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Chapter 5

ELEMENTS OF GROUP 5

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5.1 NITROGEN

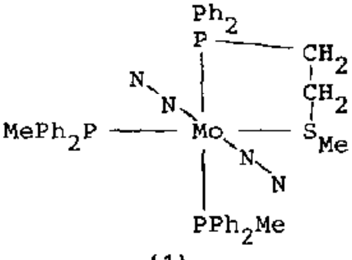
5.1.1 Elemental Nitrogen

Grevels and coworkers[1] have described how the combined application of flash photolysis with i.r. detection can be used to detect $Cr(CO)_5N_2$ in solution at room temperature. A study of the reaction of matrix(N_2 or Kr)-isolated iron atoms with excess N_2 supports the conclusion that a monomeric $Fe(N_2)_5$ species is present.[2] In dilute N_2 matrices the (N-N) i.r. absorptions were tentatively assigned to $Fe(N_2)_x$, x = 1 to 4. The first tris-dinitrogen complex has been isolated from the products of reaction (1):[3] the new Mo-complex was said to have good thermal stability.

$$\text{trans-}[Mo(N_2)_2P_4] + N_2 \rightleftharpoons \text{mer-}[Mo(N_2)_3P_3] + P \qquad ...(1)$$

The crystal structure of $[W(C_2Ph_2)(dme)Cl_