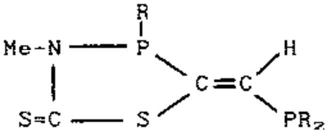
(<u>121</u>)



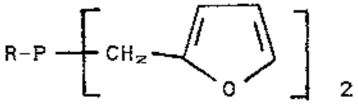
(<u>122</u>)

Structures have been determined for two bulky phosphines, $Bu^t_3C_6H_2P(SiMe_3)_2$ and $Bu^t_3C_6H_2\overline{P\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O}$.[211]

Aryl-phosphorus bonds are readily cleaved on treatment with sodium naphthalene providing the basis for convenient syntheses of a number of unsymmetrically substituted diphosphines, such as $PhHP(CH_2)_nPPh_2$ and $MePhP(CH_2)_nPPh_2$, where n = 2-6.[212] A new thiazaphospholidine (<u>123</u>) is produced by treating dimethylthiourea with acetylene bis(phosphonous dimorpholide) $R_2PC{\equiv}CPR_2$; the compound can then be oxidised by elemental sulphur at both phosphorus atoms.[213] Furfuryl phosphines (124, R = Ph, mesityl,



(123)



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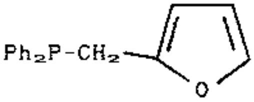

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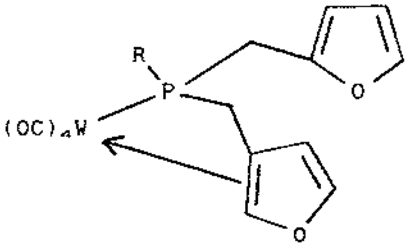


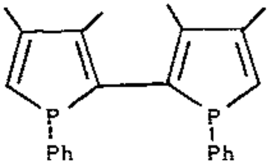
(126)

Me, Bu^t or $CH_2C_4H_3O$) and (125) can coordinate via phosphorus to $W(CO)_5$ units, and on irradiation in ether solution, carbon monoxide is lost to give (126) in which a furfuryl ring is weakly η^2-coordinated to tungsten.[214]

Sodium pentafluorobenzoate and trifluoroacetate react with Ph_2PCl in ether at ca. −20°C to give respectively $Ph_2P[OC(O)C_6F_5]$ and the phosphine oxide, $Ph_2P(O)C(O)CF_3$.[215]

Sulphur adds to the novel 2,2′-biphosphole (127) to give two isomeric P-sulphides while only one form of the $Mo(CO)_4$ complex (128) results on treatment with the hexacarbonyl.[216] Further reactions are reported with lithium and iron(II) chloride giving bis(η^5-diphosphafulvalene)diiron (129).

Reaction between $PhP(CH_2CH_2SH)_2$ and tin(II)butoxide in toluene gives the new heterocycle (130), which in the solid state forms infinite spirals from intermolecular Sn...S contacts.[217] The tin is in distorted pseudotrigonal bipyramidal coordination with phosphorus in an equatorial position (Sn...P 261.4pm) and the 8-membered ring is in the boat-boat conformation.



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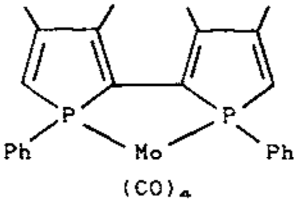
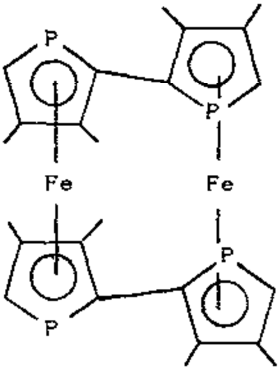


(128)



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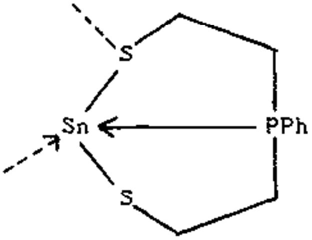
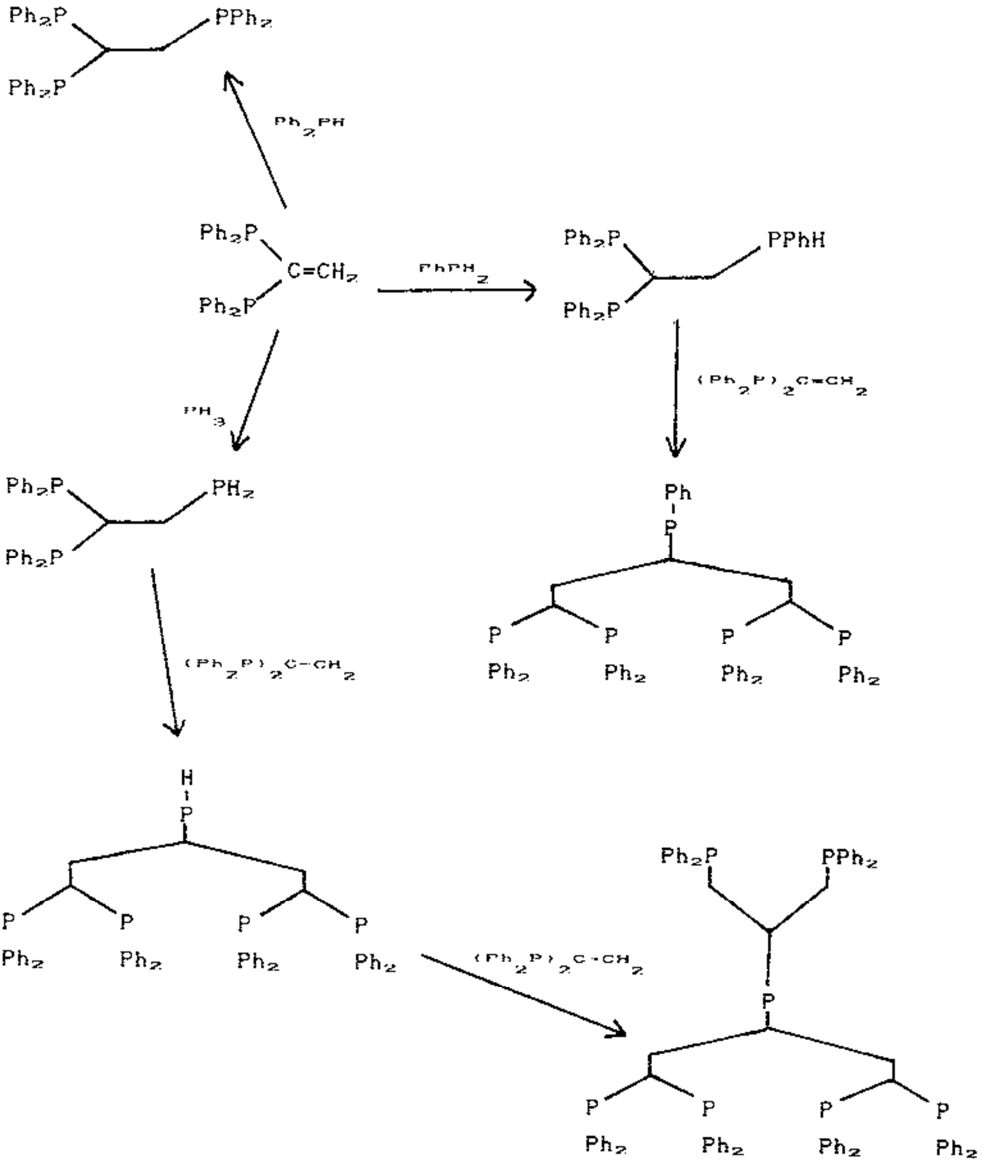


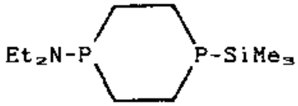
(130)

A series of new polyphosphorus ligands (see Scheme 2) has been synthesised by addition of P-H species to the double bond in (Ph$_2$P)$_2$C=CH$_2$; the compounds are expected to lead to a wide range of different transition metal complexes.[218] Further reactions of secondary phosphines R$_2$PH, for R = Me, Pr^i, Bu^t, Ph, etc., with R^{1}P(CH$_2$CH$_2$=CH$_2$)$_2$ in the presence of azobis(isobutyronitrile) and with UV irradiation show that the reaction is not general, but it has led to the successful preparation of the two new ligands, Bu^{t}P(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$ and P(CH$_2$CH$_2$CH$_2$CH$_2$PMe$_2$)$_3$.[219] Entry into a new class of 1,4-diphosphacyclohexanes (131) is possible following addition of Me$_3$SiPH$_2$ to Et$_2$NP(CH=CH$_2$)2 in the presence of AIBN. The product is interesting as it contains two oppositely polarised phosphorus atoms; an acyclic species, CH$_2$=CH.P(NEt$_2$).PCH$_2$CH$_2$P(H)-SiMe$_3$ is also obtained.[220]



Ph₂P
PPh₂
Ph₂P
Ph₂PH
Ph₂P
C=CH₂
Ph₂P
PhPH₂
Ph₂P
PPhH
Ph₂P
PH₃
(Ph₂P)₂C=CH₂
Ph₂P
PH₂
Ph₂P
Ph
P
P P P P
Ph₂ Ph₂ Ph₂ Ph₂
(Ph₂P)₂C=CH₂
H
P
P P P P
Ph₂ Ph₂ Ph₂ Ph₂
(Ph₂P)₂C=CH₂
Ph₂P
PPh₂
P
P P P P
Ph₂ Ph₂ Ph₂ Ph₂

<u>Scheme 2</u>



(131)

Continuing this theme, a range of linear polyphospha-alkanes has been synthesised from vinyl or allyl methyl phosphinic acid esters and R_2PH (R = Me, Pr^i or Ph).[221] Among the compounds isolated were $R_2P(CH_2)_3.PMe.(CH_2)_2PMeH$, $R_2P(CH_2)_2.PMe.(CH_2)_n.PMe.(CH_2)_2PR_2$ (where R = NEt_2, OH, or H and n = 2 or 3) and $RR^1P.(CH_2)_n.PMe.(CH_2)_3.PPh.(CH_2)_3.PMe.(CH_2)_n.PRR^1$ (where R, R^1 = Me, H, NEt_2 or OMe and n = 2 or 3). Iron complexes, $FeLCl_2$, have been isolated with the tetraphospha-alkanes, $Me_2P.(CH_2)_3.PMe.(CH_2)_n.PMe.(CH_2)_3.PMe_2$ where n = 2 or 3.[222]

A surprisingly easy synthetic route to tetrakis(diphenylphosphino)allene is shown in equations (17) and (18);[223] the compound can be oxidised to the tetraoxide with bis(trimethylsilyl)peroxide and sulphur and selenium also add to give tetrachalcogenides.

$$Ph_2P.C{\equiv}C.Me + BuLi \rightarrow Ph_2P.C{\equiv}C.CH_2Li + BuH \qquad ...(17)$$

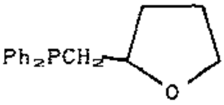
$$3Ph_2P.C{\equiv}C.CH_2Li + 3Ph_2PCl \rightarrow (Ph_2P)_2C{=}C{=}C(PPh_2)_2 + 3LiCl + 2Ph_2P.C{\equiv}CMe \qquad ...(18)$$

A novel ligand, $Ph_2P.CH_2.PPh_2.P_4.PPh_2.CH_2.PPh_2$, containing a zig-zag P_4 chain, is formed when white phosphorus and bis(diphenylphosphino)methane react with $Co(BF_4)_2$.[224] The ligand coordinates to cobalt in a distorted octahedral arrangement via all four phosphorus atoms of the opened P_4 molecule and two of the phosphorus atoms of the dppm units. A series of acetylene derivatives, such as $R^1R^2P\text{-}C{\equiv}C\text{-}PR^1R^2$ where R^1 = R^2 = morpholino, piperidino, $NHBu^t$ or F and R^1 = F, R^2 = morpholino or NEt_2, has been prepared and an X-ray structure carried out for the tetramorpholine derivative.[225]

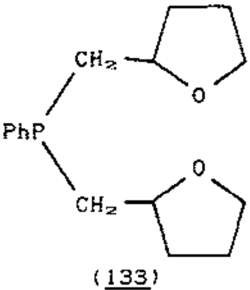
Treatment of triphenylphosphine with iodine leads to iodine disproportionation and isolation of crystals of $[(PPh_3I)_2I_3]I_3$ from dichloroethane solutions and $[PPh_3I]I_3$, with the same empirical formula, from toluene.[226] X-ray diffraction shows parallel, zig-zag chains of $[(PPh_3I)_2I_3]^+$ units between layers of I_3^- anions for the former, while strong cation-anion interaction in the latter gives "molecules" which yield infinite chains by further intermolecular contacts. Iodine oxidation of triphenyl arsenic gives $[(AsPh_3I)_2I_3]I_3$, isostructural with the phosphorus compound above.

Stabilities of the complexes, $[Ag(Ph_3M)_n]^+$ where M = P, As or Sb and n = 1-4, formed from silver nitrate in ethanol, decrease from phosphorus to antimony.[227]

Solid state ^{31}P n.m.r. spectroscopy and single crystal X-ray diffraction point to the formation of silver nitrate-triphenylphosphine complexes, $Ag(PPh_3)_nNO_3$, where n = 2-4.[228] The nitrate group is weakly coordinated for n = 2 and 3 but is ionic when n = 4; the bis and tris complexes are isomorphous with the corresponding Ph_3As complexes. CuCl and $AgBF_4$ complexes with $Pr^i_2PCH_2PHPr^i$(L) have been formulated as, respectively, $Cu_2Cl_2L_2$, containing an eight-membered ring, and $[Ag_2L_2][BF_4]_2$.[229] In the lanthanum complex $[La(Ph_2P.CH.PPh_2)_3]$, isolated from $LaCl_3$ and three mols of $K[Ph_2P.CH.PPh_2]$ in THF, the ligand behaves as an η^3-π-allyl like species.[230] Ir_3 complexes can be prepared with both $PhP(CH_2PPh_2)_2$ and $PhAs(CH_2PPh_2)_2$, [231] and although the $Mo(CO)_5$ complexes with (132) and (133) involve donation via phosphorus initially, irradiation gives tetracarbonyl species in which oxygen also donates to the metal.[232]

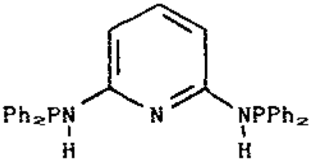


(132)

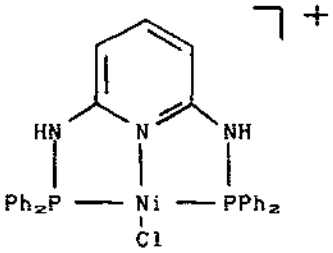


(133)

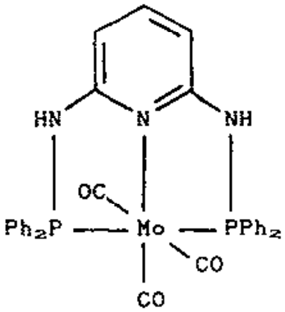
Phosphorus containing ligands continue to be synthesised in large numbers, and the following are among those noted during the period of this review. Ligands containing pyridyl groups in α- or β-positions to phosphorus, i.e. $2\text{-}C_5H_4N\text{-}(CH_2)_n\text{-}PHR$ (R = H, Pr^i, Bu^t or Ph and n = 1 or 2), are now available and the presence of a PH function allows further reaction to give NPN donor ligands, $[2\text{-}C_5H_4N\text{-}(CH_2)_2]_2PR$.[233] A range of Ru(II) and (III) complexes have been described with $PhCH_2N(CH_2CH_2MPh_2)_2$ where M = P or As, [234] and the rigid tridentate ligand (L) (<u>134</u>) has been synthesised from Ph_2PCl and 2,6-diaminopyridine.[235] Two types of complex, [MLCl]Cl.L' (for M = Ni, L' = H_2O; and M = Pd, L' = EtOH) and mer-$[ML(CO)_3]$.2THF (for M = Cr, Mo or W) are formed; each type, (<u>135</u>) and (<u>136</u>), contains an almost planar tridentate chelate system.



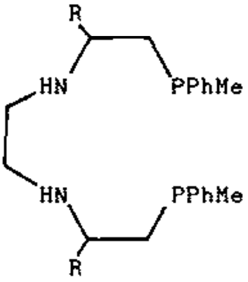
(<u>134</u>)



(<u>135</u>)



(<u>136</u>)

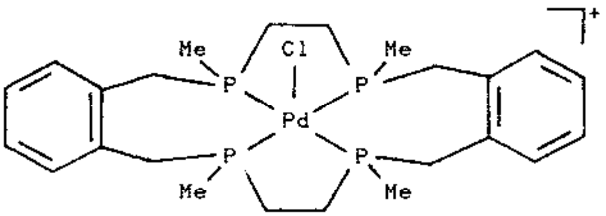


(<u>137</u>)

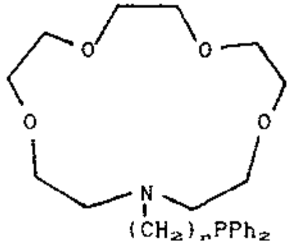
Tetra-dentate ligands, L, (<u>137</u>, R = H or Me), containing two chiral phosphorus centres, are now known giving three forms of the cobalt complex, $[trans\text{-}CoCl_2L]^+$ and four of the cis complex, $[Co(acac)L]_2^+$, which can be separated by column chromatography.[236] Anhydrous chromium(III) chloride gives a 1:1 complex with the tripod ligand $MeC(CH_2PMe_2)_3$, which contains a fac-arrangement of the three phosphorus atoms.[237] With chromium(II) chloride in THF, on the other hand, the ligand is only bidentate giving trans-$CrCl_2L_2$, which can be reduced with sodium amalgam to CrL_2.

New tripod ligands, $MeGe(OCH_2PMe_2)_3$ and $MeSi(OCH_2PMe_2)_x(CH_2CH_2PMe_2)_{3-x}$ (where x = 0-2), have been prepared from $MeGeCl_3$ or $MeSiCl_xVi_{3-x}$ with Me_2PCH_2OH.[238]

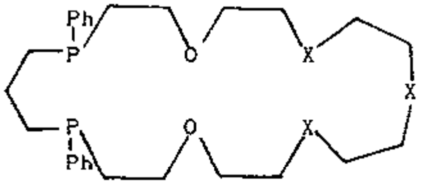
Cyclisation giving complexes of the tetradentate macrocycle (<u>138</u>) occurs when the di-secondary phosphine, $MeHP.(CH_2)_2.PMeH$, and o-xylylene dichloride react in the presence of a Pd(II) template.[239] The product is a mixture of three diastereoisomers which can be crystallised from methanol to give the pure syn-(RSRS) isomer, with palladium in square pyramidal coordination. Practical synthetic routes are now available to the aza-phospha and oxa-phospha macrocycles (<u>139</u>, X = NH or O), a new class of hard-soft binucleating ligands,[240] and to the phosphino-aza crown



(<u>138</u>)



(<u>140</u>)



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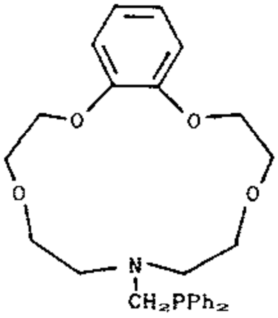
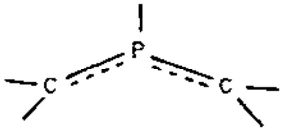


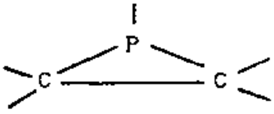
(<u>141</u>)

ethers (<u>140</u>, n = 0-3) and (<u>141</u>).[241] The latter can bind to a transition metal via the phosphorus atom and an alkali metal at the aza-crown ether.

<u>Bonds between Carbon and Phosphorus(V)</u>. Ab initio calculations for the model ylids $H_3P{=}CXY$ and the isomeric phosphines $H_2P.CHXY$, where X = Y = H, F or CF_3, point to low binding energy of $H_3P{=}CF_2$ for dissociation into PH_3 and $:CF_2$; this contrasts with binding energies of over $50 kcal.mol^{-1}$ for both $H_3P{=}CH_2$ and $H_3P{=}C(CF_3)_2$.[242] The bis(methylene)phosphorane (<u>142</u>) has also been studied, including the electrocyclic reaction to give (<u>143</u>).[243] The synthesis, structure and reactivity of three coordinate phosphorus(V) species has been reviewed discussing, inter alia, (mesityl)$P(:CPh_2)(:X)$ (X = O, S or Se), $Bu^t{}_3C_6H_2P(:S)_2$, $RP(:NR^1)(:X)$ (X = S or Se), and $RP(:NR^1)(:NR^2)$.[244]

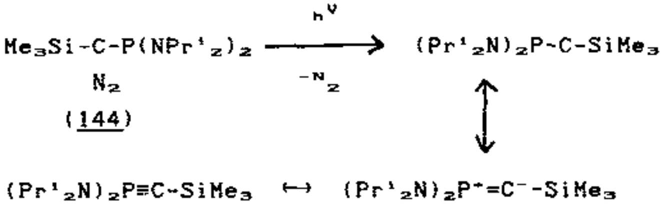


(<u>142</u>)



(<u>143</u>)

Evidence from trapping experiments suggests that the λ^3-phosphinocarbenes produced photochemically from (<u>144</u>) can be regarded as either phosphorus-vinyl ylids or λ^5-phospha-acetylenes, see equation (19).[245] Equations (20)[246] and (21)[247] summarise high yield routes to substituted bis(methylene)phosphoranes, in which P=C distances are ca. 164pm.[246] A product of equation (21), $RP[:C(SiMe_3)_2]$-$(:CPh_2)$ for R = Bu^t or Ph, rearranges to the phosphirane (<u>145</u>).[247]

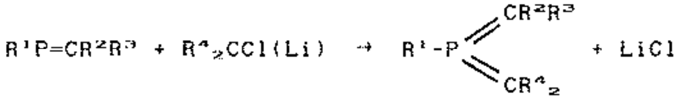


$$Me_3Si\text{-}\underset{N_2}{C}\text{-}P(NPr^i{}_2)_2 \xrightarrow[-N_2]{h\nu} (Pr^i{}_2N)_2P\text{-}\ddot{C}\text{-}SiMe_3 \longleftrightarrow (Pr^i{}_2N)_2P{\equiv}C\text{-}SiMe_3 \longleftrightarrow (Pr^i{}_2N)_2P^+{=}C^-\text{-}SiMe_3 \quad ...(19)$$

(<u>144</u>)

$$RPCl_2 + 3(Me_3Si)_2CCl(Li) \rightarrow RP[=C(SiMe_3)_2]_2 + 3LiCl + Cl_2C(SiMe_3)_2 \qquad ...(20)$$

R = Me_2N, PhS, Ph_2CH, EtMeCH

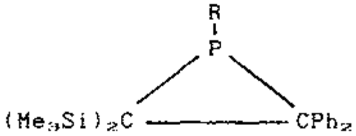


$$R^1P=CR^2R^3 + R^4{}_2CCl(Li) \rightarrow R^1\text{-}P(=CR^2R^3)(=CR^4{}_2) + LiCl \qquad ...(21)$$

R^1 = Bu^t, Ph or mesityl

$R^2/R^3/R^4$ = Me_3Si or Ph

Reaction between BuLi and $(Me_2N)_2PF_2.(CH_2)_2.PF_2(NMe_2)_2$ leads finally to the fluorinated ylid, $(Me_2N)_2PF{:}CH.CHBu.P(NMe_2)_2$,



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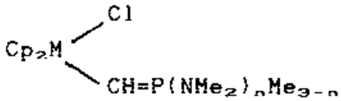

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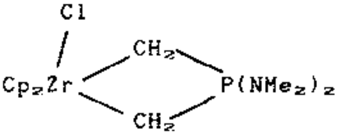
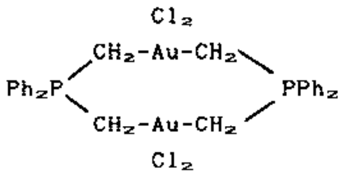


(147)

through $(Me_2N)_2PF_2.CH_2.CH{:}PF(NMe_2)_2$, $(Me_2N)_2PF{:}CH.CH{:}PF(NMe_2)_2$ as possible intermediates.[248] A range of new silylated ylids, including $(Et_2N)_3P=CHSiMe_3$, $Me(Et_2N)_2P=CHSiMe_3$, $(Me_2N)_3P=CHSiMe_3$, $(Me_3N)_3P=CHSiBu^t{}_2Cl$, has been synthesised by the action of a strong base on the silylated phosphonium salts obtained when $R_nR^1{}_{3-x}P=CH_2$ reacts with a chlorosilane, such as Me_3SiCl and $Bu^t{}_2SiCl_2$.[249] Similar transylidation reactions between $Me_{3-n}(Me_2N)_nP=CH_2$ and Cp_2MCl_2, where M = Ti, Zr or Hf, gave the complexes (146), though with Cp_2ZrCl_2 and $Me(Me_2N)_2P=CH_2$ the product was an isomeric form (147).[250]

Gold in square planar coordination to two chlorine and two carbon atoms is found in the dihydrated complex (148), with the eight membered ring adopting the chair conformation.[251] In the stable



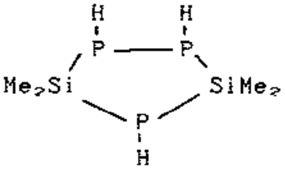
(148)

copper(I) chloride complex with $Ph_3P{=}C{=}PPh_3$ the metal is in linear coordination to chlorine and the ylidic carbon atom at distances of 211.3 and 190.6pm respectively.[252] The PCPCu system is planar with a P-C-P angle of 123.8° and the difference in the two P-C-Cu angles result from differences in the conformations of the two Ph_3P groups.

Tetraphenylphosphonium chloride, which is not isostructural with the bromide, has P-C distances ranging between 178.1 and 179.3pm and C-P-C angles between 108.1 and 111.6°.[253]

The phosphoryl-phosphines $Ph_nP[P(O)(OEt)_2]_{3-n}$ for n = 0-2 all form $Mo(CO)_5L$ complexes with $Mo(CO)_6$, and in the complex with n = 2 coordination occurs via the phosphine phosphorus atom.[254] Related ligands $[Ph_2P(O)]_n[Ph_2P(S)]_{3-n}CH$ have also been synthesised and these can be converted to anions by proton abstraction in the presence of lithium methoxide.[255] Structures for ammonium and thallium dihydrogen methylene diphosphonates, $(M^+)_2[(HO)O(O)P.CH_2P(O)O(OH)]^{2-}$ show an extensively hydrogen bonded three dimensional network.[256]

Bonds to Silicon Atoms. Dimethyldichlorosilane reacts with $LiPH_2$ and Li_2PH mixtures to give a series of silylphosphines, among which are linear products, such as $Me_2Si(PH_2)Cl$, $Me_2Si(PH_2)_2$, $H_2P.SiMe_2.PH.SiMe_2Cl$ and $(H_2P.SiMe_2)_2PH$ and the cyclic compounds $(HP.SiMe_2)_3$ and (149)-(154).[257] If Et_2SiCl_2 is used in place of Me_2SiCl_2, the major products are $(HP.SiEt_2)_{2\,\mathrm{and}\,3}$, together with the acyclic species, $Et_2Si(PH_2)Cl$, $Et_2Si(PH_2)_2$, $(ClEt_2Si)_2PH$ and $(H_2P.SiEt_2)_2PH$. $Bu^t{}_2SiCl_2$ as starting material in the reaction with $LiPH_2$ leads to PH_3 evolution and formation of the four-membered heterocycle (155). N.m.r. spectroscopy was used for structure determination but in the case of (152) an X-ray structure determination was also performed.[258] The molecule with close to C_{2v} symmetry has boat-boat conformations for the two six-membered rings, implying that it is a precursor of $(Me_2Si)_6P_4$. Reaction of $Cr(CO)_4$(norbornadiene) with (152) leads to displacement of the organic group and formation of a new $Cr(CO)_4$ complex where the silylphosphine is bonded via the two PH phosphorus atoms.



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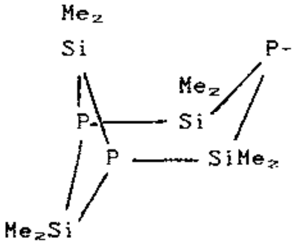

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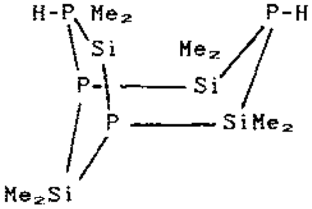

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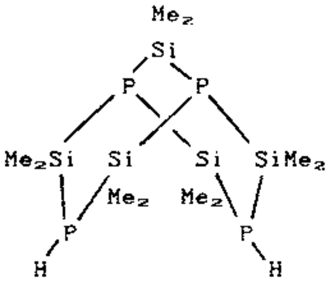

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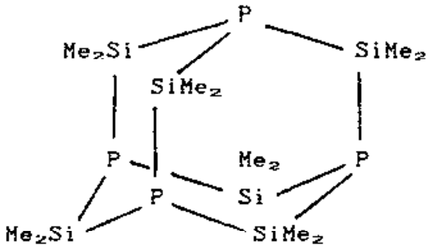

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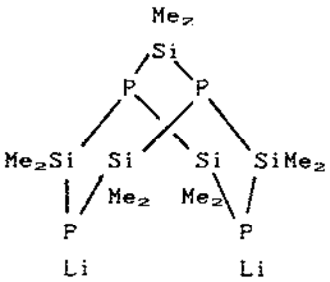

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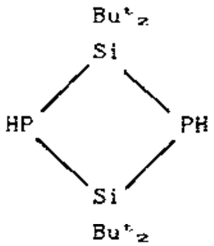

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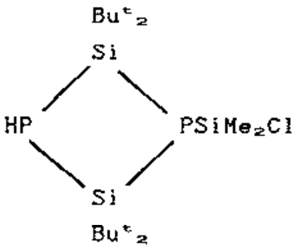

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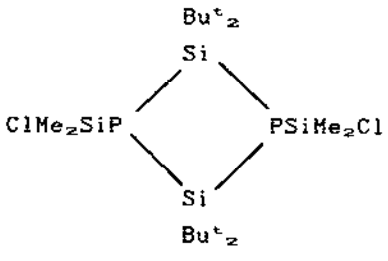

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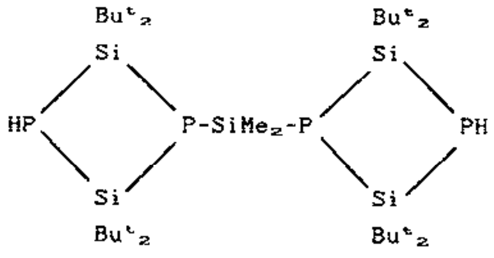

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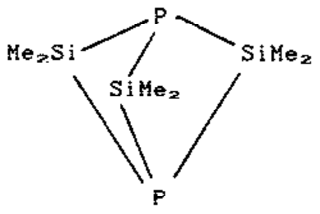

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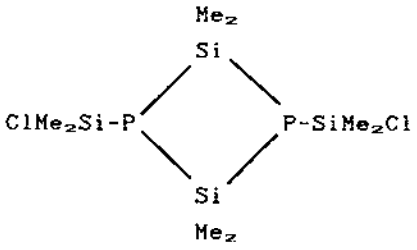


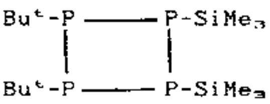
(160)

Compound (255) can be lithiated with either $LiPH_2$ or BuLi and the mono-lithiated product isolated as an adduct with two mols of DME.[259] Treatment with Me_2SiCl_2 then leads to mixtures of (156)-(158).

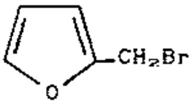
The major product when Me_2SiCl_2 reacts with Li_3P is the bicyclic compound (159), but a small quantity of a monocyclic, partially reacted species (160) is also formed.[260] The mixture cannot be separated and on attempted distillation, thermolysis leads to the adamantane-like $(SiMe_2)_6P_4$. Silyl phosphines will react with sulphur in the absence of a solvent to give products with the maximum amount of sulphur incorporation; thus Me_2PSiMe_2 gives $Me_2P(S).SSiMe_2$, while $MeP(SiMe_3)_2$ and $P(SiMe_3)_3$ give $MeP(S)(SSiMe_3)_2$ and $P(S)(SSiMe_3)_3$ respectively.[261] The by-products of these reactions are $(Me_3Si)_2S$, P_2Me_4 and $Me_2P(S)P(S)Me_2$. Reactions carried out in pentane are slower but intermediates such as $Me_2P.SSiMe_3$, and $Me_2P(S)PMe_2$ can be observed with Me_2PSiMe_2 as the starting material. With $MeP(SiMe_3)_2$, the intermediates are $MeP(SSiMe_3)(SiMe_3)$ and $MeP(SSiMe_3)_2$ and with

$P(SiMe_3)_3$, the three compounds, $P(SiMe_3)_n(SSiMe_3)_{3-n}$ with n = 0 - 2, are all observed. Depending on the reaction ratio, sulphur reacts with $P_2(SiMe_3)_4$ to give $P_2(SiMe_3)_n(SSiMe_3)_{4-n}$ where n = 0 - 3, but even at temperatures as low as 20°C only the decomposition product $(Me_3SiS)_3P(S)$ was isolated from $(Me_3Si)_3P_7$ and sulphur.

Silylated diphosphines $R(Me_3Si)P.PCl_2$, for R = Me or Bu^t, are obtained by treating $RP(SiMe_3)_2$ with PCl_3, and on treatment with $R^1P(SiMe_3)Li$ (R^1 = Bu^t or Me_3Si) can be converted to triphosphines $Bu^t(Me_3Si)P.PCl.P(SiMe_3)R^1$, which are unstable at room temperature. [262] Substitution of chlorine with either Bu^t or Me_3Si leads to more stable products, for example $(Me_3Si)_2P.P(SiMe_3).P(SiMe_3)Bu^t$ with Bu^tPCl_2 gives the cis-form of the cyclotetraphosphine (<u>161</u>).[263



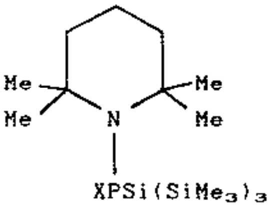
(<u>161</u>)



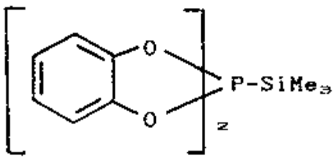
(<u>162</u>)

Furfuryl-phosphonium salts, $[RP(CH_2C_4H_3O)_3]Br$, $[P(CH_2C_4H_3O)_4]Br$ and $[Ph_2P(CH_2C_4H_3O)_2]Br$ where R = Me, Et, Bu^t, Ph or mesityl, are produced when (<u>162</u>) reacts with $RP(SiMe_3)_2$, $P(SiMe_3)_2$ or $Ph_2P(SiMe_3)$.[264] Reduction with lithium aluminium hydride gives furfurylphosphines, which are potential bi- and tridentate ligands.

Tetramethylpiperidino-substituted phosphorus(III) dihalides give thermally stable products formulated as (<u>163</u>, X = F or Cl) on reaction with tris(trimethylsilyl)silyl lithium, but the related



(<u>163</u>)

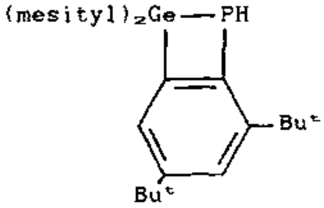


(<u>164</u>)

product, $Pr^i_2N.PClSi(SiMe_3)_3$ rearranges on heating via chlorine-Me_3Si exchange to $Pr^i_2N.P(SiMe_3).SiCl(SiMe_3)_2$.[265]

The first five-coordinate P(V)-Si compound (<u>164</u>) has been synthesised by treating tris(catechyl)chlorophosphorane $(C_6H_4O_2)_2PCl$ with the novel silylating agent $Mg(SiMe_3)_2$.DME in pentane at -28°C.[266]

<u>Bonds to Germanium</u>. Butene is lost when the phosphagermene $(mesityl)_2Ge{=}P(C_6H_2Bu^t_3)$ is heated in benzene at 160°C forming the first stable germaphosphetane (<u>165</u>).[267]



(<u>165</u>)

5.2.4 <u>Bonds to Halogens</u>

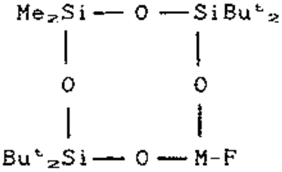
<u>The +3 Oxidation State</u>. The phosphorus analogue of NOF has recently been prepared by treating $P(O)FBr_2$ with silver in the gas phase at 1100K and 10^{-2} mbar.[268] Mass spectrometry and matrix isolation spectroscopy (ν_{P-O} 1292.2 cm^{-1} and ν_{P-F} 811.4 cm^{-1}) confirm the identification. An alternative route to POCl is the pyrolysis of allyl dichlorophosphite ($CH_2{:}CH.CH_2OPCl_2$) at 1150K in which allyl chloride is lost; again the unstable species was identified by mass spectrometry and Ar matrix i.r. spectroscopy. [691] Finally high temperature gas phase hydrolysis of PCl_3 and PBr_3 lead to POCl and POBr respectively which can be stabilised in argon matrices.[270]

An alternative to the normal inversion process (via a planar intermediate) for three coordinate Group 5 compounds has been proposed in which there is edge rather than vertex displacement leading to a T-shaped intermediate.[271,272,273] This alternative is considered to be particularly important for compounds carrying electronegative substituents and is supported by m.o. calculations showing stabilisation of the T-shaped over the planar intermediate by 35.6 and 56.2 kcal.mol^{-1} for PHF_2 and PF_3 respectively.

Substituted aryl difluorophosphines $2\text{-}MeOC_6H_4PF_2$ and $2\text{-}Me_2NC_6H_4PF_2$ have been synthesised, and although the former is stable at -30°C, it disproportionates at room temperature or above to $2\text{-MeOC}_6H_4PF_4$, and the highly puckered cyclotetraphosphine $[2\text{-MeOC}_6H_4P]_4$.[274]

Dithiols and diols on reaction with $S(PF_2)_2$ eliminate F_2PSH and give respectively $F_2PS.(CH_2)_n.SPF_2$ (n = 2-6) and $F_2PO.(CH_2)_n.OPF_2$ (n = 3-6).[275] The ligand behaviour toward molybdenum carbonyl species has been investigated.

Cyclisation with loss of two mols of LiF occurs when either PF_3 or AsF_3 reacts with the trisiloxane salt, $Li_2[OSiBu^t{}_2OSiMe_2OSiBu^t{}_2O]$ giving (166, M = P or As).[276] Hydrolysis of (166, M = P) gives the stable phosphorus acid ester (167).



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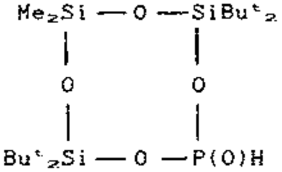

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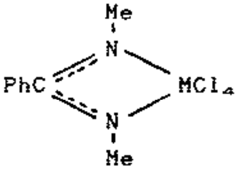


(168)

Although other products are formed, the overall reaction between phosphorus(III) chloride and hydrogen sulphide in the presence of 2-methylpyridine (B) is best represented by equation (22).[277] Phosphorus, arsenic and antimony(III) chlorides react with the

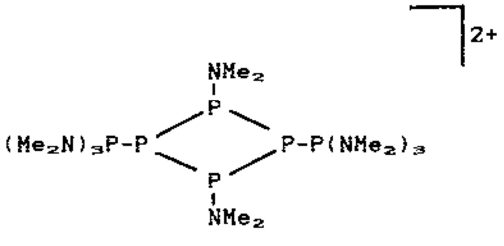
$$7PCl_3 + 9H_2S + 18B \rightarrow 3[BH][PS_2Cl] + 15BHCl + P_4S_3 \qquad ...(22)$$

substituted benzamidine PhC(:NMe)(NMeCl) to give cyclic products (168, M = P, As or Sb), for which detailed n.m.r. and mass spectrometric data are discussed. X-ray structures are very similar with M-N distances of 180.7/181.0, 195.4/194.3, and 210.0/213.0pm for phosphorus, arsenic and antimony respectively.[278]

Continued interest in phosphenium salts has led to an investigation of the reaction in equation (23).[279] The triphosphine product rapidly adds one mol of $AlCl_3$ at the central

$$PCl_3 + 3P(NMe_2)_3 + 2AlCl_3 \rightarrow [(Me_2N)_3PCl][AlCl_4] + [(Me_2N)_3P{:}P.P(NMe_2)_3][AlCl_4] \qquad ...(23)$$

phosphorus and a small amount of a second product $[(Me_2N)_3P.PH.P(NMe_2)_3][AlCl_4]_2$ is formed by addition of HCl, presumably from the solvent. During the course of this work, the all trans isomer of the cyclo-tetraphosphine (169) was also isolated. If $MePCl_2$ is treated with glycol in dichloromethane without a tertiary amine as a hydrogen chloride acceptor, the reaction course is altered giving $[MePH_3]Cl$ (structure determined) and (170).[280]



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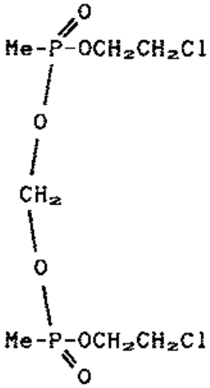


(170)

Iodine(V) fluoride rapidly oxidises R_3P, R_2PF, R_2PCl and $RPCl_2$ at 0°C to, respectively, R_3PF_2, R_2PF_3, R_2PF_3 and RPF_4 with liberation of elemental iodine,[281] and primary and secondary phosphines, etc. can be converted, e.g. equation (24), on treatment with either hexachloroethane or PCl_5 directly to $RPCl_2$, R_2PCl, $R_2P(O)Cl$ and $R_2P(S)H$ (where R = alkyl, cycloalkyl or aryl).[282]

$$R_{3-n}PH_n + nC_2Cl_6 \rightarrow nHCl + nC_2Cl_4 + R_{3-n}PCl_n \qquad \ldots(24)$$

$$RPH_2 + 3SO_2Cl_2 \rightarrow 2HCl + SOCl_2 + 2SO_2 + RP(O)Cl_2 \qquad \ldots(25)$$

$$RR'PH + 2SO_2Cl_2 \rightarrow HCl + SOCl_2 + SO_2 + RR'P(O)Cl \qquad \ldots(26)$$

Direct oxychlorination of primary and secondary phosphines is also possible on treatment with sulphuryl chloride, equations (25) and (26).

Metathesis between AgSCN and mono-substituted dihalogenophosphines gives $RP(NCS)_2$ where R = Me, Et, Ph or C_6F_5, there is evidence for the intermediate RPX(NCS) from ^{31}P n.m.r. spectroscopy and bonding via nitrogen is suggested by i.r. spectroscopy.[283] The compounds are all thermally unstable at room temperature.

A series of secondary chlorophosphines, RR'PCl, has been prepared and characterised by n.m.r. as products of reactions between a diphosphine, RR'PPRR', and either Ph_2PCl or $PhPCl_2$; among the compounds obtained were those with R = R' = Me, Et, Pr, Bu or Bu^t, and R = Me or Ph; R' = Et, Pr or Bu.[284]

Nitrogen trichloride can oxidise PCl_3 to PCl_5 and tertiary phosphines, R_3P where R = Me, Et, Bu or Ph, to R_3PCl_2 with elimination of nitrogen but the reaction of PCl_3 with cloramine leads to mixtures of the cyclophosphazenes $(NPCl_2)_{3 and 4}$.[285]

<u>The +5 Oxidation State.</u> Ozonolysis of POCl in an argon matrix gives PO_2Cl, which from i.r. data has an O-P-O angle of ca. 135° and an unexpectedly strong P-Cl bond.[286] Alternative preparative routes to PO_2Cl are high temperature reactions between either $POCl_3$ or PCl_3 and oxygen in the presence of silver.

It is interesting that an X-ray crystallographic study of PF_5 has been carried out showing the molecule has exact D_{3h} symmetry (space group $P6_3/mmc$) with axial and equatorial distances of 158.0 and 152.2pm.[287] These should be compared with gas phase values of 157.7/153.4 and 158.1/153.4pm from respectively electron diffraction and vibrational-rotational spectroscopy.

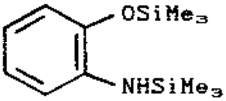
Trigonal bipyramidal structures with fluorine preferentially occupying axial positions are indicated by electron diffraction data for the mixed chloride fluorides PCl_nF_{5-n} where n = 1-4.[288] Bond distances, summarised in Table 1, show an increase in both P-F and P-Cl distances with increasing chlorine content, and the greatest effect at the axial bonds. Deviations from trigonal bipyramidal geometry are small with angles deviating from the ideal values by less than 1° for equatorial-axial and ca. 2° for equatorial-equatorial angles. Raman data for the compounds in conjunction with matrix isolation i.r. data were used to obtain valence force constants.

Table 1. Bond distances and angles for PCl_nF_{5-n} where n = 0-5.

	PF_5	$PClF_4$	PCl_2F_3	PCl_3F_2	PCl_4F	PCl_5
P-F_e	1.534(4)	1.535(3)	1.538(7)			
P-F_a	1.577(5)	1.581(4)	1.593(4)	1.596(2)	1.597(4)	
P-Cl_e		2.000(3)	2.002(3)	2.005(3)	2.011(3)	2.023(3)
P-Cl_a					2.107(6)	2.127(3)
X_ePX_e	120^a	117.8(7)^a	121.8(4)^b	120^b	120.0(1)^b	120^b
X_aPY_e	90^c	90.3(4)^c	90.0(3)^c	90^d	90.9(2)^e	90^e

$^a F_ePF_e$. $^b Cl_ePCl_e$. $^c F_aPF_e$. $^d Cl_ePF_a$. $^e Cl_aPCl_e$.

Reactions between RPF_4 (R = F, Me, Ph or adamantyl) and one mol of compound (171) lead to monocyclic benzoxazaphospholes (172) while spiro compounds (173) are the products with two mols of the aminophenol.[289]



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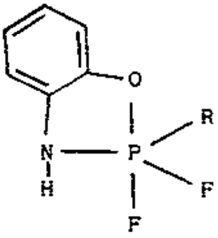

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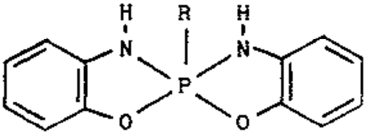


(173)

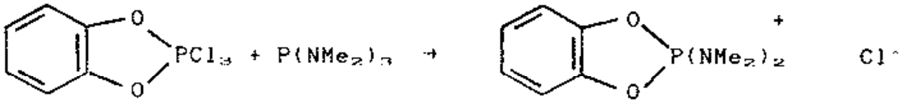
Methods for preparing the phase III modification of PCl_5, i.e. $(PCl_4)_2(PCl_6)(Cl)$, have been reviewed and the Raman shifts of the phosphorus(V) chlorides and bromides discussed.[290] Two other $(PCl_4)^+$ salts, $(PCl_4)_3(TiCl_6)(PCl_6)$ [291] and $(PCl_4)(ICl_4)$ [292] have recently been synthesised. The double salt, which results from heating a mixture of $TiCl_4$ and excess PCl_5 in either $POCl_3$ or nitromethane solution, is isostructural with the tin analogue. The tetrachloroiodate preparation involves treating a mixture of PCl_5 and iodine in either $POCl_3$ or dichloromethane with chlorine. The yellow solid contains tetrahedral PCl_4^+ and planar ICl_4^- ions but there are two secondary P-Cl...I interactions at 354 and 379pm.

Phosphorus(V) chloride treated with alkylammonium fluorides in the presence of a secondary amine leads to PF_5-amine adducts, equation (27), rather than PF_6^- salts.[293] The products give

$$3PCl_3 + 5Et_3N(HF)_3 + 13Et_2NH \rightarrow 3PF_5.HNEt_2 + 5Et_3NHCl + 10Et_2NH_2Cl \quad ...(27)$$

salts of the $(ROPF_5)$ ion with ethanol and phenol and $(ArNHPF_5)^-$ salts with primary aromatic amines.

N.m.r. data point to the formation of $(PhO)_4PCl$ or $[(PhO)_4P]$-$[PCl_6]$ when phenol reacts with phosphorus pentachloride,[294] and treatment of catechyl phosphorus trichloride with tris(dimethylamino)phosphine follows equation (28).[295] The salts $[R^1R^2P(NMe_2)_2]Cl$ and $[R^1R^2P(NMe_2)Cl]Cl$ are produced in the



$$+ Cl_2PNMe_2 \quad ...(28)$$

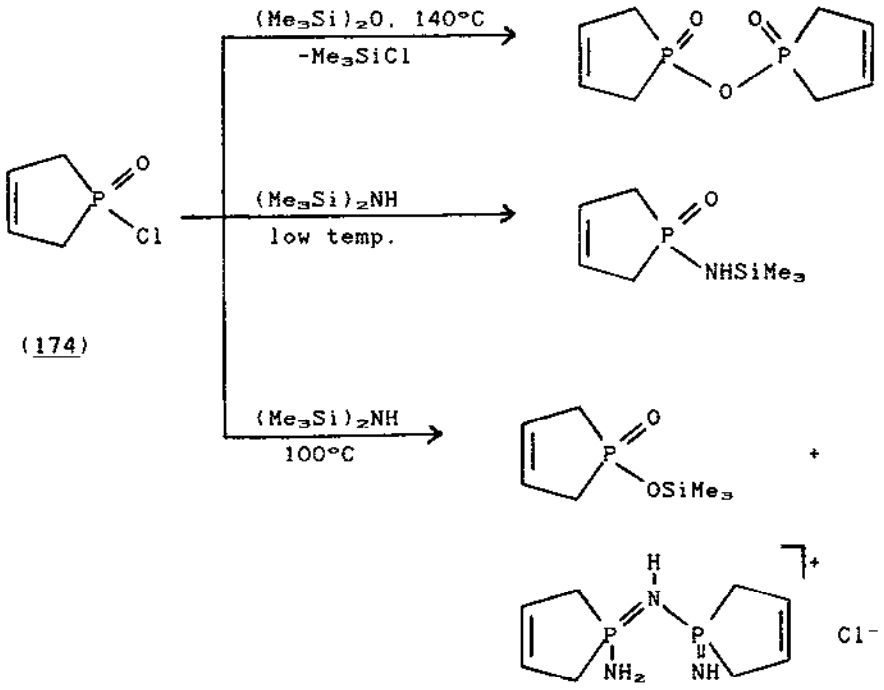
oxidation of, respectively, $R^1R^2P(NMe_2)$ and R^1R^2PCl (R^1/R^2 = OPh, NMe_2 or Cl) with N-chlorodimethylamine, Me_2NCl; with PCl_3 itself oxidation leads to $[Cl_2P(NMe_2)_2]PCl_6$.[296]

The mercury(II) halide catalysed reaction of $POCl_3$ with THF leads to compounds in the series $P(O)Cl_{3-n}[O(CH_2)_4Cl]_n$, where n = 1-3; with PBr_3 the product is $P\{P(O)[O(CH_2)_4Br]\}_3$ but with PCl_3 the catalysed reaction gives only $PCl_2[O(CH_2)_4Cl]$.[297]

Recently investigated reactions of 1-oxo-1-chlorophospholene Δ^3 (<u>174</u>) with $(Me_3Si)_2O$ and $(Me_3Si)_2NH$ are summarised in Scheme 3. [298]

The chlorine atoms in $Cl_3P{:}N.P(O)Cl_2$ can be substituted in a stepwise fashion by trifluoroethanol to give: $(CF_3CH_2O)PCl_2{:}N.P(O)Cl_2$, $(CF_3CH_2O)_2PCl{:}N.POCl_2$ and $(CF_3CH_2O)_3P{:}N.P(O)(OCH_2CF_3)_2$; on further reaction the last compound gives a diphosphorylimide, $(CF_3CH_2O)_2P(O).NH.P(O)(OCH_2CF_3)$.[299]

Two new six-coordinate phosphorus(V) anions, $[PhPCl_2(CN)_3]^-$ and $[MeP(CN)_5]^-$, result from treatment of $[RPCl_5]^-$ (R = Me or Ph) with an excess of silver cyanide.[300] A further report on the study of phosphorus(V) halides with 100% sulphuric acid and 25% oleum considers the behaviour of a range of methylated species.[301] In general solvolysis takes place which is faster for bromides than



(174)

Scheme 3

chlorides and faster in 100% H_2SO_4 than in oleum. With $MePBr_4$ in oleum there is evidence for $MeP(OH)Br_2^+$ and $MePBr_3^+$ and after long standing there is a ^{31}P n.m.r. signal assigned to $MeP(OH)_3^+$. The $MePBr_2Cl_2$ reactions show evidence for, inter alia, $MePCl_3^+$, $MePCl_2Br^+$, $MeP(OH)ClBr^+$, $MePClBr_2^+$, $MeP(OH)Br_2^+$ and $MePBr_3^+$.

5.2.5 Bonds to Nitrogen

Sub-division in this section is initially in terms of oxidation state, and within the two sections, multiple bonds to nitrogen are treated first.

The +3 Oxidation State. Treatment of MCl_3, M = P or As, with three mols of $Bu^t{}_3C_6H_2NHLi$ in ether gives the novel, isostructural, two coordinate imides, $Bu^t{}_3C_6H_2NH\text{-}M{=}NC_6H_2Bu^t{}_3$ with P-N distances of 157.3 and 163.3pm (As-N 171.4 and 174.5pm) and an angle of 103.8° at phosphorus (98.8° at arsenic).[302] The two aryl groups are magnetically distinct up to at least 400K according to n.m.r. data but there is a slow proton exchange in C_6D_6 indicating the equilibrium in equation (29). Compounds containing -P=N-, -P=P and -P=S units have been obtained from reactions between silylphosphides and acid chlorides, see equations (30)-(32).[303] An important step in introducing the double bond is a 1,3-silyl shift in intermediates of the type $RP(SiMe_2R)(X=O)$.

$M(=NAr)(NHAr) \rightleftharpoons M(NHAr)(=NAr)$ ...(29)

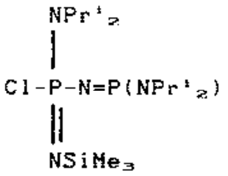
$RP(SiMe_2Bu^t)Li + NOCl \rightarrow LiCl + RP=NOSiMe_2Bu^t$ ...(30)

$RP(SiMe_3)Li + Bu^t{}_2P(O)Cl \rightarrow LiCl + RP=PBu^t{}_2(OSiMe_3)$ ...(31)

$RP(SiMe_3)Li + (mesityl)S(O)Cl \rightarrow LiCl + RP=S(mesityl)(OSiMe_3)$ ...(32)

$R = Bu^t{}_3C_6H_2$

An iminophosphine-iminophosphorane (175) is obtained when the diazadiphosphetidine (176) is treated with carbon tetrachloride; a transient diazadiphosphetine (177) formed by loss of Me_3SiCCl_3 is probably an intermediate.[304] Compound (175) is in fact, stable onl below -40°C above which it dimerises to (178); these and other reported reactions point to the instability of diazadiphosphetines such as (177), as the equilibrium is extensively displaced in favour of the open form isomer.



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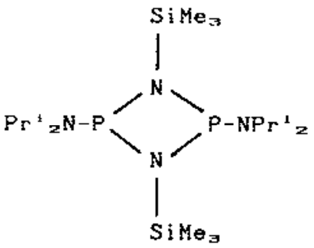

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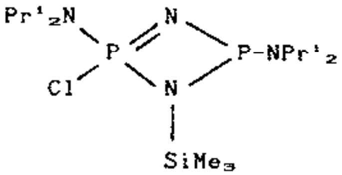

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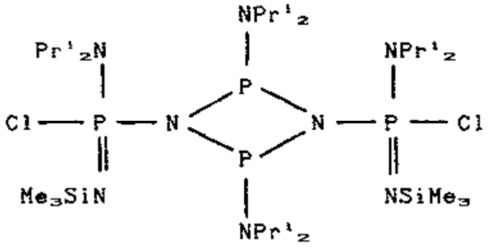

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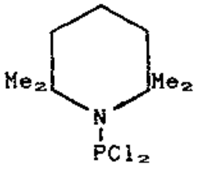

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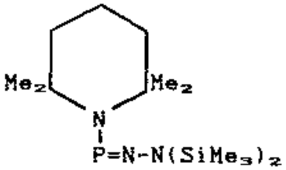
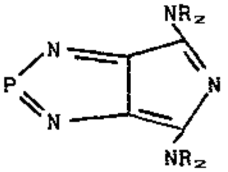


(180)

Trimethylchlorosilane is eliminated from a mixture of the substituted piperidino-phosphorus dichloride (179) and $LiN(SiMe_3)_2$ giving (180), which contains an unusually long (160pm) and highly polar P-N double bond.[305] The formal single bond to the piperidine nitrogen, on the other hand, is shorter (166pm) than would be expected. Phosphorus(III)-nitrogen double bonds also occur in the triazaphosphapentalene (181) obtained by treating dicyano-diazaphospholes (182) with secondary alkylamines.[306]



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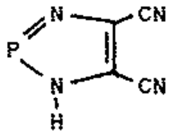
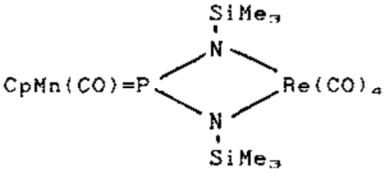


(182)

Ligand exchange between $(Me_3Si)_2N-P=NSiMe_3$ and the cis-octene complex, $CpMn(CO)_2$(octene) gives an intermediate which treated with

$Re(CO)_5Br$ loses carbon monoxide and Me_3SiBr and gives the unusual bimetallic complex (183).[307] The same amino-iminophosphine with $Fe_3(CO)_{12}$ is converted to a tridentate, six electron donor (184) stabilised as a $[Fe(CO)_3]_2$ cluster; a second species containing coordinated $(Me_3Si)_2NP$ and $Me_3SiOP{=}NSiMe_3$ groups was also isolated.[308]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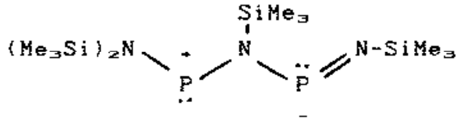
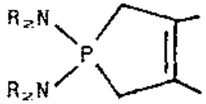

(184)

In general, phosphenium cations, $[(R_2N)_2P]^+$ (R = Me or Pr^i) and $[(Pr^i{}_2N)PCl]^+$, give phospholenium cations such as (185) on treatment with 1,3-dienes,[309] while the related $[(Me_2N)PCl]^+$ is converted in a one step process on reaction with cyclo-octatetraene to the 9-phosphabarbaralane (186).[310]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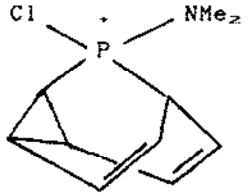

(186)

Both $MeN(PF_2)_2$ and $EtN(PF_2)_2$ are oxidised in good yields to $RN(POF_2)_2$ by N_2O_4 in hexane,[311] but silylated nucleophiles such as Me_3SiOMe and Me_3SiNEt_2, cleave the P-N-P bridge giving difluorophosphoric acid derivatives as shown in equations (33) and (34).[312]

$$EtN(POF_2)_2 + Me_3SiOMe \rightarrow F_2P(O)OMe + F_2P(O)NEt(SiMe_3) \qquad ...(33)$$

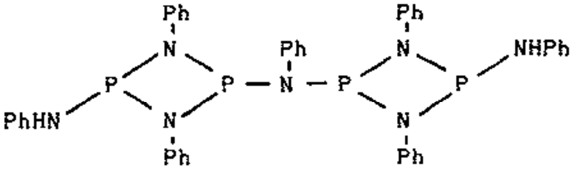
$$EtN(POF_2)_2 + Me_3SiNEt_2 \rightarrow F_2P(O)NEt_2 + F_2P(O)NEt(SiMe_3) \qquad ...(34)$$

$PhN(PCl_2)_2$ has a C_{2v} conformation in the solid state with the phosphorus lone pairs trans to the phenyl group.[313] This arrangement with P-N distances of 169pm and a P-N-P angle of 110.8° is consistent with low temperature ^{31}P n.m.r. data.

Two new members of the diazadiphosphetidine series, (187) and (188), have been isolated from experiments designed to unravel the course of the reaction of aniline with phosphorus(III) chloride (equations (35) and (36)).[314] The reaction now appears to

$19PhNH_2 + 4PCl_3 \rightarrow 12PhNH_3Cl$

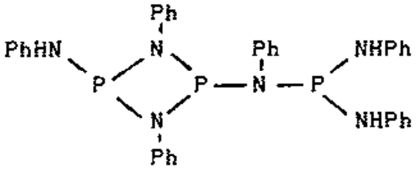
+



...(35)

(187)

$15PhNH_2 + 3PCl_3 \rightarrow 9PhNH_3Cl +$



...(36)

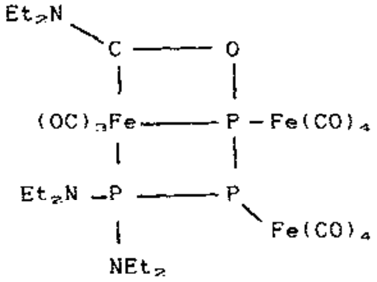
(188)

depend critically on the stoichiometry and exact conditions and involves the stepwise formation of $(Ph_2NH)_3P$, $[(PhNH)_2P]_2NPh$, $[(PhNH)PNPh]_2$ and (188) en route to the dinuclear (187).

Reaction of cis-$[ClPNPh]_2$ with trifluoroethanol and triethylamine leads to the trans form of the substitution product $[(CF_3CH_2O)PNPh]_2$, which on standing in solution slowly but almost completely, isomerises to the cis-form.[315]

The amino groups in $RP(NEt_2)_2$ and R_2PNEt_2, for R = vinyl, allyl or o-styryl, etc., can be replaced by chlorine or bromine on treatment with the appropriate hydrogen halide to give RPX_2 and R_2PX; reactions of the amine derivative with other reagents such as H_2O_2, H_2O, $LiAlH_4$ were also reported.[316]

Although a mono-substituted species, Et_2NPCl_2, was used in the reaction with $Na_2Fe(CO)_4$ in ether below 0°C, the product is a complex (189) containing a $P(NEt_2)_2$ group and both FeP_3 and FeOPC rings.[317] On decarbonylation in solution at room temperature, the original bridging diethylcarbamoyl group becomes terminal, new Fe-Fe and Fe-P bonds are formed to give (190).



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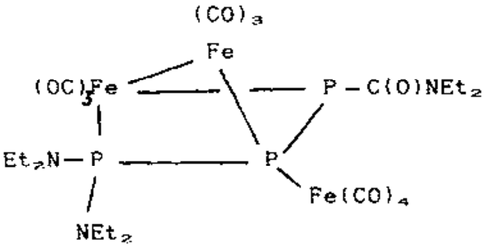
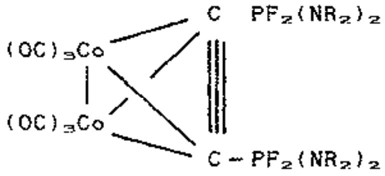


(190)

Sulphur tetrafluoride will oxidise the substituted acetylenes, $(Et_2N)_2P.C{\vdots}C.P(NEt_2)_2$ and the corresponding morpholine products, to $F_2(R_2N)_2P.C{\vdots}C.P(NR_2)F_2$ which behave as ligands in the complex $Co_2(CO)_6.L$ (191) obtained in a room temperature reaction with $Co_2(CO)_8$.[318] The chlorine atoms in fac-$[Mo(CO)_3(PCl_3)_3]$ can



(191)

be substituted by $Pr^i_2NH_2$ to give fac-$\{Mo(CO)_3[P(NHPr^i)_3]_3\}$ which has C_3 point symmetry and P-N distances of 167pm.[319]

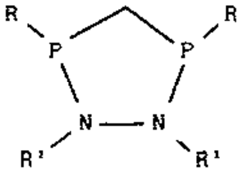
Borylaminophosphines, see equation (37),[320] and aminophosphines containing $(Me_3Si)_2CH$ groups [321] have been synthesised, the

$$(Me_3Si)_2N\text{-}BBu^t(NHLi) + ClPXY \rightarrow LiCl + (Me_3Si)_2N\text{-}BBu^t(NHPXY)$$

$X/Y = Me_2N,\ Ph,\ Cl,\ Ph/Cl,\ N(SiMe_3)_2/Cl$, etc., ...(37)

latter involves successive treatment of either PCl_3 or $PhPCl_2$ with $(Me_3Si)_2CHMgCl$ and a lithium silylamide. Among the compounds obtained are $(Me_3Si)_2CHPCl(NR_2)$, where R = $SiMe_3$ and R_2 = $SiMe_2.CH_2.CH_2.SiMe_2$ or $(SiMe_3)(SiMe_2Bu^t)$, and $(Me_3Si)_2CHPRN(SiMe_3)_2$, where R = H, Me, Ph, CH_2SiMe_3 or $CH{:}CH_2$. The latter group of compounds react with carbon tetrachloride to give a variety of products which depend on the nature of the R group and on the decomposition route of the intermediate $[(Me_3Si)_2CHPR(Cl)N(SiMe_3)_2][CCl_3]$.

Reactions between $RPClCH_2PClR$, for R = Cl, Pr^i or Bu^t, and hydrazine, N,N'-dimethylhydrazine, and phthalohydrazide yield products such as (192, R = Cl, Pr^i or Bu^t, R^1 = H or Me) and (193).[322] The structure of (192, R = Bu^t, R^1 = H) has been determined. Symmetrically substituted sulphur diimides, $Bu^t_2M.NSN.MBu^t_2$ where M = P or As, are cleaved with potassium amide to give potassium salts $K[NSNMBu^t_2]$, and treatment of the phosphorus salt with Bu^t_2AsCl gives a mixed derivative $Bu^t_2P.NSN.AsBu^t_2$.[323] On treatment with a chalcogen reaction is specifically at the phosphorus atom.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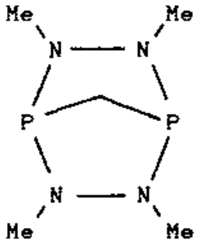

(193)

The +5 Oxidation State. Thermolysis and pyrolysis of phosphorus azides have been discussed and evidence for the formation of transient >P≡N species reviewed.[324] Although such monomeric phosphazenes are considered to be formed initially when the new azides $R^1R^2PN_3$ (R^1 = Bu^t, R^2 = Bu^t or NPr^i_2; R^1 = NMe_2, R^2 = NPr^i_2; and R^1 = $CH(SiMe_3)_2$, R^2 = $NC_5H_3Me_4$ or $N(SiMe_3)_2$) are decomposed, subsequent behaviour, whether this is dimerisation, trimerisation or rearrangement via a 1,3-silyl migration to a three coordination phosphorus(V) species, depends on the specific substituents.[325]

Primary amines, RNH_2 where R = Me, Et, Pr, Pr^i, Bu, Bu^i, Bu^s, Bu^t, CH_2Ph or cyclohexyl, react in non-polar solvents to give both mononuclear, $PhP(S)(NHR)_2$ and dinuclear, cyclophosphazane $Ph\overline{P(S).NR.PPh(S)N}R$, products.[326] The latter is formed exclusively in the trans form and is favoured with low stoichiometric quantities of amine.

Phenoxy-substituted phosphoryl-phosphazenes and imidodiphosphoric acid esters react with PCl_5 according to equations (38) and (39) respectively.[327] N-silyl phosphinimines, $R_3P{=}NSiMe_3$ (R =

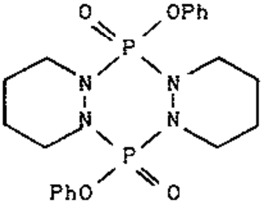
$$(PhO)_3P{:}N.P(O)(OPh)_2 + 2PCl_5 \rightarrow [(PhO)_3P{:}N.P(OPh)_2Cl]^+[PCl_6]^- + POCl_3 \quad ...(38)$$

$$(PhO)_2P(O).NH.P(O)(OPh)_2 + 3PCl_5 \rightarrow [(PhO)_2ClP{:}N.P(OPh)_2Cl]^+[PCl_6]^- + 2POCl_3 + HCl \quad ...(39)$$

$4\text{-}MeC_6H_4$ or Me, R_3 = Bu^tNH/Ph_2) react with WF_6 to give $(4\text{-}MeC_6H_4)_3P{:}NWF_5$, $[(4\text{-}MeC_6H_4)_3P{:}N]_2WF_4$, $[(Bu^tNH)(Ph_2P{:}N)]_2WF_4$ and $(Me_3P{:}N)_2WF_4$.[328] The latter is the cis form with W-N distances of 181.6 and 182.3pm and a N-W-N angle of 99.6°.

The recently synthesised sulphinyliminophosphorane $Ph_3P{:}N.S.C_6H_3(NO_2)_2\text{-}2,4$ shows P=N, S-N and C-S distances of 156.6, 166.0 and 172.8pm respectively, confirming the absence of conjugation in the system.[329]

Structures have also been determined for two phosphorus(V)-hydrazine products (194)[330] and (195)[331]. The former is centrosymmetric with all three rings in chair conformations, while the latter, a potential antitumour agent obtained by reacting $(PhO)P(S)(NMeNH_2)_2$ with $(Me_2N)P(O)Cl_2$, is the Z isomer with a twist ring conformation.



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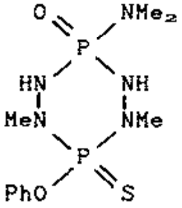
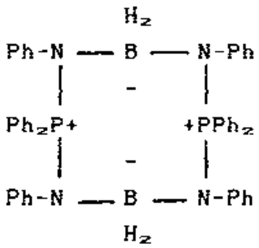


(195)

Transilylation with RMe_2SiCl, for R = Ph, $CH{:}CH_2$, CH_2Cl,

$CH_2CH_2CH_2CN$, etc., converts the phosphazene $Me_3SiN{=}P(OCH_2CF_3)Me_2$ into $RMe_2SiN{=}P(OCH_2CF_3)Me_2$ while the product using Me_2SiCl_2 is either $Me_2Si[N{=}P(OCH_2CF_3)Me_2]_2$ or $Me_2SiCl[N{=}P(OCH_2CF_3)Me_2]$ depending on the reaction stoichiometry.[332]

When borine-dimethylsulphide reacts with $PhNH.PPh_2{:}NPh$ in dichloromethane, the product is the eight-membered heterocycle (196) together with $PhNH.PPh_2.BH_3$, H_2 and Me_2S as by-products. [333] According to ^{31}P n.m.r. data, $Me_3SiNHP(S)Cl_2$ and the ring



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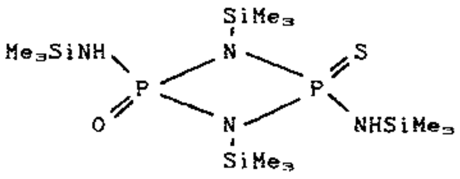
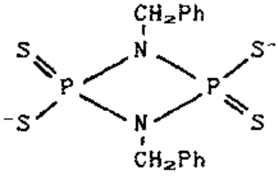


(197)

compound (197) are obtained from $PSCl_3$ and hexamethyldisilazane. [334] With $py.PS_2Cl$ and benzylamine in the presence of triethylamine, reaction gives the triethylammmonium salt of a new tetrathiodiazadiphosphetidine (198), which can be separated by fractional crystallisation into cis and trans isomeric forms.[335] Treatment with methyl iodide then gives the dimethyl ester (199).



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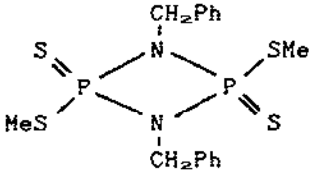


(199)

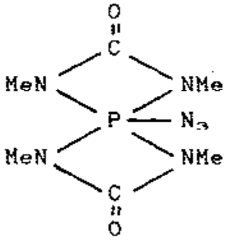
Staudinger reactions between R_nPF_{3-n}, where n = 1 or 2, R = R'_2N, $(CH_2)_5N$, $O(CH_2)_4N$, $R'O$, $(CH_2O)_2$, and substituted phenyl azides, $XC_6H_4N_3$ where X = H, Me, Cl, Br or NO_2, have been used to prepare a wide range of di- and tetrafluorodiazadiphosphetidines, equation (40), and fluorinated monophosphazenes, equation (41).[336] Substituent influence on the nature of the product and full ^{19}F and

^{31}P n.m.r. results are discussed.[337]

$$RPF_2 + XC_6H_4N_3 \rightarrow \tfrac{1}{2}(RPF_2NC_6H_4X)_2 + N_2 \qquad \ldots(40)$$

$$RR^1PF + XC_6H_4N_3 \rightarrow RR^1PF{=}NC_6H_4X + N_2 \qquad \ldots(41)$$

A normal Staudinger reaction between the azido-phosphorane (200) and triphenylphosphine gives compound (201) containing the novel λ^5-PN-λ^4-P unit.[338] A noticeable feature of the structure of (201) is the shortness of P-N(imide) bond (158.9pm); the other P-N distances are 154.9 for the double bond and 178.5/180.1 and 168.1/168.7pm for the axial and equatorial distances respectively at the central five coordinate phosphorus atom. Continuing in the area of urea substituted phosphorus(V)compounds, elimination of Me_3SiCl to give a simple μ-oxobis(spirophosphorane) was expected in the reaction of



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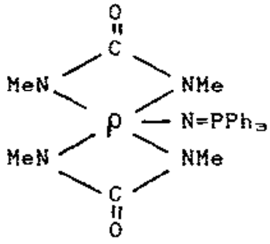
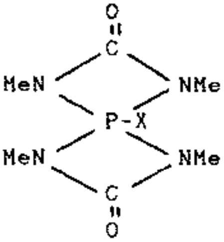


(201)



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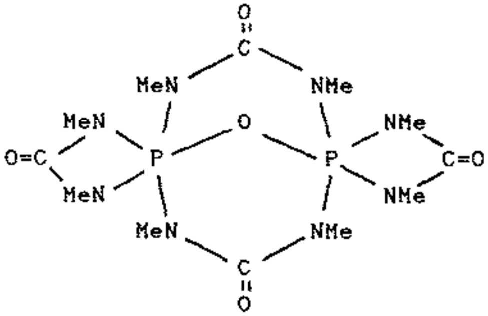


(203)

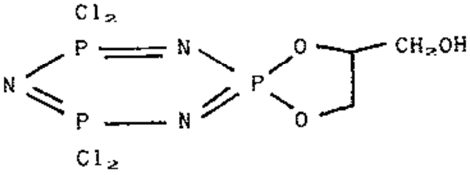
(202, X = Cl) with (202, X = OSiMe$_3$), but from a single crystal X-ray study of the product, an isomeric form with two additional dimethylurea bridges (203) is actually obtained.[339] The phosphorus atoms are in distorted trigonal bipyramidal coordina- tion with the following bond distances: P-O(axial) 163.5, P-N(axial) 179.9-181.2 and P-N(equatorial) 167.4-170.1pm; the oxygen bond angle is reduced to 126.6° and the angle at phosphorus in the four membered rings is 73.4°.

Cyclophosphazenes and Related Compounds. Ab initio calculations for the model cyclophosphazenes $(H_2PN)_2$ and $(H_2PN)_3$ show that dimerisation leads to modest stabilisation (80 kcal.mol^{-1}) of the monomer while cyclotrimerisation liberates 210 kcal.mol^{-1}.[340] The paper points out that an alternative view of the bonding in P_2N_2 systems is via formation of two three centre-four electron P-N-P bridge bonds.

A recent review concentrates on the organometallic chemistry of phosphazenes and deals with both main group (ArLi, Grignard and organoaluminium derivatives) and transition metal species.[341]

A comprehensive study of the reaction of aziridine with both $(NPCl_2)_{3 and 4}$ reveals that substitution follows both geminal and non-geminal routes and isolation of all possible isomers in the trimeric series has been achieved.[342] Structural assignments followed basically from ^{1}H and ^{31}P n.m.r. spectroscopy, supplemented by an X-ray structure of the key compound, trans-$N_3P_3(NC_2H_4)_2Cl_4$. There is evidence for all possible isomers in the first three substitution steps for the tetramer and the structure of another key compound, 2,trans-4-$N_4P_4(NC_2H_4)_2Cl_6$ was determined. A re-examination of the $(NPCl_2)_3$-thiourea reaction in pyridine solution points to formation of $N_3P_3[NHC(S)NH_2]_6$ while in acetone solution only three mols of thiourea are required, the product probably being spirocyclic with both N and S bonding.[343] Structures have been determined for gem-$N_3P_3Cl_4(NH_2)_2$, $N_3P_3Cl_4(NH_2)(NPPh_3)$ and $N_3P_3Cl_5(NPPh_3)$.[344]

Glycerol reacts with $(NPCl_2)_3$ giving compounds (204) and (205), the latter confirmed by an X-ray structure,[345] and treatment of $N_3P_3(OCH_2CF_3)_5ONa$, a hydrolysis product of $N_3P_3(OCH_2CF_3)_6$, with compounds such as benzoyl chloride, Ph_3PCl_2 and p-toluenesulphonyl chloride gives $N_3P_3(OCH_2CF_3)_5OR$ with loss of sodium chloride.[346]



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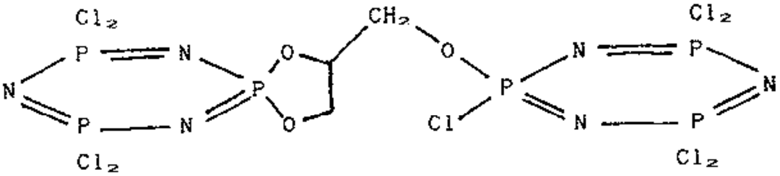
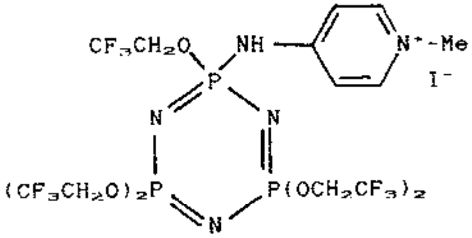


(205)

Simple cyclophosphazene-TCNQ salts have been isolated by treating quaternised derivatives such as (206) and (207) with Li(TCNQ);



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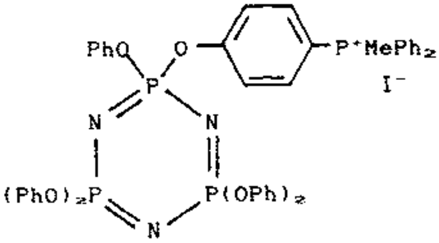
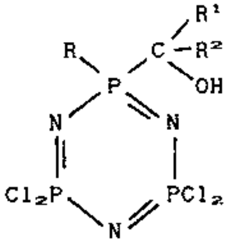


(207)

further treatment leads to "complex" salts formulated as $[\mathrm{phosphazene}]^+[\mathrm{TCNQ}]^-.\mathrm{TCNQ}$.[347] These compounds have electrical conductivities several orders of magnitude greater than related salts of the highly polymerised phosphazenes. A 1:1 complex involving coordination via a ring nitrogen atom has been obtained from $N_3P_3(OPh)_6$ and TaF_5.[348]

The remaining halogen atoms in $N_3P_3(NPPh_3)X_5$, for X = F or Cl, can be substituted with sodium methoxide to give a range of products formulated on the basis of detailed n.m.r. spectroscopy as $N_3P_3(NPPh_3)(OMe)_nX_{5-n}$, where n = 1-5.[349] Geometrical isomers were observed for n = 1-3, in unequal proportions for X = Cl but more nearly equal for X = F.

The transient copper substituted cyclophosphazenes, formed when $(NPCl_2)_3$ reacts with Grignards in the presence of $(Bu_3PCuI)_4$, react with aldehydes and ketones to give the novel geminal products (208, R = Me, R^1 = Me or Ph, R^2 = H or Me; R = Bu^t, R^1 = Me, CH_2Cl or Ph, R^2 = H or Me).[350] Complex mixtures are obtained in reactions of the trimeric chloride with either MeLi or Bu^tLi at -60°C in the presence of propan-2-ol, but (209) and a small amount of (210, R = Me) were isolated using one mol of MeLi and an excess of propanol.[351] Six products, according to n.m.r. spectroscopy, are formed with two mols of MeLi, including (209), (210, R = Me), (211) and (212), and with Bu^tLi among the products are (209) and (210, R = Bu^t). As with Grignard reagents, the first step in these alkyl lithium reactions is considered to be halogen-metal exchange.



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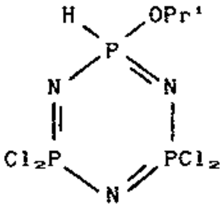

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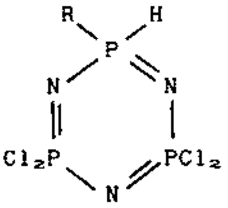

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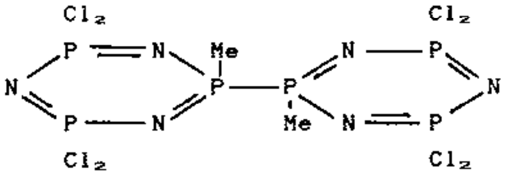

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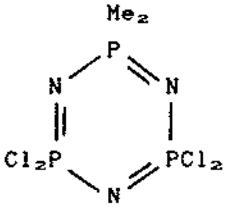
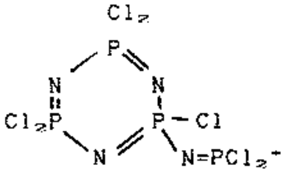


(212)

The major reaction in the electron impact mass spectrometry of $N_4P_4Cl_8$ is loss of chlorine to give $N_4P_4Cl_7^+$, considered to have the more stable ring contracted triphosphazene structure (213).[352] If the concentration of $N_4P_4Cl_8$ in the ion source is increased, oligomerisation to $(NPCl_2)_n$ with $5 \leqslant n \leqslant 12$ takes place with $N_8P_8Cl_{15}^+$ (214) being the most abundant species.



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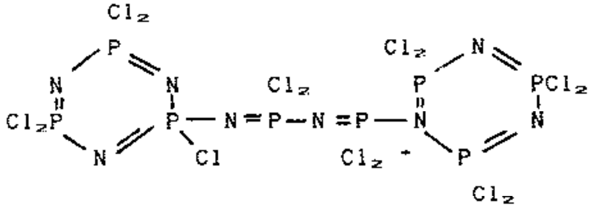
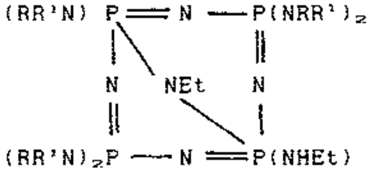


(214)

New bicyclic tetraphosphazenes (215) have been isolated when $N_4P_4Cl_6(NHEt)_2$ is treated with either pyrrolidine, piperidine, morpholine, diethylamine or cyclopropylamine and in addition the expected normal substitution product, $N_4P_4(NHEt)_2(NRR')_6$, is also isolated.[353] In some respects it is surprising that reaction of $N_4P_4Cl_8$ with cyclopropylamine also gives a bicyclic product (216).



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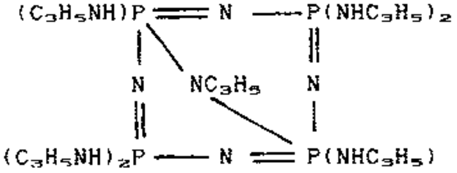
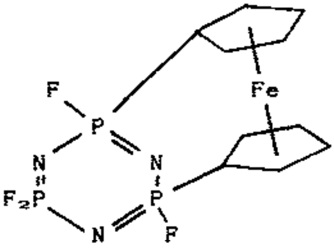


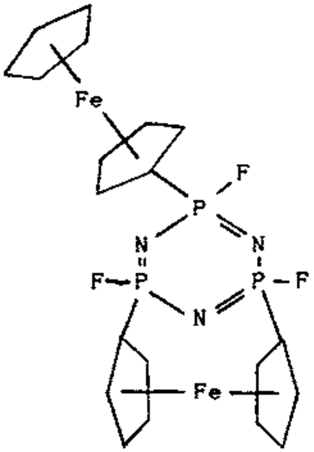
(216)

Tri- and tetrafluorophosphazenes carrying ferrocenyl or ruthenocenyl substituents can be substituted further on treatment with mono- and dilithioferrocene or ruthenocene or with methyl or phenyl lithium.[354,355] Among the compounds isolated in this comprehensive study are (217) to (221) for which crystal structures have been determined. The most intriguing compound is (220), incorporating two transannular substitutions, which is the first known example of this type of compound. Production starts with 1,5-$N_4P_4F_6[(C_5H_4)_2Ru]$ which is treated with a mixture of mono- and dilithioruthenocene to give in addition (221). An X-ray structure shows distortion of the planar $N_4P_4F_8$ structure to a boat conformation to accommodate the two transannular substituents.

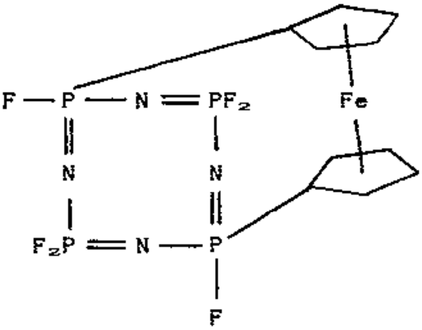
A series of vinyloxy-tetraphosphazenes is produced when $N_4P_4Cl_8$ reacts with the lithium enolate of acetaldehyde, but only



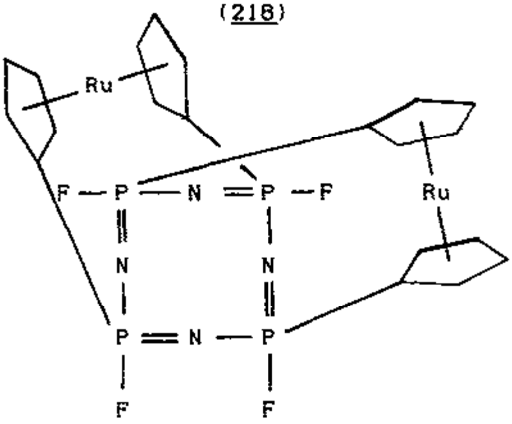
(<u>217</u>)



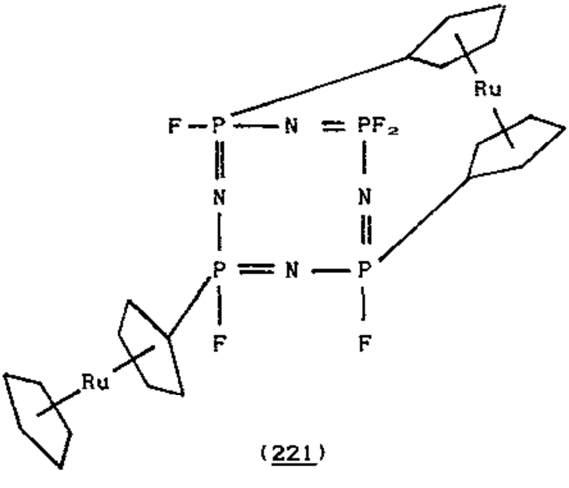
(<u>218</u>)



(<u>219</u>)



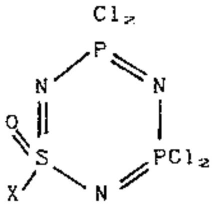
(<u>220</u>)



(<u>221</u>)

$N_4P_4Cl_7(OCH{:}CH_2)$ and $N_4P_4Cl_6(OCH{:}CH_2)_2$ were obtained in the pure state.[356] The latter was analysed by two dimensional n.m.r. spectroscopy to show a mixture of isomers, in which unusually the 2,4-compounds are major products.

Following success with $(NPCl_2)_3$,[351] Winter and van de Grampel have extended reactions of alkyl lithiums in the presence of excess 2-propanol to the mixed P-N-S heterocycles (222) and (223).[357] The products are complex mixtures containing among others >P(OPr^i)H species and alkyl hydrides (224) but in general these thia-substituted derivatives give smaller proportions of cyclic products than cyclophosphazenes. Two mols of either 1,2-diaminoethane or 2-aminoethanol react with (223, X = F, Cl or Ph) to give spirocyclic products (225) in which the two chlorines at phosphorus are replaced.[358] One such compound (225, X = Cl, Y = O) has been crystallographically investigated showing all three oxygen atoms occupying cis positions; similar spirocyclic products are formed with 1,3-propanediamine and 3-aminopropanol. In contrast to this behaviour, Friedel-Crafts reactions on (222, X = Cl) with



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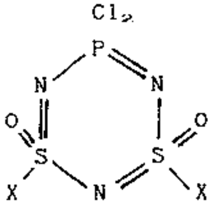

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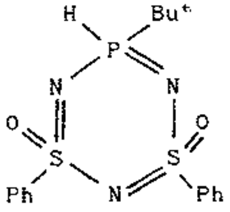

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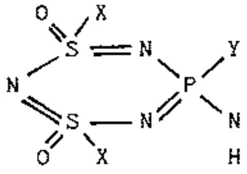

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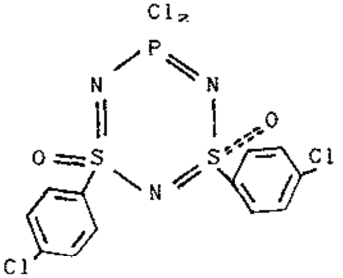

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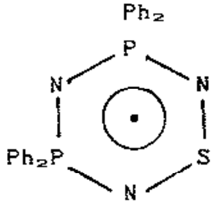
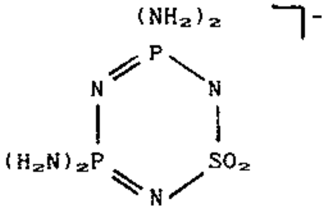


(227)

PhR, for R = Me, OMe, Et, Pr^i, Cl, Br or I, give substitution at sulphur with both ortho and para isomeric forms for R = Me or OMe.[359] Other reagents give only the para isomer. The disulphur compound (223, X = Cl) on reaction with chlorobenzene gives five of the six possible isomeric forms, which can be separated by HPLC and structurally assigned using ^{31}P and ^{1}H n.m.r. spectroscopy. The missing compound is the cis-ortho-ortho isomer. Assignments were confirmed by an X-ray structure for the trans-ortho-para isomer (226).

E.s.r. data and molecular orbital calculations support formulation (227) for the persistent radical obtained when $Ph_4P_2N_3SCl$ is reduced in dichloromethane solution with Ph_3Sb.[360] The sodium salt of (228) has been isolated and the dissociation constant of the free acid determined as 9.62 x 10^{-7}.[361]

One of the most interesting developments in this area has been the incorporation of transition metals into basically phosphazene rings. The first compound isolated, (229), resulted from a reaction between WCl_6 and the linear phosphazene $[H_2NPPh_2.N.PPh_2NH_2]Cl$.[362] Crystallisation from acetonitrile gave a disolvate containing a planar ring with P-N distances falling between 158.7 and 166.3pm; W-N distances are 177.3 and 179.8pm. In a similar fashion, but using either $MoCl_3N$ or $NbCl_5$, it was possible to obtain the molybdenum analogue of (229) and (230), respectively.[363]



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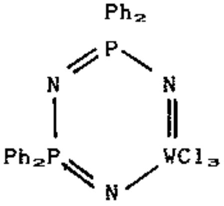

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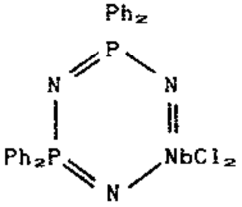
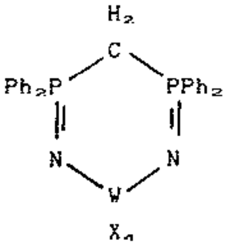
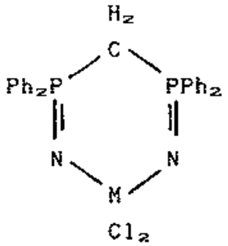


(230)

Related compounds (231, X = F or Cl) and (232, M = Se or Te) can be obtained from reactions between $CH_2(PPh_2{=}NSiMe_3)_2$ and, respectively WX_6, $SeOCl_2$ and $TeCl_4$,[364] and on treatment with DBU, (231, X = Cl) loses hydrogen chloride with conversion to the conjugated product (233).



(<u>231</u>)



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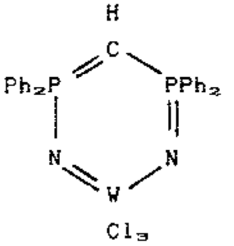
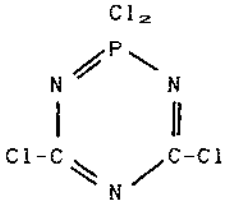


(<u>233</u>)

Regioselectivity in chlorine substitution in (<u>234</u>) by nucleophiles is shown by formation of a C-substituted products (<u>235</u>) with Me$_3$SiNMe$_2$ while P-substitution occurs with CF$_3$CH$_2$OLi to give (<u>236</u>).[365] A highly puckered 12-membered ring with P-N



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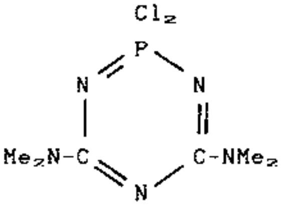

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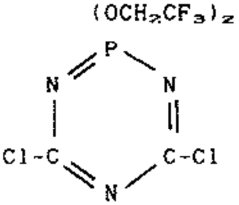

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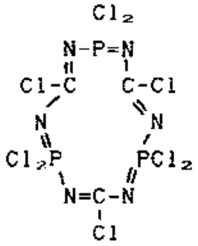


(<u>237</u>)

and C-N bond lengths of 160 and 131pm respectively is found in the trimeric product (Cl$_2$PN$_2$CCl)$_3$ (<u>237</u>) obtained in a reaction between PCl$_5$ and Me$_3$SiN:C:NSiMe$_3$ in toluene solution.[366]

5.2.6 Bonds to Oxygen

Lower Oxidation States. A series of reactions has been carried out using bis(trimethylsilyl)hypophosphite $(Me_3SiO)_2PH$. [367] The Group 6 elements, for example, are oxidised to $(Me_3SiO)_2PH(X)$, where X = O to Te, while with alkyl halides the products are $RP(OSiMe_3)_2$, sometimes together with $R_2P(O)(OSiMe_3)$. Chloroformic esters, ClC(O)OR on the other hand give $(RO)C(O)P(O)H(OSiMe_3)$, $(ROCO)_2P(O)(OSiMe_3)$ and $HP(O)(OSiMe_3)_2$.

Mixtures of organoammonium fluorides with carbon tetrachloride have proved to be good oxidative fluorination reagents for phosphorus(III) reactants and some examples of the transformations are summarised in equations (42)-(45).[368]

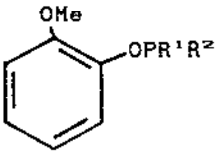
$$P(OEt)_3 \rightarrow [(EtO)PF_5]^- + (EtO)_2P(O)F \qquad \ldots(42)$$

$$P(OEt)_2(NEt_2) \rightarrow [(EtO)PF_5]^- \qquad \ldots(43)$$

$$P(OEt)(NEt_2)_2 \rightarrow (Et_2N)_2P(O)F + (Et_2N)_2(EtO)PF_2 \qquad \ldots(44)$$

$$P(NEt_2)_3 \rightarrow (Et_2N)_3PF_2 + [(Et_2N)_3PF]^+ \qquad \ldots(45)$$

Reactions between 2-methoxyphenylphosphinites, phosphonites and phosphites (238, $R^1 = R^2$ = Ph, OPh or OEt, $R^1/R_2 = OCH_2HC_2O$) and either chlorine or bromine initially give halogenophosphonium halides (239) but further reaction with starting material yields either phosphonium salts or, following elimination of methyl halides, cyclic phosphoranes.[369] Similar behaviour is observed with the substituted diarylchlorophosphite (240) which on chlorination in dichloromethane gives the spirocyclic phosphorus(V) chloride (241) with elimination of methyl chloride.[370]



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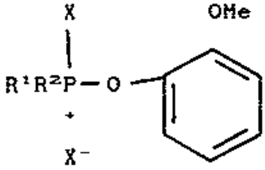

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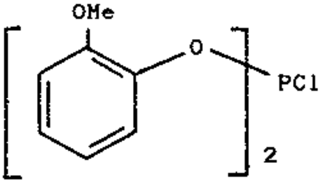

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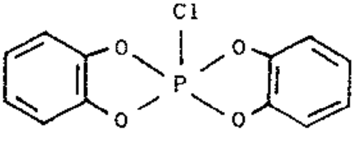

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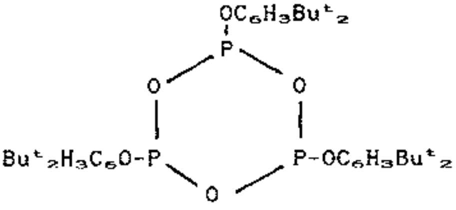
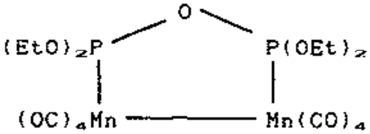


(242)

A new cyclic trioxatriphosphorinane (242) has been obtained as the hydrolysis product of 2,6-$Bu^t_2C_6H_3OPCl_2$ in the presence of two equivalents of triethylamine.[371] Related 4-substituted compounds have also been obtained and a crystal structure of the 4-methyl derivative shows the ring in a distorted boat conformation with non-equivalent phosphorus environments. The stability of the compounds to air and water is attributed to steric hindrance.

Methylenebis(phosphinic acid), $CH_2[PH(O)(OH)]_2$, an analogue of the useful diphosphite ligand, can be prepared following slow hydrolysis of $CH_2(PCl_2)_2$.[372] Like diphosphite, the ligand forms a diplatinum(II) complex, $K_4[Pt_2(pcp)_4].2H_2O$, containing four bridging P-bonded ligands; the Pt-Pt separation here is longer (298pm) than in the diphosphite analogue (292.8pm).[373] Prolonged reaction of $Mo(CO)_3[P(OMe)_3]_3$ with trifluoroacetic acid leads unexpectedly to the dimeric, $Mo_2[\mu\text{-}P(O)(OMe)_2]_2(CO)_4[P(OMe)_3]_2(CF_3COO)_2$.[374]

The complex mixture resulting from reaction between $(EtO)_2P.O.P(OEt)_2$ and $Mn_2(CO)_{10}$ contains compounds (243) and (244) while the corresponding system with $MnX(CO)_5$, for X = Br or I, can give products such as (245)-(248) depending on the



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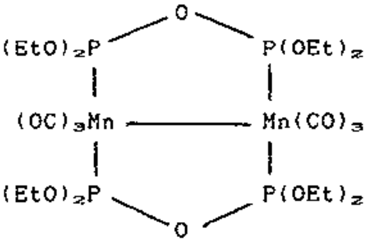

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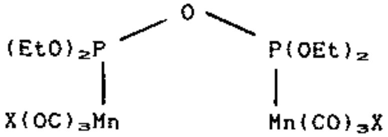

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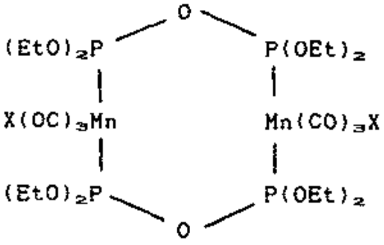

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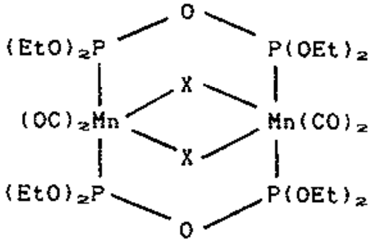

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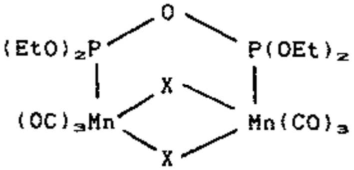
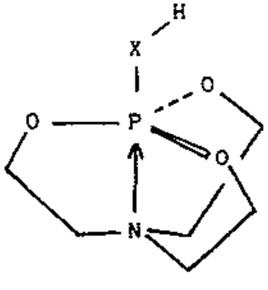


(248)

experimental conditions.[375] An X-ray structure is available for (248, X = Br).

Hypervalent mono- and dications, (249, X = O or S) and (250, X = O or S, R = H, Me or Et), based on the phosphetrane structure have



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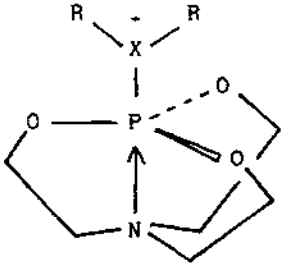
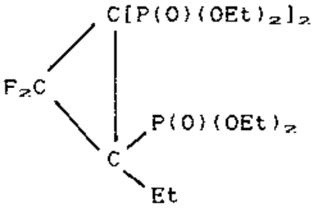


(250)

been obtained and investigated by detailed n.m.r. spectroscopy.[376] Their stability is related to the presence of three five-membered rings chelating the phosphorus atom and by the strong basicity of the apical chalcogen.

A full crystal structure has been determined for the hydrated double salt, $MnNa(H_2PO_3)_3.H_2O$.[377]

The +5 Oxidation State. Ab initio calculations are reported for the methyl esters, $PO(OMe)_3$, $HPO(OMe)_2$ and $H_2PO(OMe)$.[378] Detailed multinuclear n.m.r. spectroscopy on the phosphorylated cyclopropane (251) has shown, inter alia, that there is free rotation for one phosphoryl group but a barrier of 75 $kJmol^{-1}$ for the other two.[379]



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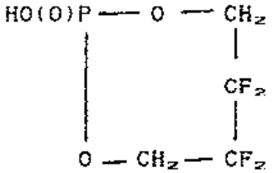
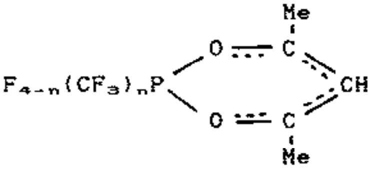


(252)

The synthesis is reported of a series of phosphonic, phosphinic,[380] and phosphoric acids,[381] by oxidation of appropriate phosphorus(III) precursors with N_2O_4. For example, with the iodides R_2PI and RPI_2, where R = CF_3, C_2F_5 or C_4F_9, the first step is conversion to the corresponding chloride with silver chloride in the dark followed by oxidation with N_2O_4, giving a mixture of $R_2P(O)Cl$ and the anhydride, $R_2P(O)OP(O)R_2$. Hydrolysis leads to the free acids, $R_2P(O)OH$ and $RP(O)(OH)_2$. Two new dibasic acid phosphates, $ROP(O)(OH)_2$ for R = $(CF_3)_2CH$ and $(CF_3)MeCH$, and the monobasic phosphates, $(RO)_2P(O)OH$ for R = $(CF_3)_2CH$, $(CF_3)MeCH$, $(CF_3)_2MeC$ and $(CF_3)Me_2C$ were also prepared [381] together with the tetrabasic bis(phosphates), $(HO)_2P(O)OCH_2(CF_2)_nCH_2OP(O)(OH)_2$ where n = 2-4 and the monobasic dioxaphosphepane oxide (252).[382]

Dimethylphosphinic acid and Me_3SnNEt_2 react to form $Me_2PO_2SnMe_3$ in which alternating Me_2PO_2 and Me_3Sn groups are arranged in a helical chain.[383] Similar Cl_2PO_2 and Me_3Sn groups alternate in the related $Cl_2PO_2SnMe_3$ structure but here the chain is almost planar. A number of new addition compounds between the bidentate ligands $Ph_2P(O)CH_2P(O)Ph_2(L)$, trans-$Ph_2P(O)CH{:}CHP(O)Ph_2(L^1)$ or $Ph_2As(O)CH_2CH_2As(O)Ph_2(L^2)$ and $Ph_2Sn(NO_3)_2$ or Ph_3SnNO_3 have been sythesised.[384] X-ray structures show pentagonal bipyramidal coordination about tin in $Ph_2Sn(NO_3)_2.L$ from two oxygens of the chelating ligand and three oxygens of two nitrate groups in the equatorial positions and phenyl groups in the apical sites. In $(Ph_3SnNO_3)_2L^2$, the ligand bridges between the tin atoms which show trigonal bipyramidal coordination.

The phosphorus(V) pentane-2,4-dionate complexes (253, n = 1-3) and (254), recently prepared, are characterised by high field ^{31}P n.m.r. shifts indicative of six-fold coordination.[385] This has been confirmed for (253, n = 2) by an X-ray structure which shows acac and two fluorine atoms in a plane; for (253, n = 3) the unique CF_3 group is perpendicular to the plane which now contains two CF_3 groups and the oxygens of the ligand.



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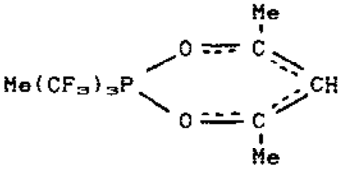
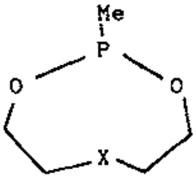
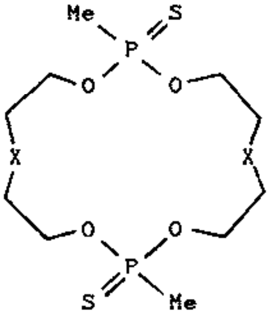


(254)

Although the trioxaphosphocanes (255, X = O) can spontaneously dimerise to 16-membered crown type products, which can be isolated as sulphides (256), specific synthetic routes to (256) have now



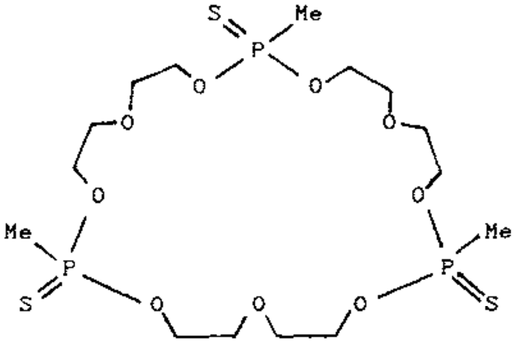
(255, X = O or NMe)



(256, X = O or NMe)

been devised.[386] An example is the reaction of (255, X = O) with $O(CH_2CH_2OH)_2$ giving $MeP[O(CH_2)_2O(CH_2)_2OH]_2$ which can be oxidised by sulphur. Subsequent treatment of the diol with $MePCl_2$ and sulphur leads to cyclisation. A 24-membered homologue of

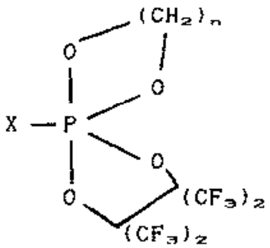
(256) is (257), which is produced when the diol above reacts with a molecule of (255, X = O) followed by treatment with MePCl$_2$ and sulphur.



(257)

Stable hydrophosphoranes (258, X = H, n = 2 or 3) can be obtained by treating cyclic chlorophosphites Cl$\overline{\text{P-O(CH}_2\text{)}_n\text{-O}}$ (n = 2 or 3) with an ammonium or substituted ammonium perfluoropinacolate.[387,388] Irradiation of (258, X = H, n = 2) in the presence of dimethyldisulphide gives (258, X = SMe, n = 2),[387] while with (258, X = H, n = 3) hexafluoroacetone inserts into the P-H bond to give a pentaoxaphosphorane (259).[388]

Hexafluoroacetone will also react with diphosphines R^{1}R^{2}PPR^{1}R^2, where R^1 = R^2 = Me or Et and R^1 = Me, R^2 = Bu^t to produce dioxaphospholanes (260), and tetraethyldiphosphine in addition gives a 1,3,4-dioxaphospholane (261).[389] With mercury(II) thiocyanate and hexafluoroacetone give an addition compound (262) which with



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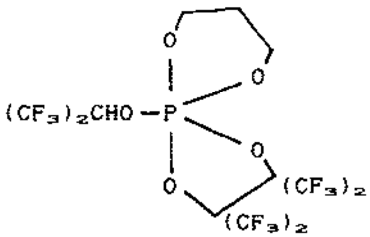

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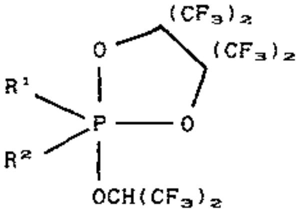

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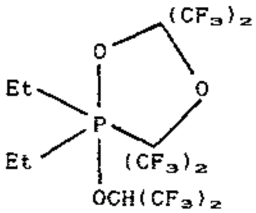

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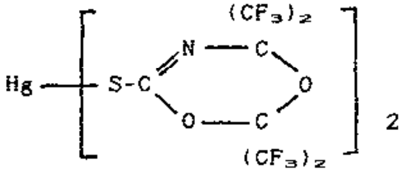

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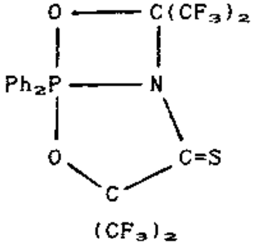

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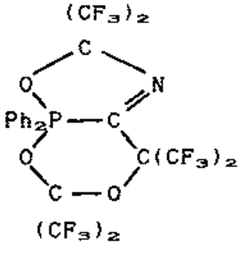

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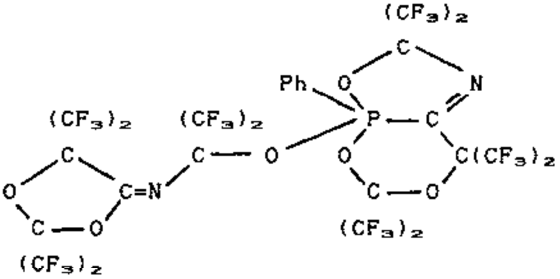
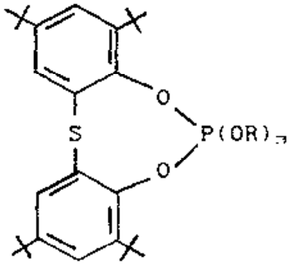


(265)

Ph$_2$PCl eliminates mercury(II) chloride yielding the five coordinate bicyclic (263).[390] Use of mercury(II) cyanide in place of the thiocyanate gives (264), and the same bicyclic phosphorus unit occurs in (265) obtained when PhP(CN)$_2$ reacts with hexafluoroacetone. X-ray structures are available for (263)-(265).

Two new phosphorus(V) pentaoxyphosphoranes (266, R = CH_2CF_3 or Et) have been synthesised from, initially, phosphorus(III) chloride and the diol (267) in ethanol; n.m.r. data show a significant barrier to pseudorotation in the trifluoroethanol compound.[392]



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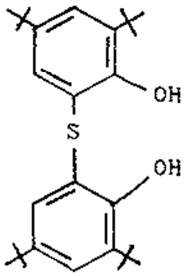

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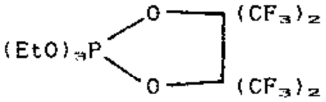


(268)

Hydrolysis of the pentaoxyphosphorane (268) gives a mixture of acyclic $(HO)_2P(O).OC(CF_3)_2.C(CF_3)_2OH$ and cyclic $HO(O)\overline{P\text{-}O\text{-}C(CF_3)_2.C(CF_3)_2.O}$.[392]

The tripod ligand $P[P(O)(OR)_2]_3$ (≡L) forms stable 2:1 complexes in liquid sulphur dioxide solution with $M(AsF_6)_2$, where M = Mn, Fe, Co or Ni, which are formulated as $[ML_2][AsF_6]_2$ and involve the metal in six fold coordination to the phosphoryl oxygens of the ligands.[393]

Oxidation of hypophosphate $[O_3P.PO_3]^{4-}$ by bromine in aqueous solution gives diphosphate $[O_3P.O.PO_3]^{4-}$ but using ^{18}O labelled water and ^{31}P n.m.r. spectroscopy it is possible to show that only one ^{18}O atom is incorporated into a non-bridging position.[394] The mechanism probably involves attack by a hypophosphate oxygen on ^{18}O-hypobromous acid to give the intermediate $(HO)_2P(O^-)\text{-}P(O^-)(:O)OBr$. Europium hypophosphate, $EuHP_2O_6.4H_2O$ is isostructural with the Nd, Er and Yb analogues and shows a P-P separation of 218.4pm.[395] Possible reasons for the variation in P-P distances with change in lanthanide element are discussed.

Further evidence supporting the formation of monomeric metaphosphate, $ArPOP_2$, comes from flash vacuum pyrolysis of 2-aryloxy-1,3,2-dioxaphospholanes.[396] Enantiomers of the thiophosphate anion $[^{16}O^{17}O^{18}OPS]^{3-}$ have been prepared by treating

[1-^{18}O]-dihydroxy-1,2-diphenylethane with thiophosphoryl chloride, followed by hydrolysis with ^{17}O-water.[397] The two forms can be distinguished by ^{31}P n.m.r. spectroscopy.

Two papers consider different aspects of m.a.s. ^{31}P n.m.r. spectroscopy. The first [398] for a series of condensed phosphates shows changes due to phosphorus coordination, counter ion, chain length, crystalline form, hydration state and inequivalence within the unit cell while the second [399] shows, that as with ^{29}Si spectra, there is a correlation between the isotropic chemical shift and P-O bond strength.

Crystals of $H_3PO_4.3H_2O.\frac{1}{2}$(18-crown-6) from an X-ray investigation contain hydrogen bonded H_3PO_4 dimers, which are linked by water molecules to the crown ether, each oxygen of which forms one hydrogen bond.[400] X-ray data for a series of hydrogen phosphates have been analysed showing increased distortion of the PO_4 tetrahedra with increase in the O-H...O hydrogen bond strength.[401] Structures for two further acid phosphates, $Me_4N[H_2PO_4].H_2O$[402] and $(cyclohexylNH_3)_2HPO_4$[403], have been determined by X-ray crystallography and hydrogen bonding in struvite, $MgNH_4PO_4.6H_2O$, has been probed by neutron diffraction.[404]

Aluminium orthophosphate formation in the Al_2O_3-P_2O_5-H_2O system has been reviewed.[405] Conditions for obtaining the previously unknown $Na_5AlF_2(PO_4)_2$ from either aqueous or solid state systems have been optimised;[406] the compound contains tetrahedral PO_4 and octahedral AlO_4F_2 units connected by common vertices to give a heteropolyanionic sheet structure. The structure of $Li_3In_2(PO_4)_3$ has been determined,[407] and in Tl_3PO_4 the thallium atoms are coordinated to oxygens from three different phosphate groups.[408] Two new mixed phosphates, $Na_3Bi(PO_4)_2$ and $Na_3Bi_5(PO_4)_6$, have been identified in the Na_3PO_4-$BiPO_4$ system.[409] A vanadium n.m.r. study of the interaction of vanadate with phosphate, diphosphate and arsenate points in all cases to the formation of mixed analogues of di- and triphosphates.[410]

A high pressure form of $Mn_3(PO_4)_2$, prepared at 2.5 GPa and 600°C, has been identified by X-ray powder diffraction.[411] An important feature in the structure of $Mn_7[PO_3(OH)]_4(PO_4)_2$ is the presence of three different manganese polyhedra, MnO_6, $MnO_4(OH)_2$ and MnO_5, which are interlinked by $PO_3(OH)$ and PO_4 tetrahedra in three dimensions.[412] The structure of $(H_3O)Fe_3(HPO_4)_2(H_2PO_4)_6$.-

$4H_2O$, obtained by long reaction between iron powder and 85% phosphoric acid at room temperature, consists of iron(III) phosphate layers alternating with water layers.[413] The phosphate layers contain FeO_6 octahedra sharing vertices with both $O_2P(OH)_2$ and $O_3P(OH)$ tetrahedra.

A triply bridging $O_3P(OH)$ group is found in $H_2Os_3(CO)_9(\mu_3\text{-}O_3POH)$, isolated from the reaction of $H_3Os_3(CO)_9(\mu_3\text{-}CH)$ with phosphoric acid saturated with P_4O_{10} in the presence of trifluoromethanesulphonic acid; the analogue containing a $\mu_3\text{-}O_3SO$ group has also been synthesised and its structure determined.[414]

Treatment of $[Co(NH_3)_4(PO_4)]$ with $[Cr(H_2O)_6]^{2+}$ gives $[Cr(H_2O)_5(H_2PO_4)]^{2+}$ and the kinetics of formation of this ion from $[Cr(H_2O)_6]^{2+}$ and $H_2PO_4^-$ have been investigated.[415]

Water molecules in the quadruply bridged platinum(II) complex $[Pt_2(\mu\text{-}HPO_4)_4(H_2O)_2]^{2-}$ can be replaed by halide, amine, thioether and thiolate ligands and a structure is available for the bis(tetrahydrothiophene) complex.[416] The structure has also been obtained for the recently prepared doubly deprotonated guanidine-diplatinum tetraphosphate complex, $Na_{10}[Pt_2(\mu\text{-}PO_4)_4\text{-}(C_5H_3N_5O_2]$.[417] Both ZnO_6 and ZnO_5 units linked by $PO_3(OH)$ tetrahedra are found in solid $Zn(HPO_4).H_2O$.[418]

I.r. spectra of $\alpha\text{-}Ti(HPO_4)_2.H_2O$, the anhydrous compound and their deuterated derivatives recorded at room temperature and -180°C have been interpreted as showing two structurally non-equivalent HPO_4^{2-} groups in the unit cell, which form different length hydrogen bonds to the water of crystallisation.[419] $H^+\text{-}Ca^{2+}$ exchange on γ-titanium phosphate leads to $TiH_{1.25}Ca_{0.37}\text{-}(PO_4)_{2.3}.5H_2O$, but on raising the temperature, water is lost decreasing the basal spacing from 1310 to 1020pm in the anhydrous material.[420] Half exchanged copper phases, $TiHCu_{0.5}(PO_4)_2$ have been detected with 2.5, 1 and zero molecules of water of crystallisation in similar $H^+\text{-}Cu^{2+}$ exchanges on the same material.[421]

Histidine intercalation into γ-zirconium phosphate appears to proceed via partial replacement of the interlayer water to give $Zr(HPO_4)_2(Hist)_{0.2}.1.9H_2O$ followed by successive conversion to $Zr(HPO_4)_2(Hist)_{0.2}.0.8H_2O$ and $Zr(HPO_4)_2(Hist)_{0.9}.3H_2O$, where the interlayer spacing is 2290pm and great molecules are intercalated as a bilayer.[422] With lysine and arginine on the other hand low uptake leads to one or two monolayered phases but there is disorder at higher loadings. M.a.s. ^{31}P n.m.r. measurements on γ-$Zr(HPO_4)_2.2H_2O$ show two phosphate environments, only one of which undergoes exchange with phosphate and phosphonate esters.[423]

Diffusion of $[Cu(phen)_2]^{2+}$ into layers of the diethanol intercalate of α-zirconium phosphate leads at maximum uptake to $ZrH_{1.6}[Cu(phen)_2]_{0.20}(PO_4)_2.3H_2O$, while 1,10-phenanthroline itself can be intercalated to give α-$Zr(HPO_4)_2(phen)_{0.5}.2H_2O$, a pure well ordered stage 1 phase with interlayer separation of 1358pm.[424]

Vanadium(III) diphosphate, $V_4(P_2O_7)_3$ obtained by heating a mixture of V_2O_5, H_3PO_3 and H_3PO_4 contains face sharing octahedral V_2O_9 units and three types of staggered conformation diphosphate groups, each with C_s symmetry.[425] The P-O-P angles are ca. 170°. Three sparingly soluble iron(II) diphosphates, $K_2Fe(OH)P_2O_7.2.5H_2O$, $KFeP_2O_7.4H_2O$ and $Fe_3(P_2O_7)_2(OH).12H_2O$, have been prepared from aqueous solutions of iron(II) nitrate and $K_4P_2O_7$,[426] and the protons in $FeHP_2O_7$ can be replaced by an alkali metal on heating with MNO_3 where M = Na, K, Rb or Cs.[427] The double diphosphate, $LiInP_2O_7$, contains InO_6 octahedral units and P_2O_7 groups in which the P-O-P angle is 132.7°.[428]

An unusual product, $CaNb_2O(P_4O_{13})(P_2O_7)$, obtained when a $CaCO_3$-Nb_2O_7-H_3PO_4 mixture was heated to 500°C contains two different phosphate ions, i.e. P_2O_7 units with mirror symmetry and the tetrapolyphosphate $P_4O_{13}^{6-}$ ion with two fold symmetry.[429]

Discrete $[MnP_3O_{10}.3H_2O]^{3-}$ units, in which the triphosphate group is α,β,γ-coordinated, are held together by Na-O interactions and hydrogen bonds in the structure of $MnNa_3P_3O_{10}.12H_2O$.[430] An interesting point here is the formation of four hydrogen bonds (O...O separations 273.8 to 300.3pm) at an oxygen atom of a terminal phosphorus. A crystalline mixed triphosphate, $NH_4Mn_2P_3O_{10}.5H_2O$ has been isolated from aqueous solutions of ammonium triphosphate and manganese(II) chloride.[431] High resoluti solid state ^{31}P n.m.r. data have been collected for the I and II modifications of $Na_5P_3O_{10}$ and for $Na_3P_3O_{10}.6H_2O$.[432]

Full crystal structures have been determined for the following trimetaphosphates: $BaNaP_3O_9.3H_2O$,[433] $Co(NH_4)_4(P_3O_9)_2.4H_2O$,[434] $Na_4Ni(P_3O_9)_2.6H_2O$,[435] $(NH_4)_2Na_2Hg(P_3O_9)_2$,[436] and $HgK(P_3O_9)$.[437] The cobalt ammine derivative contains the octahedral $[Co(P_3O_9)_2(H_2O)_4]^{4-}$ anion with trans arranged P_3O_9

units.

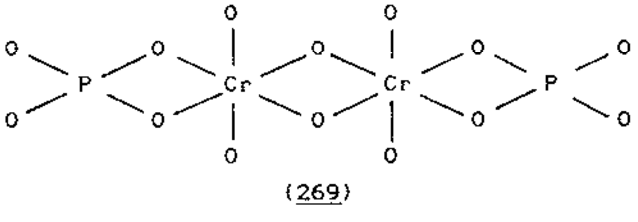
The tetrapolyphosphate, $[Co(NH_3)_6]_2P_4O_{13}.5H_2O$, contains the isolated $[P_4O_{13}]^{6-}$ ion with P-O-P bridge distance varying between 155.7 and 165.2pm with some alternation of distances along the chain.[438] In $Pb_3P_4O_{13}$, all phosphorus atoms in the anion are crystallographically independent.[439]

Structures of the cyclic tetrametaphosphate investigated recently include $Li_4P_4O_{12}.5H_2O$ (containing two crystallographically independent rings with two-fold symmetry),[440] $Cs_4P_4O_{12}.4H_2O$ [441] and $Sr_2(P_4O_{12}).6H_2O$ (containing centrosymmetric anions at the origin, linked by $SrO_4(H_2O)_3$ polyhedra and hydrogen bonds).[442] $Pb_2Cs_3(P_4O_{12})(PO_3)_3$, isolated from a solid state reaction between Cs_2CO_3, $PbCO_3$ and H_3PO_4 at 400°C, is interesting as this is the first compound containing both cyclic P_4O_{12} and infinite chain anions.[443]

In a study of lithium phosphate dehydration, seeding LiH_2PO_4 with $Li_6P_6O_{18}$ led to pure hexaphosphate.[444]

The repeat unit in the polyphosphate chain in $Pb_2Li(PO_3)_5$ is five, the first time that this has been observed,[445] while the period in $LiCs(PO_3)_2$ is eight [446] and four in $BaCs_4(PO_3)_6$.[447]

Single crystal data for $BaNb_2P_2O_{11}$ show a structure in which PO_4 tetrahedra are grouped about barium in palmierite-type layers together with NbO_6 octahedra and a refinement of the $NbPO_5$ structure shows a three dimensional framework of linked chains of NbO_6 octahedra and PO_4 tetrahedra.[448] Dark green crystals of α-$CrPO_4$, obtained by chemical transport in chlorine, contain chains of edge sharing CrO_6 octahedra with PO_4 tetrahedra at the ends (<u>269</u>), and large channels extending through the structure.[449]



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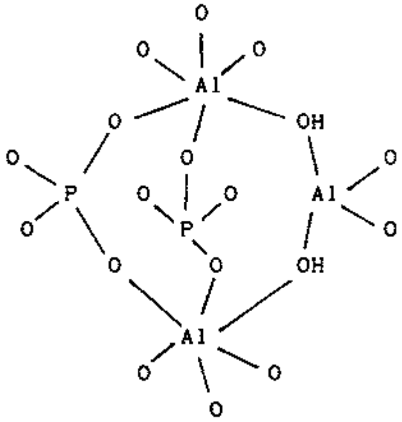
The new molybdenum phosphates, $Cs_3Mo_5P_6O_{25}$, obtained from a 3:9:3:6 mixture of Cs_2MoO_4, MoO_2, Mo and P_2O_5 at 900°C, contains a tetrahedral Mo_4 cluster each face of which is capped by a μ_3-

oxygen.[450] The three crystallographically equivalent molybdenum atoms forming the base of the tetrahedron each carry a chelating P_2O_7 ligand while the three slant edges are bridged by P_2O_7 groups.

Two open framework transition metal phosphates, $Fe_5P_4O_{20}H_{10}$ and $NaFe_3P_3O_{12}$, have been prepared hydrothermally by heating a mixture of H_3PO_4, R_4NOH (R = Pr or Bu), $Fe(CO)_5$ and acetone.[451] The former is a pure iron analogue of the mineral hurealite, the latter of alluaudite arising from a small mount of sodium impurity in the original mixture. Full structural details are available.

Structures have been determined for a number of new hydrated aluminophosphates, including: $AlPO_4.1.5H_2O$, based on a framework of PO_4 tetrahedra interposed between AlO_4 tetrahedra and $AlO_4(H_2O)_2$ octahedra,[452] $7AlPO_4.2Pr^iNH_2.2H_2O$,[453] and $Al_{18}P_{18}O_{72}.4$(piperidine.H_2O).[454] The second compound was isolated from a preparation giving mainly $AlPO_4$-14 using i-propylamine as the template. Both tetrahedral and octahedral aluminium units are present and the best representation is $Al_7P_7O_{28}(OH)_2.2Pr^iNH_2$. The structure is built from two octahedral aluminium units connected as shown in (270) by two PO_4 and one AlO_4 unit to give a five atom cluster consisting of three eight-membered rings. Two of these units are linked into cages by two PO_4 tetrahedra and zig-zag chains formed by further cross linking. The amine is encapsulated as $[Pr^iNH_3]^+OH^-$ connecting two aluminium atoms in the framework. The final compound is a precursor of $AlPO_4$-17, the analogue of the



(270)

zeolite erionite, and is obtained from hydrated alumina, phosphoric acid and piperidine. The $AlPO_4$-17 structure, shown in Figure 2, consists a tetrahedral network of alternating aluminium and phosphorus with bridging between two aluminium atoms by an extra framework oxygen. In these systems it is not always easy to remove the templating compound by calcination and carbonaceous material can block active sites. Treating with methanolic hydrogen chloride at 420K for 16 hours in a sealed system has recently been found to be effective and causes no adverse effects.[455]

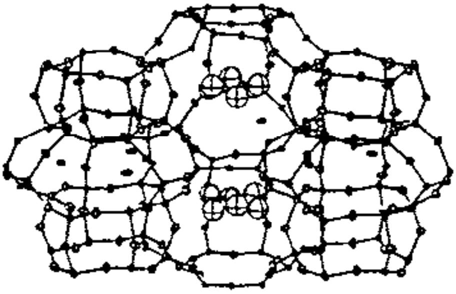


Figure 2. The $AlPO_4$-17 structure (reproduced by permission from Acta Crystallogr., C42(1986)283).

Structures have been determined for two gallium analogues of the aluminophosphates discussed above. That for $GaPO_4$-21, obtained as prisms using i-propylamine as template, is similar to the $AlPO_4$-21 structure with the framework formed by crosslinking between corrugated sheets of ribbons of edge sharing three and five-membered rings containing gallium in five-fold coordination.[456] The template molecules are disordered over two sites. The $GaPO_4$-14 structure, $Ga_4(PO_4)_4OH.Pr^iNH_2.1.09H_2O$, consists of crosslinking between units of five- and six-fold coordinated gallium polyhedra by gallium and phosphorus tetrahedra to give a framework enclosing the protonated amine.[457]

Crystalline samples of $(NH_4)_2(PO_3F).H_2O$ and K_2PO_3F can be obtained by a new synthetic route based on reaction of concentrated aqueous solutions of either $(NH_4)HF_2$ or KHF_2 with phosphoric acid when the products can be precipitated by ethanol.[458] Crystals of the mixed fluoride-fluorophosphate, $K_3F(PO_3F)$, which are isostructural with $K_3F(SO_4)$ have been obtained by melting together the components, KF and K_2PO_3F.[459] The structure of $Co(PO_3F).3H_2O$, obtained from Ag_2PO_3F and cobalt(II) chloride, contains tetrahedral PO_3F and octahedral CoO_6 units held together by hydrogen bonding,[560] and insoluble $Cu_2K(PO_3F)(OH).H_2O$ has been isolated from aqueous solutions of KPO_3F and copper(II) salts for thermal decomposition and X-ray studies.[461] X-ray powder data for mixed phosphate-vanadate fluoroapatites, $M_{10}(PO_4)_{6-x}(VO_4)_xF_2$ for M = Ca, Sr or Ba and x = 1-3, have been analysed to show an inrease in unit cell dimensions with increase in vanadium content.[462]

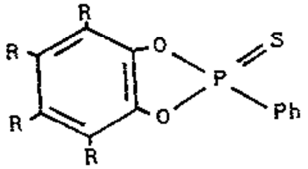
POF_3 is eliminated when difluorophosphates, $M(PO_2F_2)_2$, are heated giving monofluorophosphates, $M_2(PO_3F)$; similarly it is possible to convert HPO_2F_2 to H_2PO_3F in 50% yield.[463]

Manganese and zinc amidophosphates, $M(HPO_3NH_2)_2$, result from the potassium salt and, respectively, $MnCl_2$ and zinc acetate,[464] and a new method for preparing salts of the imidodiphosphate anion $[O_3P.NH.PO_3]^{4-}$ has been reported.[465] The process starts with $POCl_3$ and proceeds via $(PhO)_2P(O)Cl$, $(PhO)_2P(O)NH_2$, $(PhO)_2P(O)N{:}PCl_3$, $(PhO)_2P(O)NHP(O)(OH)_2$. Detailed i.r. and Raman data were obtained and a normal coordinate analysis carried out.

High temperature reactions between $(PNO)_x$ and $Na_5P_3O_{10}$ in the presence of a range of metal oxides gives nitridophosphates, $M(I)_3M(III)P_3O_9N$, where M(I) = Na or K and M(III) = Al, Ga, Cr, Fe or Mn.[466,467] A magnesium analogue, $Na_2Mg_2P_3O_9N$, has also been prepared.

5.2.7 Bonds to Sulphur, Selenium or Tellurium

Phosphorus(III)-Sulphur Compounds. Thermally produced PhP:S has been trapped with o-quinones as the cycloaddition products (271),[468] and further data are available on the stabilisation of



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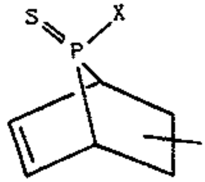

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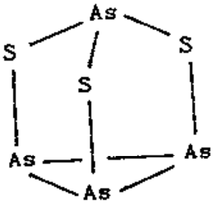


(273)

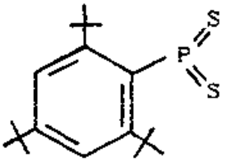
of such two coordinate thioxophosphines, RP:S where R = Me, Et, Ph, 4-$MeOC_6H_4$, etc., in molybdenum and manganese carbonyl complexes.[469] Among the reactions investigated was the dehalogenation of $RPSCl_2$ with $Na[CpMo(CO)_3]$. Evidence has also been produced from trapping experiments for the previously unknown derivatives ROP:S and R_2NP:S generated by retro-cycloadditions from compounds such as (272, X = OR or NR_2).[470]

Structure and reactivity for P_4S_3, P_4S_4, P_4S_5 and P_4S_6 have been investigated using the rule of topological charge stabilisation, i.e. that "nature prefers to locate heteroatoms at those positions in a molecular structure where connectivity and electron filling level tend to accumulate or deplete electron density in an isoelectronic, isostructural, homoatomic system."[471]

$P_2Al_2S_3$, isomorphous with β-dimorphite, As_4S_3 (273), has been obtained by vacuum sublimation of a 2:2:3 melt of phosphorus, arsenic and sulphur.[472] Although phosphorus and arsenic atoms are disordered between apical and basal positions, phosphorus shows a preference for the apical position, with basal occupancies of 43, 35 and 35% phosphorus. Analysis of the P_4S_3-P_4Se_3-As_4S_3-As_4Se_3 system by thermal methods, mass spectrometry, and X-ray diffraction indicates formation of all compounds in the series $P_nAs_{4-n}S_mSe_{3-m}$, where n = 0-4 and m = 0-3.[473] The ranges of existence are influenced by annealing temperature and in the P_4Se_3-As_4Se_3-As_4S_3 region decomposition gives A_4B_4 species and an amorphous phase.

Primary aliphatic amines, RNH_2 for R = Et or Pr, react with $P(SEt)_3$ in the presence of carbon tetrachloride to give $(EtS)_2PCCl_3$, EtSNHR and RNH_3Cl.[474] No reaction occurs with $(RO)_2P(O)NH_2$ while with $(EtO)_2P(O)H$ and sodium azide, $P(SEt)_3$ and CCl_4 give the monophosphazene, $(EtO)_2P(O).N:P(SEt)_2$.

Phosphorus(V)-Sulphur Compounds. The properties of tri(t-butyl)-phenyldithiophosphorane (274) including its conversion at 110°C to the phosphaindane (275), desulphurisation to (276), and reactivity to MeOH, HCl, etc., have been reviewed.[475] The monomeric trithiometaphosphate anion, PS_3^-, stabilised as a tetraphenylarsonium salt is produced from the reaction between P_4S_{10}, KCN and H_2S in acetonitrile solution.[476] Successful refinement of the X-ray data was ruled out by thermal motion problems but a pyramidal



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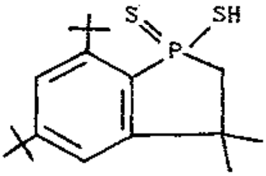

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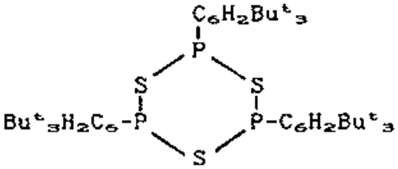

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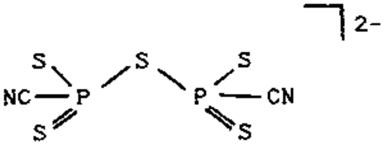
structure is suggested. SCF-MO calculations on the other hand predict a planar structure in the gas phase, but if the molecule is n rigid, a solid state pyramidal structure cannot be ruled out. The initial reaction also yields the known cyanodiphosphate, $(NCPS_2.S.PS_2CN)^{2-}$.

Coordination of $Me_2PH{:}S$ to zinc and cadmium halides takes place via the sulphur atom according to recent i.r. and Raman spectroscopy.[477]

P_4S_{10} continues to be a versatile reagent, giving on treatment with sodium azide in acetonitrile salts of the diazidodithiophosphate anion, $[PS_2(N_3)_2]^-$.[478] The anion has distorted tetrahedral geometry with a small (93.8°) angle at phosphorus between the two azide nitrogens. The related reactions of P_4S_{10} with



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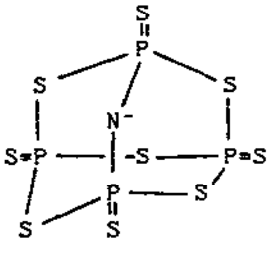

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sodium cyanide, on the other hand, gives salts of the sulphur bridged anion (<u>277</u>), which has bridging and terminal P-S distances of 212.1 and 184.5pm respectively and a 122.6° angle at the bridging sulphur.

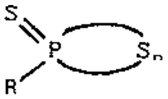
Benzonitrile and P_4S_{10} give the diphenyldithiazolium salt of $(P_4NS_9)^-$,[479] and the same anion, as the tetrapropylammonium salt, results when P_4S_{10} reacts with the diazide mentioned above.[480] Structures for both compounds show the anion (<u>278</u>) based on the P_4S_{10} structure in which one P-S-P link is replaced by P-N-P. P-N distances are 159.6 and 162.0pm and in comparison with P-S-P angles of ca. 106°, the P-N-P angle is opened to 130.0°.

Methanolysis of P_4S_{10} in carbon disulphide at 0° to 35°C gives $(MeO)_2PS_2H$ as the sole product; the reaction, which is first order in P_4S_{10} and second order in methanol, is controlled kinetically by the initial attack of the alcohol on P_4S_{10}.[481]

Sulphur rich phosphorus sulphides, P_4S_{10+m}, react with metal fluorides in either acetonitrile or 1,2-dimethyoxyethane to produce sulphanebis(fluorodithiophosphate) mixtures $(S_2PF.S_n.FPS_2)^{2-}$ for n = 1-8.[482]

Treatment of $[CpFe(CO)_2(THF)]^+$ with the Group 5 sulphides or selenides, R_3MX for M = P, As or Sb, leads to $[CpFe(CO)_2(R_3MX)]^+$ in which coordination is via the chalcogen atom.[483]

Silylesters, $RP(S)(SSiMe_3)_2$ where R = Me, Bu^t or Ph, can be synthesised in high yield from $RP(SiMe_3)_2$ and elemental sulphur in toluene.[484] The related stannyl esters can be prepared similarly but they are more readily obtained by treating silyl derivatives with Me_3SnCl. Low temperature hydrolysis of the silyl esters yields free trithiophosphonic acids, $RP(S)(SH)_2$ for R = Me or Bu^t, isolated as white solids at -30°C, and on reaction with chlorosulphanes S_nCl_2, n = 3-5, both the silyl and stannyl esters undergo ring closure to give (<u>279</u>). These compounds are



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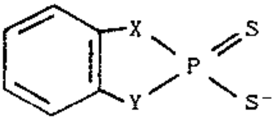

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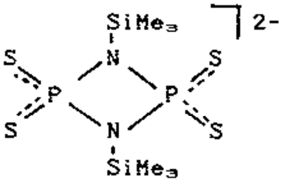

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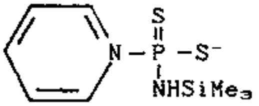

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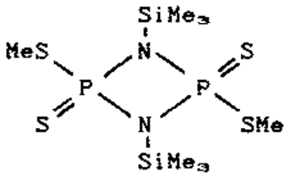


(283)

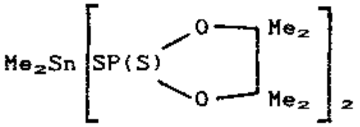
stable in the solid state but disproportionate and oligomerise in solution.[485]

Recent n.m.r. results have been interpreted as showing that in phosphorothioates the sulphur atom largely carries the negative charge and is singly bonded to phosphorus.[486]

Cyclic dithiophosphates (280, X,Y = O, S, NH, CH_2O or (S)CNH) are obtained when bifunctional reagents, e.g. $C_6H_4(XH)(YH)$, react with the betaine, $pyPS_2Cl$, in the presence of a base.[487] Hexamethyl disilazane also reacts with the betaine to give the diazadiphosphetidine salt (281), probably via the monomer (282); on treatment with methyl iodide (281) is converted into (283).[488]

The following section concerns dithio-phosphates and -phosphinates, and main group compounds in order of their periodic groups are treated before transition metal derivatives.

Organo-germanium derivatives $R_{4-n}Ge[S_2P(OR^1)_2]_n$, where n = 1-3, R = Me or Ph and R^1 = Me or Et, have monodentate dithiophosphate groups according to i.r. and n.m.r. spectroscopy; this has been confirmed by a partial X-ray structure for $PhGe[SP(S)(OMe)_2]_3$.[489] The dimethyl tin complex (284) on the other hand shows aniso-



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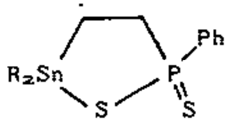


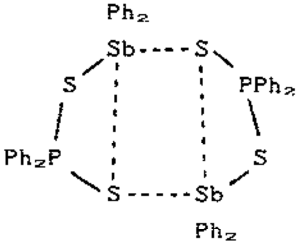
(285)

bidentate character with P-S and Sn-S distances of 193.2/203.1 and 313.0/249.5pm respectively and very distorted octahedral coordination about tin.[490] The bidentate character of the ligand is reduced even further in $Ph_3Sn[\overline{SP(S)OCMe_2CMe_2O}]$ where Sn-S distances are 243.6 and 341.1pm and P-S distances 203.9 and 190.3pm.[491] Cyclic dithiophosphinates such as (285, R = Me or

Bu^t) can be produced by oxidising $R_2SnH(CH_2)_2PHPh$ with sulphur.[492]

Structures have been reported for both $Sb(S_2PPh_2)_3$ and $Bi(S_2PPh_2)_3$.[493] The former consists of isolated molecules in which the antimony atom is in distorted pentagonal pyramidal coordination by three anisobidentate ligands. The basal plane thus contains two short (mean 259.5pm) and three longer (292.3-318.7pm) Sb-S distances. Coordination about bismuth is very similar except that there is effective dimerisation through short intermolecular Bi...S contacts (317.3 and 330.1pm). As this is trans to the apical atom it is evidence against stereochemical activity of the lone pair in these systems.

Structures are also available for $Ph_2Sb(S_2PPh_2)$, $Ph_2Sb(SOPPh_2)$ and $Ph_2Sb(O_2PPh_2)$[494,495] The dithiophosphinate was prepared from Ph_2SbOAc with either $Ph_2P(S)SH$ or the sodium salt and, as for the corresponding dithioarsinate, has a centrosymmetric dimeric structure (286) with one short and two longer Sb-S contacts giving an eight-membered $Sb_2S_4P_2$ ring. The thiophosphinate and phosphinate structures are completely different from that of the dithiophosphinate, with bridging ligands leading to infinite chains. Antimony atoms are in pseudo-trigonal bipyramidal coordination to two equatorial phenyl groups with axial positions occupied either by two oxygen atoms or by one oxygen and one sulphur atom.



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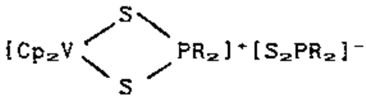


(287)

In the vanadium complexes (287, R = Et, OEt or OPr^i) obtained by treating Cp_2V with the appropriate disulphide $[R_2P(S)S]_2$ in THF solution, the dithiophosphorus group is coordinated in the cation and also serves as the counter anion.[496] Stable crystals of $Fe[S_2P(OPr^i)_2]_3$ have been obtained for the first time by treating either iron metal or Fe_2O_3 with the free acid in hexane solution.[497] The molecule with overall C_2 symmetry and iron in distorted octahedral coordination shows unique Fe-S distances of 246.1, 249.2 and 247.2pm. The ligand in $CpFe(CO)_2[S_2P(OPr^i)_2]$ is unidentate (Fe-S 232.2pm; P-S 194.4 and 202.6pm).[498]

The molybdenum cluster compound, $Mo_3S_4(S_2PEt_2)_4$, has close to C_{3v} symmetry with each metal carrying an almost symmetrically chelating dithiophosphinate ligand.[499] The fourth ligand bridges between a pair of molybdenums reducing the symmetry to approximately Cs.

The Rh(I) dithiophosphates, $Rh(COD)[S_2P(OR)_2]$ where R = Et, Pr or Pr^i and R/R = Me_2CCMe_2, isolated from reactions with $[Rh(COD)Cl]_2$ are monomeric from ^{31}P n.m.r. data.[500]

N.m.r. measurements on solutions of $Zn[S_2P(OR)_2]_2$, where R = Et or Pr^i, in $CDCl_3$ or toluene point to the presence of dimers, most probably involving two bridging dithiophosphate groups between zinc centres, while in ethanol or THF solutions, conductance data point to ionisation of a ligand with coordination of a solvent molecule.[501] The compounds form 1:1 addition compounds with a range of nitrogen donors, including pyridine, ethylenediamine, N,N'-diethylenediamine, terpyridine, 1,11-diamino-3,6,9-triazaundecane [502], N,N'-dimethyl and N-tetramethylethylenediamine, and 2,9-dimethylphenanthroline.[503] X-ray structures for the pyridine adduct of the i-propyl compound show zinc in five fold coordination with one symmetrical and one strongly asymmetrically chelating dithiophosphate group,[502,503] while for the en adduct, the zinc is coordinated to two en nitrogen atoms and two sulphurs from unidentate thiophosphate groups.[503] In the bipy complex, zinc coordination is irregular to the nitrogens and sulphurs from one unidentate and one anisobidentate phosphate group.[502] The terpyridine compound contains only unidentate thiophosphate groups but all three nitrogen donors of the ligand are in bonding distance giving again irregular five fold coordination at zinc. The five nitrogen donor, 1,11-diamino-3,6,9-triazaundecane, on the other hand, gives an ionic compound with a chelated zinc cation and two ionic dithiophosphate groups. Two other ionic compounds $[ZnL_3][S_2P(OR)_2]_2$ where L = en or NN'-Me_2en have also been isolated.[503]

Zinc dithiophosphates are hydrolysed by atmospheric moisture, a process promoted by amines such as di- and triethylamine, to give the tetrazinc products, $Zn_4O[S_2P(OR)_2]_6$ and small amounts of $Zn_4S[S_2P(OR)_2]_6$.[504] The latter contains a Zn_4S tetrahedral core with almost symmetrical dithiophosphate groups bridging between pairs of zinc atoms. Under anhydrous conditions, the amines gave $Zn[S_2P(OEt)_2]_2.2.75Et_2NH$ and $Zn[S_2P(OPr^i)_2]_2.nEt_3N$, where n = 1 or 2.75. EXAFS data for the basic $Zn_4O[S_2P(OBu)_2]_6$ salt point to a tetrahedral structure analogous to that for the thio analogue above.[505]

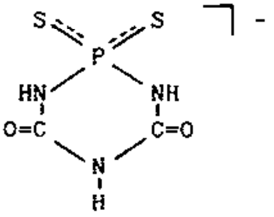
The $Cd(S_2PEt_2)_2$ structure contains centrosymmetric dimers with one chelating and one bridging ligand giving a distorted chair type eight membered $Cd_2P_2S_4$ ring.[506] The exocyclic ligand is disordered, as had been found previously for a related zinc compound.[507]

There is dodecahedral coordination about lanthanum in $La[S_2P(OEt)_2]_3[(PhCH_2)_2SO]_2$ from three almost symmetrically chelating phosphorus groups and oxygens of the dibenzylsulphoxide ligands.[508] This and the neodynium complex represent one type of behaviour by lanthanoids, the second type is shown by the ionic europium compound formulated from X-ray diffraction as $\{Eu[S_2P(OPr^i)_2]_2(DMSO)_3\}\{Eu[S_2P(OPr^i)_2]_4\}$.[509] Dodecahedral coordination is maintained for europium in the anion but the metal in the cation shows seven fold, pentagonal bipyramidal coordination.

A compound $Ti_4P_8S_{29}$ obtained from the elements at 400°C contains the previously unknown $P_2S_7^{2-}$ anion, which is structurally related to the $P_2S_6^{2-}$ structure (two PS_4 tetrahedra sharing a common edge) by replacement of a bridging sulphur by an S_2 unit.[510] From an X-ray structure the compound is formulated as $Ti_4(PS_4)_4(P_2S_6)(P_2S_7)$.

Reactions between metal halides and $Li[Et_2P(S)NR]$, R = Me, Et, Pr^i, Bu^t, Hex^c or Ph, lead to readily hydrolysable aminophosphinates, $M[Et_2P(S)NR]_n$ where n = 2 for M = Ni[511], Co[512] and Zn, and n = 3 for M = Ti, V or Cr, containing four membered chelate rings. Ligand field parameters for $Et_2P(S)NR^-$ are similar to those for $R_2PS_2^-$.

Biuretodithiophosphate (288) can be converted successfully to the monothiophosphate (289) and the phosphate (290).[513]



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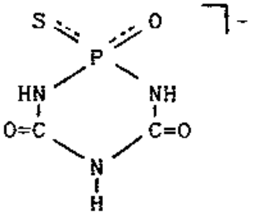

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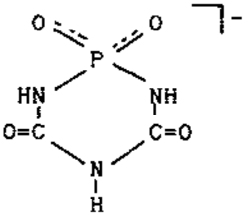

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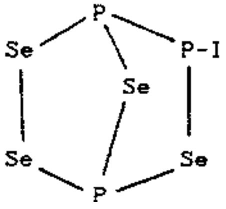
Phosphorus-Selenium Compounds. Raman and resonance Raman spectra are now available for P_4Se_3.[514] The major product of the I_2-P_4Se_3 reaction at 463K is α-$P_4Se_3I_2$ but a new selenoiodide P_3Se_4I, whose structure (291) is related to that of α-$P_4Se_3I_2$ (292) is also formed.[515]



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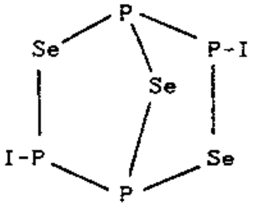


(292)

Phosphorus-Tellurium Compounds. New compounds in this category are p-$MeC_6H_4TePR_2$, where R = Pr^i or Bu^t, obtained from mixtures of diphosphines R_4P_2 and di-p-tolylditelluride.[516] The products are yellow, can be purified by vacuum distillation and characterised by the usual spectroscopic methods.

The P-Te separation in Bu^t_3PTe is 236.8pm, equivalent to a bond order of 1.5,[517] and this compound and its methyl, i-propyl, butyl and dimethylamino analogues can be converted by methyl iodide in benzene to tellurophosphonium salts, $(R_3PTeMe)^+I^-$.[518]

5.3 ARSENIC

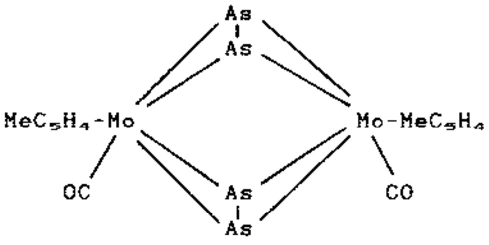
5.3.1 Polyarsines and Arsenides

The reaction in equation (46) provides a convenient method for preparing pure samples of polyarsines; on account of its volatility

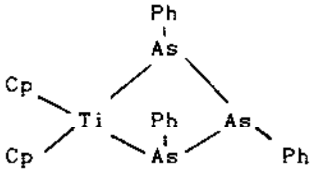
$$n(MeAs)_5 + 5nRAsH_2 \rightarrow 5(RAs)_n + 5nMeAsH_2 \qquad ...(46)$$

R = Et or Pr, n = 5
R = Ph or 4-MeC_6H_4, n = 6

separation of methylarsine is very easy and is, indeed, necessary otherwise the product is a mixture of reactants, polyarsine and intermediate oligomers.[519] An X-ray structure of $[Mo(CO)_4(PhAs)_6]$, first prepared in 1967 shows the polyarsine behaving as a 1,4-bidentate group with the ring in a twist boat conformation.[520] A complex containing two μ_2-η^2-As_2 ligands (<u>293</u>), with short As-As separations (227.2, 230.2pm), has been obtained by thermolysis of a mixture of $(MeAs)_5$ and $[MeC_5H_4Mo(CO)_3]_2$,[521] and related compounds, formulated as



(<u>293</u>)



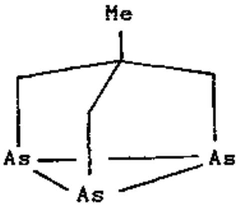
(<u>294</u>)

$Cp^*Mo(CO)_2(\eta^3$-$As_3)$, $Cp^*Mo_2(CO)_4(\mu,\eta^2$-$As_2)$ and cis-$[Cp^*Mo(CO)(\mu,\eta^2$-$As_2)]_2$, result from $[Cp^*Mo(CO)_3]_2$ on long heating with arsenic in xylene at 140°C.[522] The third compound is probably isostructural with both (<u>293</u>) and the phosphorus analogue $[Cp^*Mo(CO)(P_2)]_2$ whose complex with two $Cr(CO)_5$ groups has been structurally investigated.

In the presence of dissolved oxygen, solutions of $Mo(CO)_6$ and $(MeAs)_5$ in toluene at 150°C give crystals of a complex $[Mo(CO)_3]_2(MeAsO)_6$, containing a stabilised cyclo-hexa-arsoxane, and $[Mo(CO)_3]_2(AsMe)_{10}$ as a byproduct.[523] The twelve membered As_6O_6 ring takes the form of a flattened cubo-octahedron with a plane of six oxygens sandwiched between two planes each containing three arsenic atoms. These then coordinate in a facial arrangement to the molybdenum atoms. Treatment of $(PhAs)_6$ with

Cp_2TiCl_2 in the presence of magnesium metal gives good yields of the moderately air stable complex, $Cp_2Ti(AsPh)_3$, (294) which contains normal As-As bond distances but the As-As-As angle (109.5°) is the largest yet known.[524] The related methyl substituted compound results if $(MeAs)_5$ is the starting material.

Cleavage of one As-As bond is promoted on treatment of (295) with one mol of either PCl_5, Br_2, or I_2 to give the dihalides (296), but with two mols of the reagents yields of



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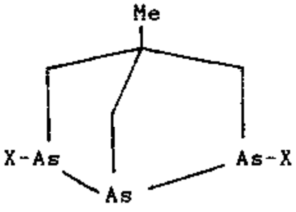

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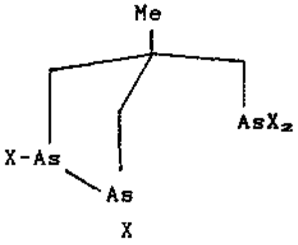


(297)

$MeC(CH_2AsX_2)_3$ are poor.[525] ^{1}H n.m.r. spectra however suggest that these products are formed via the tetrahalides (297).

The structures of two new Zintl phases $As_{10}Te_3{}^{2-}$ and $As_{11}Te^{3-}$ are shown in Figures 3 and 4. The first consists of six edge sharing five-membered rings, related structurally to $P_{11}{}^{3-}$, and is obtained when As_2Te_3 reacts with potassium in ethylenediamine.[526] Addition of Ph_4PBr then gave the salt used for the structure determination. The second, again prepared in ethylenediamine solution, resulted from reaction of $K_{1.6}As_{1.6}Te$ with the bicyclic cryptand $N[(CH_2)_2O(CH_2)_2O(CH_2)_2]_3N$.[527] A tin-arsenic phase, $Ca_5Sn_2As_6$, containing corner linked $SnAs_4$ tetrahedra can be isolated from a mixture of the elements in a 5:2:6 ratio heated to 150°C.[528] Arsenic-tin distances fall between 257.2 and 263.8pm.

During attempts to synthesise rubidium polyarsenides from the elements in a niobium tube, the novel niobium compound $[Rb(2,2,2\text{-crypt})]_2[Rb(NbAs_8)]$ was obtained from a solution of the reaction mixture in ethylenediamine containing the cryptand.[529] X-ray data show the presence of anionic chains containing alternate rubidium atoms and complex $[NbAs_8]^{3-}$ anions. The latter with D_{4d} symmetry consists of a crown shaped $(As^-)_8$ unit and a central Nb(V) atom. A number of binary arsenides and related compounds, including SrPtAs, SrPtSb, BaPtSb, SrPt$_{0.70}$As$_{0.90}$, BaPtAs, BaPtAs, have also been synthesised.[530]

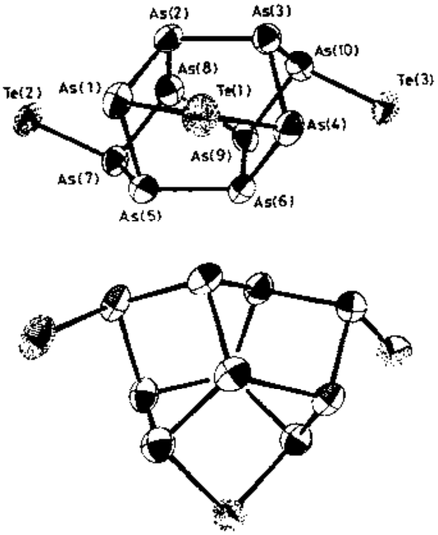


Figure 3. Two views of the As$_{10}$Te$_3^{2-}$ anion (reproduced by permission from J. Chem. Soc., Chem. Commun., (1987) 196).

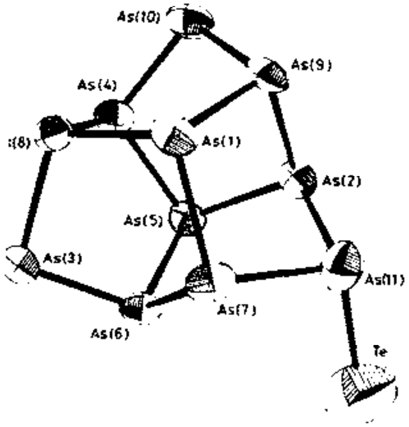


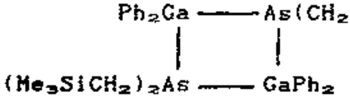
Figure 4. The As$_{11}$Te^{3-} anion (reproduced by permission from J. Chem. Soc., Chem. Commun., (1987)190).

5.3.2 Bonds to Boron or Gallium

Four-membered As$_2$B$_2$ units are formed in reactions of (mesityl)AsLi$_2$ with RBCl$_2$ where R = mesityl or 2,2,6,6-tetramethylpiperidino.[142] The corresponding phosphorus compounds were discussed in section 5.2.2.

Hydrogen is evolved when dimethylarsine reacts with solid Ga$_2$X$_4$ (X = Cl, Br or I) in a vacuum to give Me$_2$AsGaX$_2$, which are probably dimeric from their vibrational spectra.[531] With Me$_2$AsI and Ga$_2$I$_4$, on the other hand, the product is Me$_4$As$_2$GaI$_5$ (In$_2$I$_4$ gives an analogous product) containing discrete, slightly distorted, tetrahedral GaI$_4^-$ anions and the novel $[Me_2AsAsMe_2I]^+$ cation (As-As 242.7pm).

The silylmethyl substituted arsine (Me$_3$SiCH$_2$)$_2$AsH and Ph$_3$Ga eliminate benzene to give dimeric (298) with a planar, centrosymmetric ring and the following important dimensions: Ga-As 251.8 and 253.0pm, As-Ga-As 85.08°, and Ga-As-Ga 94.92°.[532] Gallium



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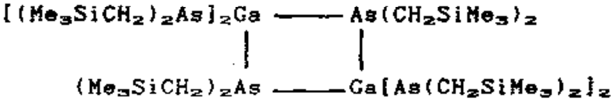


(299)

trichloride and $(Me_3SiCH_2)_2AsLi$ also gives a dimer (299) but here the ring is distinctly non-planar.[533]

Other methods for synthesising arsino-gallanes, in particular sterically hindered products, are summarised in equations (47)-(50)[534] and (51) and (52).[535] Rather unusually for compounds

$$R_2AsLi + GaCl_3 \rightarrow 1/n(R_2AsGaCl_2)_n + LiCl \qquad ...(47)$$

$$R_2AsLi + Me_2GaCl \rightarrow 1/n(R_2AsGaMe_2)_n + LiCl \qquad ...(48)$$

$$2R_2AsLi + GaCl_3 \rightarrow 1/n[(R_2As)_2GaCl)_n + 2LiCl \qquad ...(49)$$

$$R_2AsLi + GaCl_3 \rightarrow (R_2As)_3Ga + 3LiCl \qquad ...(50)$$

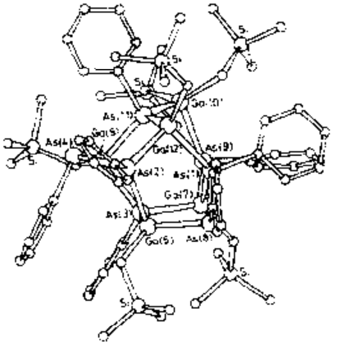
$$R_2AsSiMe_3 + (R_2As)_2GaCl \rightarrow (R_2As)_3Ga + Me_3SiCl \qquad ...(51)$$

R = mesityl

$$R_2AsSiMe_3 + GaCl_3 \rightarrow 1/n(R_2AsGaCl_2)_n + Me_3SiCl \qquad ...(52)$$

of this type, X-ray diffraction shows that tris(dimesitylarsino)-gallane is monomeric,[534] and the dimer $\{[(Me_3SiCH_2)_2As]_2GaCl\}_2$, from detailed n.m.r. spectroscopy is fluxional.[535] A monomeric trisubstituted arsino-gallane, $Ga(AsBu^t_2)_3$, can also be obtained by treating the trichloride with three mols of Bu^t_2AsLi, but a cyclic dimer, $(R_2GaAsBu^t{}_2)_2$, similar to (<u>298</u>), is produced when $GaCl_3$ reacts successively with $Bu^t{}_2AsLi$ and two mols of either methyl or butyl lithium.[147]

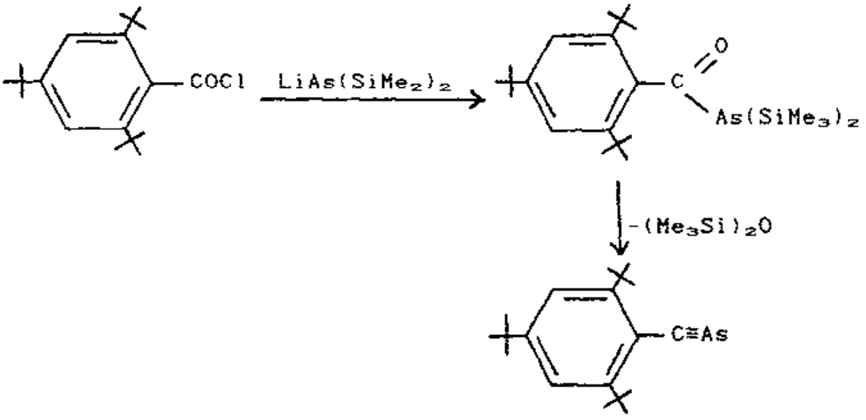
A novel cluster compound containing an As_7Ga_5 core has been obtained, along with a range of other products including $(PhAs)_6$, in a reaction between $PhAsH_2$ and $(Me_3SiCH_2)_3Ga$.[536] X-ray analysis shows the compound is $\{(PhAsH)[(Me_3SiCH_2)_2Ga](PhAs)_6$-$(Me_3SiCH_2Ga)_4\}$; structural details are shown in Figure 5.



<u>Figure 5</u>. Structure of the organogallium-arsenic cluster compound, $[(PhAsH)(R_2Ga)(PhAs)_6(RGa)_4]$ where R = Me_3SiCH_2 (reproduced by permission from J. Chem. Soc., Chem. Commun., (1986)487).

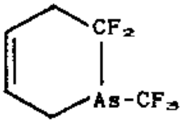
5.3.3 <u>Bonds to Carbon or Silicon</u>

<u>Arsenic(III) Compounds</u>. The first compound (mp. 114-6°C) containing an arsenic-carbon triple bond has been synthesised as outlined in equation (53).[537]



...(53)

The fluorinated arsapropene, $CF_3-As=CF_2$, prepared in situ by thermolysis of $(Me_3Sn)(CF_3)_2As$, undergoes [2+4] cycloadditions with a range of 1,3-dienes (Diels-Alder adducts) giving a series of new compounds including (300)-(303).[538] Arsa-alkenyl transition metal complexes, e.g. $Cp(CO)_2Fe-As=C(OSiMe_3)R$, where R = Bu^t, mesityl or $C_6H_2Bu^t{}_3$, can be obtained by treating $Cp(CO)_2FeAs(SiMe_3)_2$ with RCOCl; the structure of the t-butyl compound contains a short As-C bond (182.1pm) in keeping with the double bond character.[539]



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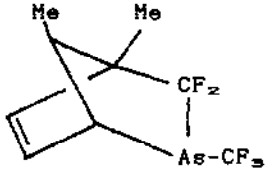

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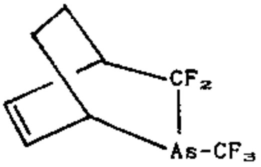

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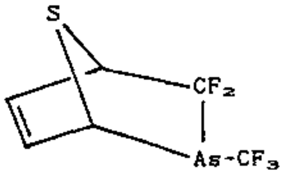
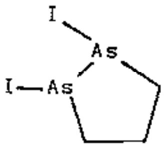


(303)

A series of methylarsine-boron adducts, $Me_nAsH_{3-n}.BX_3$, for n = 1-3, X = Cl or Br, has been prepared and ^1H n.m.r. data obtained.[540]

1,3-Bis(diphenylarsino)propane, $Ph_2As(CH_2)_3AsPh_2$, on treatment with hydrogen iodide gives the corresponding tetraiodide which can be reduced by sodium in THF to give the red, air sensitive, heterocycle (304).[541] The tetraiodide can be oxidised by aqueous hydrogen peroxide to $(HO)_2As(O)(CH_2)_3As(O)(OH)_2$ and treatment with concentrated aqueous ammonia in THF gives the tricyclic (305). Treatment with Ph_2AsNa replaces the covalently bonded chlorine atoms in $[HN(CH_2CH_2Cl)_2(CH_2CHMeCl)]Cl$ by $AsPh_2$ groups and the compound can be subsequently converted to an HI adduct of $N(CH_2CH_2AsI_2)_2(CH_2CHMeAsI_2)$ by benzene elimination with



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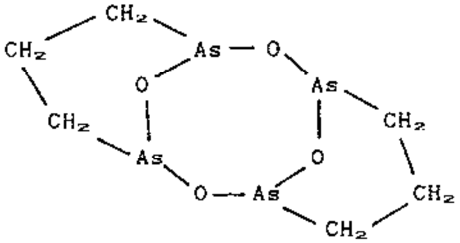

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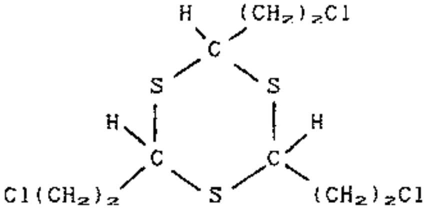
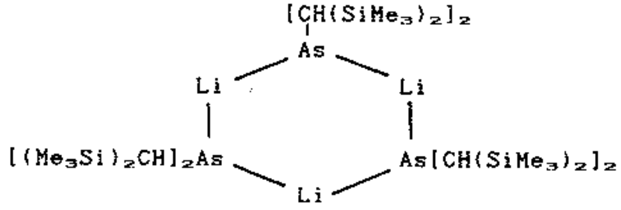


(306)

hydrogen iodide.[542] This compound serves as a precursor for two new compounds, $[N(CH_2CH_2)_2CH_2CHMe]_8(As_4X_4)_6$ for X = O or S, which are formed on treatment with, respectively, aqueous ammonia or H_2S in triethylamine. Other substituted alkyl chlorides, including $[HN(CH_2CHMeCl)_3]Cl$ and the trithiahexane derivative (306), were also used as starting materials in this series of reactions.

Bu^tCOCl will react with both $PhAs(SiMe_3)_2$ and $PhP(SiMe_3)_2$ giving $PhM[C(O)Bu^t]_2$ in which the As-C(O) and P-C(O) distances of 205 and 191pm, somewhat longer than normal but similar to those in trifluoromethyl derivatives.[543]

Reaction of $[(Me_3Si)_2CH]AsCl$ with lithium metal gives the trimer (307), which can behave both as a strong reducing agent, e.g. $SnCl_2$ is reduced to metallic tin, and as an arsenic centred nucleophile, e.g. on treatment with, respectively, HCl or MeCl, it is converted to R_2AsH or R_2AsMe.[544] An alternative route to such lithium salts uses butyl lithium and both $Li(dioxan)_3AsPh_2$ and $[Li(Et_2O)_2AsPh_2]$ have been prepared from Ph_2AsH; the second product contains a four membered As_2Li_2 ring.[545] Related antimony compounds, e.g. $[Li(12\text{-crown-}4)]_2[SbPh_2]$.½THF and $[Li(12\text{-crown-}4)_2][Sb_3Ph_4]$.THF, and a nitrogen analogue $[Li(12\text{-crown-}4)NPh_2]$ were also obtained.



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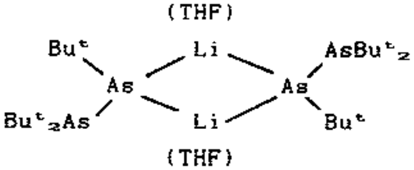
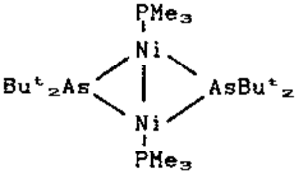


(308)

In what must be a highly complex reaction, Bu^t_2AsLi with anhydrous magnesium bromide gives the dimer (308), containing ring arsenic atoms coordinated to two lithium atoms (As-Li 258pm) and t-butyl and Bu^t_2As groups.[546] The same arsenic reagent yields an unusual dinickel complex (309) with a direct Ni-Ni bond on treatment with $NiCl_2(PMe_3)_2$; the coordinated trimethylphosphine can be displaced with p-tolyl isocyanide.[547]



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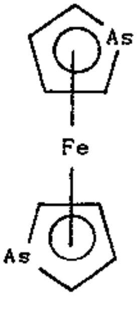

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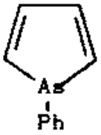


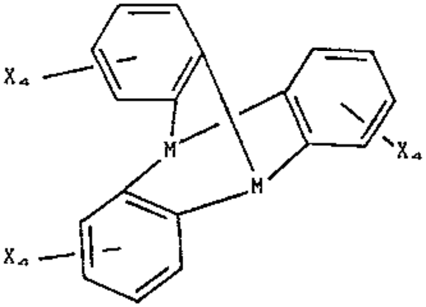
(311)

Bromine substitution takes place when trans-$WBr(CO)_2(bipy)CNEt_2$ is treated with Ph_2AsNa,[548] and, while treatment of $FeCl_2(PPh_3)_2$ with $PhAs(SiMe_3)_2$ leads to a redox process giving iron, $(PhAs)_n$ and Me_3SiCl, reaction with the cobalt chloride complex gives a green solution from which can be isolated the cobalt cluster $[Co_4(\mu_3\text{-}As)_3(\mu_3,\eta^3As_3)(PPh_3)_4]$.[549] The compound contains a tetrahedral Co_4 cluster, with three faces capped by μ_3-As ligands and one face linked to an As_3 ring. The structure is completed by coordination of a Ph_3P group to each cobalt. An unusual feature of this reaction is that As-Ph bonds are broken at room temperature.

Co-condensation of the ligand and chromium atoms leads to the η^6-arsabenzene complex, $(C_5H_5As)_2Cr$,[550] and the parent arsaferrocene (310) has now been isolated following an efficient preparative route to 1-phenylarsole (311) from 1,4-dichloro-1,3-butadiene and $PhAsLi_2$.[551] Compound (310) then follows by successive reaction of (311) with lithium and iron(II) chloride.

Freshly prepared solutions of IN_3 and INCO add oxidatively to Ar_3M, where Ar = 4-Me, 4-Cl or 4-FC_6H_4 and M = As, Sb or Bi, to give monomeric Ar_3MIX species,[552] but for $Ph_3As.I_2$, isolated as a purple solid during an investigation of reaction of manganese(II) iodide and Ph_3AsO, the product contains an As-I-I system which is slightly bent.[553] Triphenylarsine and iodine in dichloroethane solution give a compound with the stoichiometry $Ph_3As.2I_2$, which has an ionic structure, $[(Ph_3AsI)_2I_3]I_3$, like the corresponding Ph_3P product.[226]

Elemental arsenic, antimony or bismuth on treatment with phenyl mercurials $(C_6X_4Hg)_3$ where X = H, F or Cl give the heterocycles (312).[554]



(312)

Arsenic(V) Compounds. The structure of $(C_6F_5)_3AsF_2$ contains a two-fold axis passing through arsenic and one organic group giving trigonal bipyramidal coordination about antimony with fluorine atoms (As-F 178.1pm) in axial positions.[555]

Treatment of $MePh_3AsI$ with PhLi generates methylene triphenylarsorane in situ, which with ethyl trifluoroacetate, gives a new stable ylid, $Ph_3As:CHCOCF_3$.[556] A crystal structure determination points to a bond order of ca. 1.6 for the arsenic-ylidic carbon bond. The corresponding reaction with trifluoroacetic anhydride yields $Ph_3As:C(COCF_3)_2$ but there is no comparable reaction with benzaldehyde.

Arsenic-Silicon Compounds. The arsasilicate, Rb_2SiAs_2, isolated initially in the synthesis of RbAs in a quartz reactor, can be prepared directly from the elements as red needles.[557] The compound is an isotype of K_2SiP_2 containing a polymeric chain anion of edge sharing $SiAs_4$ tetrahedra (Si-As 238.1pm, As-Si-As 95.7°, Si-As-Si 84.3°).

5.3.4 Bonds to Halogens

Continuing investigations into arene adducts with Group 5 trihalides have shown that a discrete 2:1 complex of $AsBr_3$ with hexaethylbenzene can be isolated, which is only slightly air and moisture sensitive.[558] In the solid state, the arene is sandwiched between two $AsBr_3$ molecules and the data show strict η^6 coordination of the arene to arsenic (As-centre of arene 316pm).

Iodine(V) fluoride is a useful oxidising agent for a range of organochloro derivatives of arsenic, antimony or bismuth, $R_{3-n}MCl_n$ for R = Bu, Ph, C_6F_5 etc., M = As, Sb or Bi and n = 0-2.[599] The arsenic and antimony reactants yield the appropriate +5 oxidation state fluoride except for Ph_2AsF_3, which decomposes to Ph_3AsF_2 and AsF_5.

Trithiazyl chloride, $N_3S_3Cl_3$, does not react with phosphorus(V) oxide but with the heavier Group 5 trioxides, reaction gives salts identified as: $(S_5N_5)_4(As_8Cl_{28}).2S_4N_4$, $(S_5N_5)(SbCl_6)$ and mixtures of $(S_4N_5)(BiCl_4)$ and $(S_4N_4Cl)(BiCl_4)$.[560] An X-ray study on the first compound shows an octameric anion with S_4 point symmetry (see Figure 6) which arises by addition of four $AsCl_3$ molecules to a cubane-type $As_4Cl_{16}^{4-}$ species.

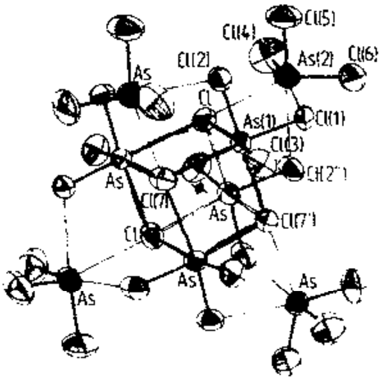


Figure 6. Structure of the $As_8Cl_{28}^{4-}$ anion (reproduced by permission from Z. Anorg. Allg. Chem., 537(1896)145).

The low temperature form of $H_3O(AsF_6)$ shows distortion of both the pyramidal cation and the octahedral anion through three independent O-H...F hydrogen bonds.[561] In the solid state, $AgF_2.AsF_5$ consists of octahedral AsF_6^- ions and infinite chain $(AgF^+)_n$ cations lying along the a axis (Ag-F 200.0pm, F-Ag-F 175.5°).[562] The chains are then cross linked via fluorine bridges from AsF_6^- anions to give effective pentagonal bipyramidal coordination about arsenic. Of the six As-F distances, five which involve bridging fluorines fall between 171.4 and 172.9pm while the single non-bridging fluorine forms a substantially shorter contact (167.7pm). The compound is clearly structurally different from $SnF_2.AsF_5$, which contains cyclic $(SnF)_3^{3+}$ cations. Structures for the AsF_5 adducts formed in liquid sulphur dioxide solution with both benzo-2,1,3-thiadiazole and benzo-1,2,3-thiadiazole show interaction via a nitrogen atom of the ligand.[563]

U.v. and p.e. spectroscopy point to the presence of $AsCl_4F$, the least stable arsenic(V) chloride fluoride, in the gas phase over heated $[AsCl_4][AsF_6]$,[564] and the compound has been isolated during sublimation of $[AsCl_4][AsF_6]$ in the presence of potassium fluoride.[565] The related dichloride, $AsCl_2F_3$, characterised by matrix i.r. and Raman spectroscopy, can be obtained from $AsCl_3F_2$ by halogen exchange with calcium chloride.[566]

5.3.5 Bonds to Nitrogen

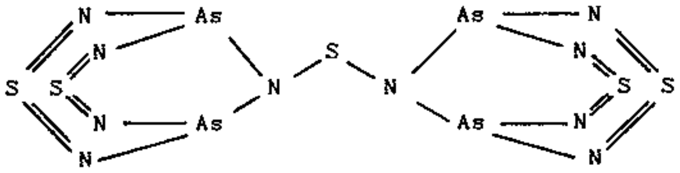
The novel two-coordinate arsenic imide, $Bu^t_3C_6H_2N.As{:}NC_6H_2Bu^t_3$, obtained from the trichloride and $Bu^t_3C_6H_2NHLi$ has already been mentioned in section 5.2.5.[302]

Multinuclear n.m.r. spectroscopy has been used to follow reactions of Me_2AsH with Me_2AsNMe_2 and $Me_2AsNMe_2.BH_3$, which in each case give good yields of the diarsine, $Me_2AsAsMe_2$.[567] In cases where $MeAsH_2$ is substituted for the dimethyl compound, the n.m.r. results suggest formation of unstable $Me_2AsAsMeH$ as an intermediate which decomposes giving $(MeAs)_5$ among other products.[568]

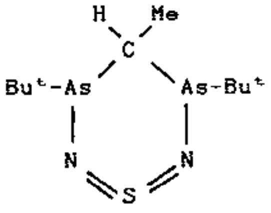
An unsymmetrically substituted diarsine, $Me_2AsAsEt_2$, is probably the initial product of reactions between Me_2AsNR_2 and $Et_2AsAsEt_2$ or between $Me_2AsAsMe_2$ and $Et_2AsAsNR_2$ (R = Me or Et) but results point to subsequent symmetrisation.[569] Coordination between Me_2AsNR_2 and $BH_3.THF$ apparently occurs only at low temperatures with decomposition to give $(Me_2NBH_2)_2$ and diarsines occurring on warming.[570]

A new series of aminoarsonium chlorides $[R_3AsNR_2{}^1]Cl$, where R = Me, Et, Pr or Ph and R^1 = H or Me, results when R_3As reacts with $R_2{}^1NCl$.[571]

Extending reactions already reported between substituted arsenic(III) chlorides and K_2SN_2, reactions with AsX_3, for X = Cl, Br or I point to formation of (<u>313</u>) as a result of SN_2 loss from the expected cage structure.[572] When the substrate is a bis-



(<u>313</u>)



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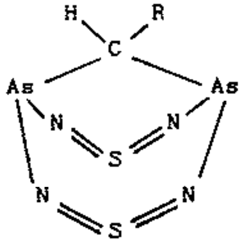
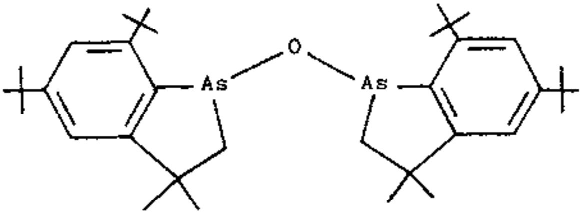


(<u>315</u>)

(chloroarsine), e.g. $MeCH(AsBu^tCl)_2$ or $RCH(AsCl_2)_2$, for R = H or Me, reaction with K_2SN_2 gives the novel heterocycles (314) and (315) respectively.[573]

5.3.6 Bonds to Oxygen

Crystals of a tetrameric arsine oxide $[(mesityl)AsO]_4$, together with a small amount of a reorganisation product $(mesityl)_2AsOAs(mesityl)_2$, have been isolated from hydrolysis of (mesityl)arsenic dichloride with potassium hydroxide in dimethoxyethane solution.[574] The eight-membered ring adopts a crown conformation (mean As-O 179.0pm, O-As-O 98.9°). Hydrolysis of the related compound $Bu^t{}_3C_6H_2AsF_2$ by the same method however led to (316).



(316)

Synthesis of an arsa-aza-oxa cryptand has already been mentioned,[542] and the chromium pentacarbonyl complex of a related cryptand, $[N(CH_2CH_2)_3]_8(As_4O_4)$, has been obtained on reaction with $Cr(CO)_5.THF$.[575]

A barium salt, $Ba_2As_6O_{11}$, containing a new highly condensed polyarsenate anion has been isolated from hydrothermal reactions with barium oxide and As_2O_3 at 200°C.[576] The structure can be considered as pairs of $(AsO_2)_n$ chains linked by As(O)OAs(O) units to give a series of condensed $As_{10}O_{10}$ rings. These double chains are further linked into sheets by relatively strong (As...O 268pm) secondary bonds. Full structures have now been published for four condensed arsenites, i.e. $Na_3(H_2As_4O_8)$, $NaAsO_2.4H_2O$, $Na_2(HAsO_3).5H_2O$ and $Na_5(HAsO_3)(AsO_3).12H_2O$, isolated from the Na_2O-As_2O_3-H_2O system at 6°C.[577]

Low temperature matrix isolation shows that oxygen is lost on heating arsenic(V) oxide in a vacuum giving lower oxides formulated as As_4O_n for n = 6-10.[578] I.r. spectra were interpreted on the basis of an As_4O_6 cage with the required number of terminal As=O bonds which absorb at ca. $1020cm^{-1}$.

Strong hydrogen bonding (O...O 255.5pm) is important in stabilising the 1:1 adduct of Ph_3AsO and p-nitrophenol with basically tetrahedral geometry (mean C-As-C 108°) about arsenic and an As-O distance of 166.8pm.[579] The hydronium salt $H[As(O_2C_6H_4)_3].nH_2O$, first prepared in 1919, is now known to be a dioxan complex of $[H_7O_3]^+[As(O_2C_6H_4)_3]^-$.[580]

New compounds, $Na_2As_4O_{11}$ (m.incongruent 670°C), $NaAs_3O_8$ (peritectoid reaction at 600°C) and $Na_3As_7O_{19}$, have been observed in the Na_3AsO_4-As_2O_5 system.[581] and the double tin arsenates, $MSn_2(AsO_4)_3$ for M = Li-Cs, can be synthesised from mixtures of $Sn(HAsO_4)_2$ and 2MCl, heated finally to 600°C.[582] The compounds are also isostructural, crystallising in the space group R3c and stable to 950°C.

The following arsenate structures have been determined:

LiH_2AsO_4, orthorhombic form, isostructural with LiH_2PO_4 and obtained from concentrated aqueous solutions of LiOH and arsenic acid,[583]

partially deuterated TlH_2AsO_4,[584]

PbCu(I)AsO_4 obtained from a 1:1:1 mixture of PbO, CuO and As_2O_3 in 1M acetic acid heated to 490K,[585]

$NaCu_4(AsO_4)_3$ hydrothermal synthesis using Na_2HAsO_4, $Cu(OAc)_2$ at 490K for 100 days, a significant feature of the structure is common edge sharing between an AsO_4 tetrahedron and a CuO_4 square leading to significant distortion of both polyhedra.[586]

$Na_5Cu_3H(AsO_4)_4$ hydrothermal synthesis with $Na_2HAsO_4.7H_2O$, $NaNO_3$ and copper wire at 493K for 48 hours, the compound is isostructural with the corresponding phosphate and contains a very strong hydrogen bond (O...O 242.7pm) between two of the arsenate groups so that formulation should be $Na_5Cu_3(AsO_4)_2(AsO_4HAsO_4)$,[587]

$CuH_{10}(AsO_4)_4$, from aqueous $Cu(HCO_3)_2$ and arsenic acid, the structure shows Jahn-Teller distorted CuO_6 octahedra and AsO_4 tetrahedra, cross linked by hydrogen bonds,[588]

$AgCu_3Cu(AsO_4)_3$, from As_2O_5, $AgNO_3$, $CuSO_4.5H_2O$ and water at 300°C for 7 days, the structure is related to those of $AgCo_3H_2(AsO_4)_3$ and $AgZn_3H_2(AsO_4)_3$ by replacement of two hydrogen atoms by a further copper atom,[589]

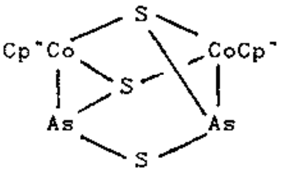
$As_2V_4O_{13}$, from a 1:2 mixture of As_2O_3 and V_2O_5 heated to 833K for 24 hours, the structure is best considered as composed of close packed oxygens with four crystallographically different vanadium(IV) atoms in octahedral sites and two arsenic(V) atoms in tetrahedral sites.[590]

$Ca_{10}(AsO_4)_6(OH)_2$, the arsenic analogue of hydroxyapatite, synthesised from stoichiometric quantities of $Ca(NO_3)_2$ and $(NH_4)_2HAsO_4$ in boiling water, among other properties determined is the solubility product (2.1×10^{-91} at 318K).[591]

5.3.7 Bonds to Sulphur, Selenium or Tellurium

New heat of formation data are available for β-As_4S_4, As_2S_3, As_2S_4, As_4S_5 and As_4S_3.[592] From Knudsen effusion and mass spectrometric experiments, As_4S_4 molecules are the basic component of the vapour over β-As_4S_4 but a range of species including As_4S_4, As_4S_5, As_2S_4, As_2S_3 and S_2 are found with As_2S_3.[593]

Transition metals containing stabilised AsS_3, AsS and As_2S groups are already known and recently a compound containing an As_2S_3 group has been isolated from photolysis of As_4S_4 in THF solution in the presence of $Cp^*Co(CO)_2$.[594] The structure (317) shows the As_2S_3 group behaves as a four electron donor.



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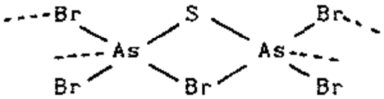
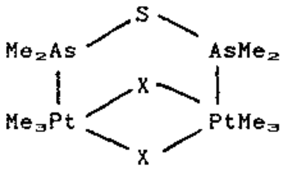


(318)

Treatment of a solution of the appropriate trisulphide and Ph_4PBr in boiling dibromomethane with hydrogen bromide leads to $Ph_4P[M_2SBr_5]$ for M = As or Sb.[595] The arsenic compound (318) is similar to $Ph_4P[As_2SCl_5]$ but intermolecular interactions, shown by the dotted lines lead to chains in the solid. Intermolecular interactions are substantially stronger in the antimony compound leading to discrete dimers.

Monomeric products, fac-$PtXMe_3L_2$, are obtained when $[Me_3PtX]_4$ reacts with diarsine sulphide, $Me_2As.S.AsMe_2$(≡L).[596] The ligands are unidentate here but binuclear complexes (319) in which the ligand is a bridging group can also be obtained. Arsenic bonded Re(I), Ru(II) and Rh(III) complexes have also been obtained



(319)

both with this ligand and with Me_2AsSMe.[597] The dithioarsenate, $Ph_2Sb(S_2AsPh_2)$, is isostructural with the corresponding dithiophosphinate (see section 5.2.7).[494]

As_4Se_3, As_2Se_3 and As_2Te_3 all react with $Co(BF_4)_2.6H_2O$ in the presence of triphos, $MeC(CH_2PPh_2)_3$, to give solvated complexes formulated as $[(triphos)Co(As_2X)][BF_4]$, where X = Se or Te.[598] The cobalt atom is coordinated, as in the related P_3, P_2S, P_2Se and As_2S complexes investigated earlier, by three phosphorus atoms from triphos and the atoms of the cyclic As_2Se or As_2Te units but here the three membered rings are disordered.

Hydrothermal syntheses from an alkali metal carbonate and As_2Se_3 at 135°C have led to three new selenoarsenates, $KAsSe_3.H_2O$, $RbAsSe_3.½H_2O$ and $CsAsSe_3.½H_2O$.[599] The structures all show linking of pseudo-tetrahedral $AsSe_3$ units into infinite chains via Se-Se bonds; As-Se distances for the potassium salt fall between 231.9 and 242.5pm with Se-Se distances of 234.8pm. A related barium compound, $Ba_2AsSe_4(OH).2H_2O$, contains isolated $AsSe_4^{3-}$ ions (As-Se 230.3-232.9pm) with C_s symmetry.[600]

$PbAs_2SSe_3$, melting incongruently at 690K, has been observed in the As_2Se_3-PbS system,[601] and $SnAs_2SeS_3$, melting incongruently at 325°C in the related As_2S_3-SnSe system.[602] There is also evidence for $NiAs_2Se_4$ from As_2Se_3-NiSe phase studies.[603]

5.4 ANTIMONY

5.4.1 Antimonides

Ten new stibines (R_2SbMR^1) have been characterised as products of exchange reactions in the R_4Sb_2-$R_2{}^1M_2$ series where R/R¹ = Me or Et and M = S, Se or Te; reactions with both Ph_2S_2 and Ph_2Se_2 were also investigated.[604] Two of the compounds, $Me_2SbTeMe$ and $Et_2SbTeMe$, are thermochromic. A similar exchange reaction produces the mixed stibine-bismuthine, $Pr^i{}_2BiSbMe_2$ in equilibrium with $Pr^i{}_4Bi_2$ and

Me_4Sb_2.[605]

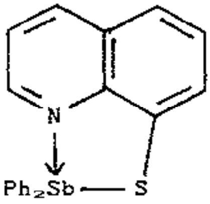
Crystal structure determinations for the isomorphous compounds $(PhSb)_6.S$, where S = dioxan, benzene or toluene show a chair shaped centrosymmetric Sb_6 ring with phenyl groups in equatorial positions.[606] The compound has overall symmetry close to D_{3d} with ring angles at antimony of 90°; Sb-Sb and Sb-C distances are 284 and 216pm respectively. Contributing to the stability of the system is the stacking of rings where the Sb...Sb separation is 420pm.

An intermetallic phase, $Ba_7Ga_4Sb_9$, can be prepared from the elements and has a structure based on $GaSb_4$ tetrahedra sharing vertices and edges to produce ribbons.[607] These are interconnected further into sheets by long (329.6pm) Sb...Sb contacts; Sb-Ga distances in edge sharing tetrahedra are 273.9 and 274.1pm, in the vertex sharing units 266.9pm.

5.4.2 Bonds to Carbon and Silicon

Reviews on organoantimony chemistry are available for 1984[608] and 1985.[609]

Good yields of mesitylhalogenostibines, $(mesityl)_nSbX_{3-n}$ where X = Cl or Br and n = 1 or 2 can be obtained by reorganisation reactions between SbX_3 and $(mesityl)_3Sb$ at 80-100°C.[610] In the presence of Me_3SiCl, both $(mesityl)_2SbBr$ and $(mesityl)SbBr_2$ can be dehalogenated by magnesium in THF to give, respectively, $(mesityl)_2SbSiMe_3$ and $(mesityl)Sb(SiMe_3)_2$. Oxidation of the former in air leads to $(mesityl)_2SbOSiMe_3$. Dehalogenation of $(mesityl)_2SbBr$ itself gives the distibine, $(mesityl)_4Sb_2$ but with $(mesityl)SbBr_2$ the product is either $[(mesityl)Sb]_6.PhH$ or $[(mesityl)Sb]_4PhMe$, depending on which aromatic is used in the work-up.



(320)

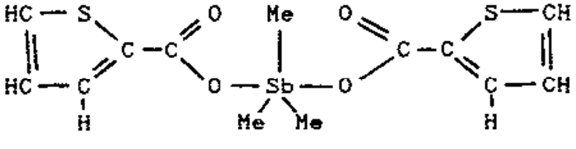
Treatment of Ph_2SbCl with the sodium salt of 8-mercaptoquinoline in ethanol gives (320) in which the Sb-S bond is normal (244.4pm) but Sb-N interaction (267.7pm) is much weaker; significant Sb...Sb interaction is indicated by the 388.4pm separation and if this is also considered, coordination about antimony becomes distorted square pyramidal with a phenyl group in the apical position.[611]

Two compounds containing phenylantimony anions, $[Li(12\text{-crown-}4)_2][SbPh_2]$.½THF and $[Li(12\text{-crown-}4)_2][Sb_3Ph_4]$.THF have been obtained, the former from a reaction of BuLi with Ph_2SbH and the latter from Ph_3Sb with lithium metal in the presence of the crown ether.[545] In both compounds, the antimony is in two fold coordination.

Although the amine derivatives, Et_2SbNPh_2 and Ph_2SbNPh_2 can be obtained, related reactions designed to give $R_2SbPR_2^1$ and $R_2SbAsR_2^1$ were unsuccessful and gave either $R_2^1PPR_2^1$ or $R_2^1AsAsR_2^1$ instead.[612]

The stiboranes, $Ph_3Sb(O_2C_6Cl_4)$ and solvated (2,2'-biphenylene)-$PhSb(O_2C_6Cl_4)$, obtained via oxidation reactions with tetrachlorobenzoquinone, have respectively trigonal bipyramidal and square pyramidal geometry with the phenyl group in the apical position.[613] Trigonal bipyramidal geometry is also found for both $Ph_3Sb[S_2C_2(CN)_2]$ and $Ph_3Sb(O_2C_6H_3\text{-}4\text{-}NO_2)$ but in $4\text{-}MeC_6H_4(O_2C_4Me_4)_2$, prepared from the stibonic acid and pinacol, the antimony is closer to the square pyramidal alternative.[614] The authors conclude that stabilisation of square pyramidal geometry requires two unsaturated five membered rings at antimony with the same donor atoms in the individual rings. An attempt to form a neutral stiborane from Ph_3SbCl_2 and 2,3-naphthalene diol in the presence of triethylamine led instead to the salt $Et_3NH[Ph_3SbCl(O_2C_{10}H_6)]$ with a distorted octahedral anion.[613]

Compound (321) obtained from $Me_3Sb(OH)_2$ and 2-thenoic acid in chloroform has a trigonal bipyramidal antimony with apical oxygen ato but one of the C-Sb-C angles is widened by donation from the second oxygen of each carboxylate group.[615] 8-Quinolinato complexes,



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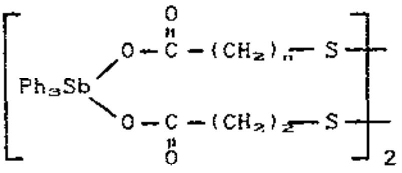


(322)

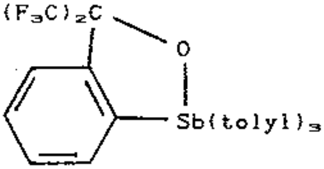
R_3SbQ_2 where R = Me, Et or Ph, are considered to be five coordinate with essentially no chelation by the ligand from n.m.r. and u.v. spectroscopy but substantial chelation is suggested in solutions of the monosubstituted compounds, R_3SbClQ.[616]

Hydrolysis of $Ph_3Sb{:}C(SO_2C_6H_4Me)_2$ gives $(Ph_3SbO)_2$,[617] and the disulphonates, $R_3Sb(O_3SR^1)_2$ where R = Me or Ph and R^1 = Me, CH_2CH_2OH, Ph, 4-MeC_6H_4; $Me_3Sb(O_3SCF_3)_2.2H_2O$ and $Ph_3Bi(O_3SR^1)_2$, where R^1 = Me, CF_3, CH_2CH_2OH, Ph or 4-MeC_6H_4, have been obtained from $(Ph_3SbO)_2$, $Me_3Sb(OH)_2$ or Ph_3BiCO_3 and the appropriate sulphonic acid.[618] Vibrational data point to essentially ionic structures for $Me_3Sb(O_3SCF_3)_2.2H_2O$ and $Me_3Sb(O_3SCH_2CH_2OH)_2$ but five coordinate covalent structures with unidentate axial sulphonic acid groups for the remainder. This was confirmed by an X-ray study on the isostructural antimony and bismuth compounds $Ph_3M(O_3SPh)_2$, which showed Sb-O and Bi-O distances of 210.6/212.8 and 227.6/228.0pm respectively. There is an addition short contact with a second oxygen of one sulphonate group at 327.4 for antimony and 312.9pm for bismuth which, as found in (321) above, causes distortion of the equatorial angles. Structures for the oxygen bridged sulphonates $[Ph_3Sb(O_3SR]_2O$ where R = Ph or CF_3 show slightly distorted trigonal bipyramidal geometry with oxygen atoms in apical positions.[619] The sulphonate groups are formally unidentate but Sb-O separations in the 225-237pm range point to substantial ionic character. Angles at the bridging oxygen are 139.8 and 136.5° for the phenyl and trifluoromethyl derivatives respectively with Sb-O bridging distances between 193 and 198pm.

Triphenylantimony oxide, unexpectedly, gives high yields of the macrocyclic antimony carboxylates (322, n = 1 or 2) on treatment with thioglycolic or β-thiopropionic acids.[620]

Oxidation of trimesityl stibine with hydrogen peroxide in acetone gives the dihydroxide, $(mesityl)_3Sb(OH)_2$ which with sulphonic acids, RSO_3H for R = Ph or CF_3, gives hydrogen bonded addition compounds formulated as $(mesityl)_3SbO.HO_3SR$.[621] A structure determination for the phenyl compound indicates distorted tetrahedral coordination about antimony with the smallest Sb-O separation (189.4pm) yet observed indicating appreciable double bond character. An i.r. band at $690cm^{-1}$ is assigned to ν(Sb-O).

Addition of methyllithium to the five coordinate tolyl derivative (323) gives three isomeric forms of the hypervalent anion (324).[622]



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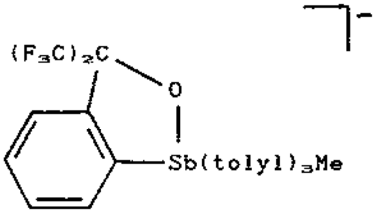


(324)

Exposure to oxygen in the air leads, via insertion into the Sb-Si bond, to $PhSb(OSiMe_3)_2$ and $Ph_2Sb(OSiMe_3)$ from respectively $PhSb(SiMe_3)_2$ and $Ph_2SbSiMe_3$.[606]

5.4.3 Bonds to Halogens

The +3 Oxidation State. Calculations on SbF_5^{2-} and the isoelectronic TeF_5^-, XeF_5^+ and IF_5 compounds point to the absence of lone pair effects in determining the overall geometry.[623]

A new mixed antimony(III)-antimony(V) fluoride, identified as $5SbF_3.3SbF_5$ can be obtained by reducing either $SbF_3.SbF_5$ or SbF_5 itself with PF_3 in arsenic(III) fluoride solution.[624] As shown by X-ray diffraction, the solid consists of a three dimensional, croos-linked cation, $(Sb_5F_{12})_n^{3n+}$ which forms strong interactions with the SbF_6^- counteranions. Simplification of the cation structure shows that it consists of planar, eclipsed $Sb_2F_3^{3+}$ units, three types of $Sb_2F_5^+$ cations in different conformations and SbF_3 moieties. Full details of the bond distances in this complex structure are discussed.

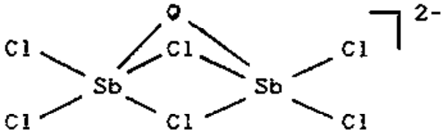
Evaporation of solutions of $MnCO_3$ and SbF_3 in dilute hydrofluoric acid gives crystals of $Mn(SbF_4)_2.2H_2O$ shown to contain infinite SbF_4 layers, similar to those in $NaSbF_4$.[625] The basic unit is pseudo trigonal bipyramidal with axial and equatorial Sb-F distances of 207.8/211.2 and 192.7/192.6pm respectively, but three further contacts in the range 295-301pm raise the coordination number to seven.

An X-ray structure of the Menshutkin complex, $(SbCl_3)_2$.benzene shows $SbCl_3$ molecules on opposite sides of the ring at distances of 322 and 330pm.[626] As in other complexes of this type, two of the Sb-Cl bonds are effectively parallel to the plane of the ring with the third at right angles giving overall geometry close to that in the pure trihalide. Each antimony atom is also involved in three longer contacts, again raising the coordination number to seven which here describes a pentagonal bipyramid with the benzene ring in an axial position.

The 1:1 antimony(III) chloride-N,N'-dimethyloxamide adduct is polymeric, based on bridging oxygen atoms of the ligand,[627] and both $SbCl_3.2POCl_3$ and $SbCl_5.P_2OS_2Cl_3$, i.e. $[P_2OS_2Cl_3][SbCl_6]$, have been isolated.[628] The antimony-iron cluster compound, $[Fe_2(CO)_8(\mu_4\text{-}Sb)]_2[Fe_2(CO)_6]$ has been prepared from $SbCl_3$, [629,630] and an open structure stibinidine complex, $(Me_3Si)_2CHSb[W(CO)_5]_2$, results from reaction of $(Me_3Si)_2CHSbCl_2$ with $[W(CO)_5)^{2-}$.[631]

Compounds in the series $[C^+]_3[Sb_2Br_nCl_{9-n}]^{3-}$, where C = Hpy and n = 0-9, C = Me_4N or Cs and n = 3, 6 or 9, have been prepared by a variety of methods for spectroscopic and X-ray investigation.[632] Crystallisation of $[Hpy]_3[Sb_2X_9]$, for X = Br or I, from concentrated hydrochloric acid was also shown to give mixed tetrahalides, $Hpy[SbX_2Cl_2]$. An X-ray structure for $[Hpy]_3[Sb_2Cl_9]$ shows a polymeric, ribbon-type structure with each antimony surrounded by a distorted octahedron of three terminal and three bridging chlorine atoms. Antimony atoms in the isostructural $[Me_4N]_3[Sb_2Br_9]$ and $[Me_4N][Sb_2Br_3Cl_6]$ are again octahedrally coordinated to three terminal and three bridging halogens but these compounds have discrete confacial bioctahedral structures, with the three bromine atoms in $[Sb_2Br_3Cl_6]^{3-}$ occupying bridging positions.

All members of the halogeno-oxydiantimonate series $[Hpy]_2[Sb_2OBr_nCl_{6-n}]$, where n = 0-6, can be prepared by hydrolysis of the appropriate nonahalide, $[Hpy]_3[Sb_2Br_nCl_{9-n}]$ but it was not possible to prepare the related cesium or tetramethylammonium salts by hydrolysing the corresponding $[Sb_2Br_nCl_{9-n}]^{3-}$ salts.[633] The hexachloride, $(Hpy)_2[Sb_2OCl_6]$, can also be obtained from the action of adventitious water on solutions of antimony(III) chloride and pyridine in dichloromethane solution. The oxydiantimonates are all soluble in a range of organic solvents and are characterised by an i.r. absorption at ca. 500cm-1. Three of these compounds, $[Hpy]_2[Sb_2OBr_nCl_{6-n}]$ with n = 0, 2 or 4, are isostructural and contain discrete $Sb_2OX_6^{2-}$ anions (325) with strong hydrogen bonding between one of the pyridinium cations and the bridging oxygen atom (N...O 268pm).[634] Halogen disorder occurs in both the mixed halides and although the bridging positions are uniquely occupied by bromine for n = 4, these positions show only 53% bromine occupancy for the dibromide anions.



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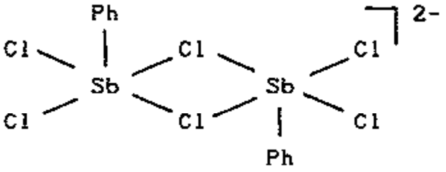


(326)

Reduction of $NH_4[PhSbCl_5]$ with sodium sulphite followed by addition of bipyridine leads to the bipyridinium salt of the centrosymmetric $[Ph_2Sb_2Cl_6]^-$ anion (326).[635] Bridging is slightly asymmetric (300.7 and 310.3pm) with terminal Sb-Cl distances substantially shorter (243.2 and 244.4pm) leading to square pyramidal coordination about antimony. There is however a weaker intermolecular Sb...Cl contact at 375.6pm.

Three new anionic antimony(III) iodides have been isolated. The first containing polymeric $[Sb_3I_{10}]^-$ can be obtained by treating

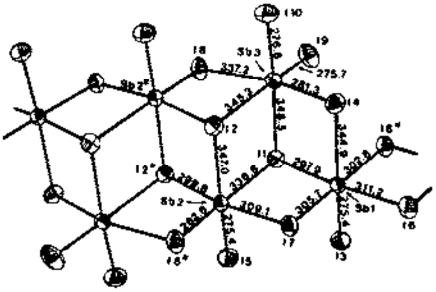
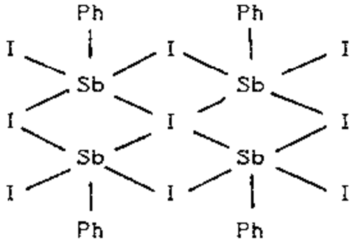


Figure 7. Structure of the $[Sb_3I_{10}]^-$ anion (reproduced by permission from Angew. Chem., Int. Ed. Engl., 25(1986)825).

tris(dimethylamino)cyclo-propenylium iodide with three mols of antimony(III) iodide in acetonitrile.[636] As shown in Figure 7, there are 18 independent Sb-I contacts falling into the three ranges, 275-282, 298-311 and 337-349pm; if all are considered to be bonding the structure is composed of edge sharing distorted SbI_6 octahedra. The second compound, $(Ph_4P)_2[Sb_2I_8].2MeCN$, results from interaction between Ph_4PI and SbI_3, and has a double iodine bridged structure with square pyramidal geometry about antimony.[637] Curious features in this structure are the weak interactions between antimony and a phenyl group of each cation at distances of 343-358pm. The final compound is an (18-crown-6)-potassium salt of a $[Ph_4Sb_4I_9]^-$ anion obtained from $Cr(CO)_5(PhSbI_2)$ and potassium with the crown compound in THF solution.[638] Here X-ray diffraction shows a central iodide anion in square planar coordination to four $PhSbI_2$ groups (<u>327</u>).

<u>The +5 Oxidation State.</u> I.r. and single crystal X-ray data for the 1:1 addition compound of $SbCl_5$ with $Pr^iN:C:NPr^i$ show Sb-Cl distances between 235.6 and 236.8pm and an Sb-N separation of 215.4pm.[639] Complexes of $SbCl_5$ with nitriles, phosphine oxides ($R_{3-n}R'PO$), or ethers, etc. have C_{4v} point symmetry in both the solid state and dibromoethane solution acording to i.r. and Raman spectroscopy and self ionisation to give $[SbCl_4.2L]^+[SbCl_6]^-$ is considered to be less than 3% from ^{121}Sb n.m.r. spectroscopy.[640] Ligand exchange reactions, equation (45), follow a first order



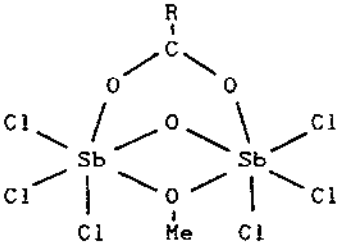
(<u>327</u>)

$$SbCl_5L + L' \rightleftharpoons SbCl_5L' + L \qquad \ldots(45)$$

rate law from ^1H n.m.r. investigations in dichloromethane or tetrachloroethane pointing to a limiting dissociative mechanism.[641]

Intercalation of $SbCl_5$ into both natural and synthetic graphites either neat or in carbon tetrachloride solution shows an induction period,[642] which is not observed when $SbCl_4F$ is used.[643] It is also possible to intercalate simultaneously into graphite both $SbCl_5$ and trichlorides, such as $AsCl_3$, $SbCl_3$, $BiCl_3$, $AlCl_3$, $GaCl_3$ and $FeCl_3$, giving products with $SbCl_5$:MCl_3 ratios of between 1:0.16 and 1:4.5.[643]

Two new carboxylate bridged antimony(V) chlorides, also containing either a bridging methoxy group (328, R = CF_3 or Et) or a hydroxy bridge (329, R = CF_3 or Et), have been obtained from the carboxylic acid with either $SbCl_5$-MeOH mixtures or $SbCl_5.H_2O$.[645]



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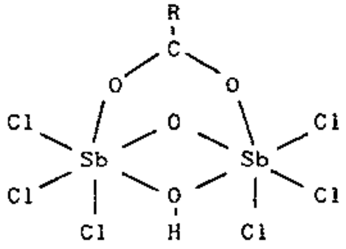


(329)

Three charge transfer complexes, $NaSbCl_6.2PhMe$, $NOSbF_6.C_6Me_6$ and $NOAsF_6.C_6Me_6$ obtained from liquid sulphur dioxide solutions have been examined by n.m.r. and optical spectroscopy and X-ray diffraction.[646] Among the results is the observation that the nitrogen atom in $NOSbCl_6.C_6Me_6$ is almost symmetrically placed with respect to the six ring atoms.

5.4.4 Bonds to Oxygen

The $Sb(OMe)_3$ structure consists of layers in which each antimony is coordinated by six oxygen atoms, three at short distances (198.6-201.2pm) and three at longer separations (256.4-300.3pm), with pairs of antimony atoms forming Sb_2O_2 rings.[647] By reorganisation of mixtures of $Sb(OMe)_3$ and SbX_3, X = Cl or Br, it has been possible to prepare members of the two mixed ligand series $SbX(OMe)_2$ and $SbX_2(OMe)$. Their i.r. and Raman spectra show structures similar to that of $Sb(OMe)_3$ for the former, but for $SbX_2(OMe)$ there are Sb_2X_2 rings in addition to Sb_2O_2 rings.

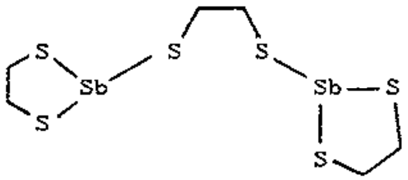
The negative ion mass spectrum of $Sb(OBu)_3$ shows formation of the new species SbH_2O^-, Sb_4^- and $Sb_3O_5^-$; for the former, formulation as H_2SbO^- rather than $HSbOH^-$ is preferred following its greater stability on the basis of STO-3G level m.o. calculations.[648]

Structures have been determined for both the Δ and Λ isomers of bis(ethylenediamine)glycinato cobalt(III) di-μ-(RR)-tartrato-diantimonate(III) tetrahydrate.[649] Four new oxide pyrochlores, $Pb_2[M_{0.33}Sb_{1.67}]O_{6.50}$, for M = Mg, Ni, Cu or Zn, result from heating mixtures of the appropriate oxides.[650] Investigations by ^{121}Sb Mossbauer and e.s.r. spectroscopy show that although antimony is in the +3 oxidation state with tungsten as +6 in Sb_2WO_6, both the corresponding molybdenum compound, Sb_2MoO_6, and $Sb_2Mo_3O_{12}$ contain both +3 and +5 antimony with the implication that molybdenum is partially reduced.[651]

Reaction of $Sb(OMe)_5$ with tetramethylammonium methoxide gives $[Me_4Sb][Sb(OMe)_6]$ for which i.r. and Raman data are now available.[652] Analysis of these data give the Sb-O stretching force constant as $2.56Ncm^{-1}$, a value similar to that for W-O stretching in a parallel investigation of the spectrum of $W(OMe)_6$.

5.4.5 Bonds to Sulphur or Selenium

Good yields of antimony(III) dithiocarbamates can be obtained by treating the trioxide with dithiocarbamic acids prepared in situ from dialkylamines and carbon disulphide.[653] The reaction can be extended to give novel β-hydroxy and β-cyanoethyl derivatives, but reduction occurs with antimony(V) starting materials, e.g. Sb_2O_5, Sb_2S_5 and $PhSbO_3H_2$, and only antimony(III) compounds were obtained. Diantimony tris(dithiolates), $Sb_2(S_2X)_3$ where X = CH_2CH_2, $CH_2CH_2OCH_2CH_2$ and $CH_2CH_2SCH_2CH_2$, have been prepared either from SbF_3 and a sodium dithiolate solution in ethanol or by refluxing $Sb(OEt)_3$ and the dithiol in chloroform.[654] The structure of $Sb_2(SCH_2CH_2S)_3$ (330) shows SbS_2C_2 rings in both the envelope and half chair conformations and additional intramolecular Sb...S bonding at 347 and 350pm. The pentagonal pyramidal structure of $Sb(S_2PPh_2)_3$ has already been referred to in section 5.2.7.[493] The $Ph_4P[Sb_2SBr_5]$ structure is similar to that of the arsenic analogue also mentioned previously but here intermolecular interactions are substantially stronger leading to discrete dimeric units (<u>331</u>).[595]



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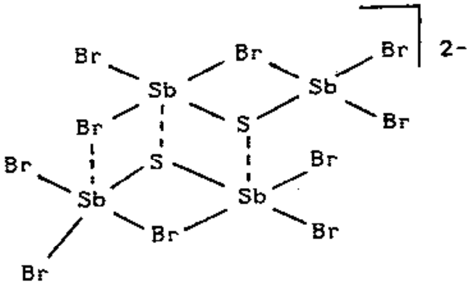
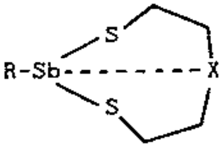


(<u>331</u>)

Although it has not yet been possible to prepare $PhSb(OAc)_2$ - the monoacetate is however well known - the corresponding thioacetate, $PhSb(SAc)_2$ is readily obtainable by metathesis between $PhSbCl_2$ and potassium monothioacetate in ethanol.[655] Primary bonding is via sulphur (mean Sb-S 246pm) but there is also substantial Sb...O secondary interaction at ca. 281pm leading to distorted square pyramidal coordination about antimony. The solid state structure is completed by weak dimer formation via Sb...S contacts (380pm) completing distorted octahedral coordination about antimony. In contrast to the acetate series, isolation of $Ph_2Sb(SAc)$ has not proved possible and possible reasons for the instability of this compound and $PhSb(OAc)_2$ are discussed.

Di- and trithiostibocanes (<u>332</u>, X = O or S and R = 4-tolyl or 4-nitrophenyl) can be obtained from $RSbCl_2$ and the appropriate dithiol, $X(CH_2CH_2SH)_2$ in the presence of triethylamine.[656] The



(<u>332</u>)

4-nitrophenyl derivative with X = S shows a boat-chair conformation for the eight-membered ring with a transannular Sb...S interaction at 319pm but there is an additional intermolecular interaction which raises the antimony coordination to six. Preparative and structural data have already been discussed for $Ph_2SbS_2PPh_2$.[494] $Ph_2Sb(S_2AsPh_2)$, $Ph_2Sb(OSPPh_2)$ [495] and $Ph_2Sb(O_2PPh_2)$.

A range of substituted antimony(V) selenocyanates, including $R_3Sb(SeCN)_2$, for R = Me, Ph, 4-ClC_6H_4, 4-FC_6H_4 and C_6F_5, $Ph_4Sb(SeCN)$ and the oxygen bridged species $R_3Sb(SeCN)OSbR_3(SeCN)$ can be obtained from the corresponding halide and potassium selenocyanate in the presence of 18-crown-6.[657]

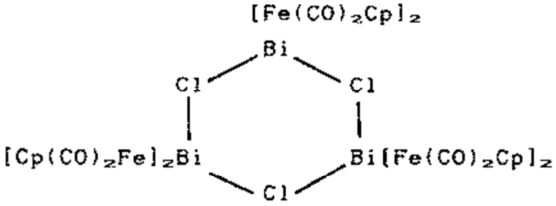
$CsSb_2Se_4$, which contains both pseudo-tetrahedral and pseudo-trigonal bipyramidal Sb-Se units interconnected by both Sb-Se and Se-Se bridges, has been obtained in a hydrothermal reaction of Cs_2CO_3 and Sb_2Se_3 at 115°C.[658]

5.5 BISMUTH

5.5.1 Dibismuthines and Bismuthides

Tetra-i-propyldibismuthine reacts with free chalcogens with insertion into the Bi-Bi bond to give Pr^i_2Bi-X-$BiPr^i_2$ X = O, S, Se or Te and exchange in the $Pr^i_2BiBiPr^i_2$-Me_4Sb_2 system leads to an equilibrium with $Pr^i_2BiSbMe_2$.[605] Low temperature stable (p-tolyl)$_4Bi_2$, obtained from (p-tolyl)$_2$BiBr and sodium in liquid ammonia, shows the same chalcogen insertion discussed above but p-benzoquinone will also insert to give (p-tolyl)$_2BiOC_6H_4OBi$-(p-tolyl)$_2$. With Ph_2S_2 and the selenium and tellurium analogues the products are (p-tolyl)$_2$BiXPh where X = S, Se or Te.[659]

Among the anionic clusters generated by dissolving alkali metal alloys in ethylenediamine is $Sn_2Bi_2^{2-}$, identified for the first time by tin n.m.r. spectroscopy.[660] Bismuth can behave as a bridging atom in organometallic compounds as shown by reactions of bismuth(III) chloride with two and three equivalents of $Na[CpFe(CO)_2]$,[661] or three equivalents of $Na[Mn(CO)_5]$.[662] The first product, $[CpFe(CO)_2]_2BiCl$, is trimeric (333) while the



(333)

second compound $[CpFe(CO)_2]_3Bi$ can be decarbonylated photochemically to give $[CpFe(\mu_2\text{-}CO)]_3Bi$. The manganese derivative,

$[Mn(CO)_5]_3Bi$, is pyramidal with Mn-Bi-Mn angles of 106.9, 107.5 and 110.3° and Bi-Mn distances falling between 288.4 and 291.6pm.

All the metal atoms are retained when $Bi_2Fe_3(CO)_9$ reacts with $[Fe(CO)_4]^{2-}$ giving $[Bi_2Fe_4(CO)_{13}]^{2-}$ but with $[Co(CO)_4]^-$, one iron atom is lost giving $[Bi_2Fe_2Co(CO)_{10}]^-$. This contains a Bi_2Fe_2 tetrahedron, bridged on the Bi-Bi edge by a $Co(CO)_4$ group.[663]

5.5.2 Bonds to Carbon

Organobismuth chemistry for 1984 and 1985 has been reviewed.[664,665] Reactions of R_3Bi, where R = Ph or p-tolyl, with an arenesulphonic acid give diarylsulphonates, R_2BiO_3SR and under more reactive conditions a second aryl group can be displaced to give impure p-tolyl $Bi(O_3SPh)_2$.[666] Treatment of Ph_3Bi with sulphur trioxide does not give the 1:1 addition compound previously reported but rather the sulphonate, Ph_2BiO_3SPh, mentioned above.

5.5.3 Bonds to Halogens

Reexamination of the products from solutions of bismuth(III) chloride in mesitylene or in hexamethylbenzene-toluene mixtures shows formation of $(Me_3C_6H_3).BiCl_3$ and $(Me_6C_6).2(BiCl_3)$.[667] The former contains sheets based on rings of six $BiCl_3$ molecules (see Figure 8a) with each bismuth in octahedral coordination to three chlorine atoms at between 246.5 and 248.9pm, two further chlorines at 330.2 and 336.8pm, with the sixth position occupied by η^6-mesitylene groups disposed alternately above and below the $BiCl_3$ sheets. The hexamethylbenzene adduct contains a tetrameric $(BiCl_3)_4$ unit with D_{2d} symmetry, (see Figure 8b) in which bismuth is coordinated to an η^6-arene molecule lying on a crystallographic inversion centre. As a consequence a bismuth chloride unit must also be attached to the other side of the ring.

Related reactions in the presence of aluminium chloride however give hydrolytically unstable compounds, $AlBiCl_6.A$, A = toluene or hexamethylbenzene, which contain a centrosymmetric dimeric arrangement of $AlCl_4^-$ and arene complexed $BiCl_2$ units.[668] The bismuth-arene separation is 272pm and bismuth coordination is completed by longer contacts to three further chlorine atoms.

Slightly distorted octahedral geometry is found for $[BiCl_6]^{3-}$ in both the diethylammonium salt [669] and the salt with the protonated 4,6-dimethylpyrimidine-2(1H)-thione.[670] In the former, bismuth is trigonally distorted and coordinated to three

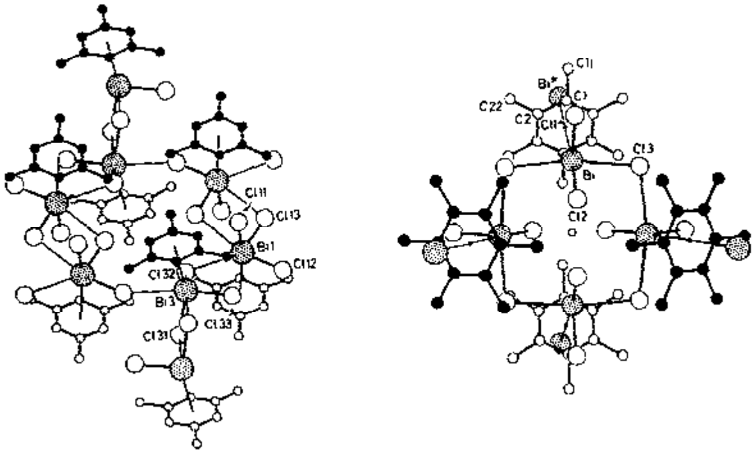


Figure 8. a) Section of the structure of $BiCl_3.(Me_3C_6H_3)$ showing a $(BiCl_3)_6$ section of the sheet. The mesitylene groups are alternately above (filled circles) and below (open circles) the sheet.
b) The tetrameric unit in $(BiCl_3)_2.(Me_6C_6)$ with bismuth atoms above and below each arene molecule. The chlorine environment of the bismuth atoms generated by inversion is not shown (reproduced by permission from Angew. Chem., Int. Ed. Engl., 25(1986)757).

close (258.3pm) and three more distant (289.2pm) chlorine atoms; in neither case is the lone pair considered to be stereochemically active but hydrogen bonding to the less tightly bound chlorines is thought to cause the distortion.

Face sharing bioctahedral $[Bi_2I_9]^{3-}$ units with bridging and terminal Bi-I distances of 316.9-327.7 and 293.4-303.2pm are present in solid $(Et_2NH_2)_3[Bi_2I_9]$.[671]

$BaBiBr_5$, decomposing in a peritectic reaction qt 184°C, has been identified in a DTA and X-ray powder diffraction study of the $BiBr_3$-$BaBr_2$ system.[672] and the related Na_2BiI_5 melting incongruently, is formed from NaI and BiI_3.[673] Three lower bismuth iodides formulated as $Bi_{4.4}I$, $Bi_{3.3}I$ and BiI are formed in the bismuth rich section of the Bi-BiI_3 system.[674]

5.5.4 Bonds to Oxygen

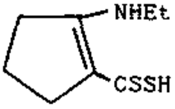
Refinement of the BiOBr structure indicates that, as for the corresponding chloride, the compound belongs to the PbFCl layer family of structures; the bismuth atom forms contacts to oxygen at 232.5pm and to bromine at 317.0pm.[675]

Bi_2GeO_5 crystallises in the space group Cc and consists of infinite $[Bi_2O_2]^{2+}$ layers parallel to the a axis alternating with infinite $(GeO_3)_n^{2n-}$ chains.[676] The germanium atoms are tetrahedrally coordinated but, while bismuth forms two short contacts to oxygen (218 and 226pm), there are a total of six oxygen contacts within 261pm and five others if the distance is extended to 381pm. The latter in fact account for ca. 12% of the bismuth bonding and coordination at bismuth is best considered as trigonal prismatic with five additional long contacts.

Single crystals of a new phase formulated as $Bi_4V_2O_{11}$ have been isolated from molten mixtures of $2Bi_2O_3$ and V_2O_5.[677]

5.5.5 Bonds to Sulphur

The dimeric structure of $Bi(S_2PPh_2)_3$ has already been discussed in section 5.2.7.[493] On coordination to bismuth(III), the dithiocarboxylic acid (334) loses a proton giving a tris complex in which bismuth is surounded by three sulphur atoms at 261.7-264.7pm and three further sulphurs at 296.3-310.8pm.[678] Nitrogen is not involved in coordination but a further Bi...S contact at 368.9pm leads to weak dimerisation. Complexes formulated as $[Bi(SC_6H_4NH_3)Cl_3]$ and $[Bi(SC_6H_4NH_2)_3]$ have been obtained from 2-aminobenzene thiol.[679]



(334)

The highly sulphur rich anion $[Bi_2S_{34}]^{4-}$ results when $BiCl_3$ reacts with an ammonium polysulphide solution in acetonitrile.[680] The unusual structure shows two bismuth atoms linked by an S_6^{2-} chain and each atom coordinated by two chelating S_7^{2-} chains leading to distorted square pyramidal geometry about bismuth. The axial positions are occupied by the S_6 chain which forms the shorter Bi-S contacts (268.3pm); basal Bi-S distances are 281.7pm.

A europium(II) compound, $Eu_{1.1}Bi_2S_4$, has been obtained from either EuS and Bi_2S_3 mixtures at 1073K or mixtures of EuS. 2Bi and 3S at the same temperature.[681] The bismuth atoms are octahedrally coordinated (Bi-S 252-363pm) while the eight fold coordination at europium is described as bicapped-trigonal prismatic. Bi-S octahedra are also present in $Pb_4In_2Bi_4S_{13}$ together with both tetrahedral and octahedral InS_n units and mono- and bi-capped trigonal prismatic PbS_n units.[682] The related $Pb_4In_3Bi_7S_{16}$ contains both BiS_6 octahedral and BiS_5 square pyramidal units.[683]

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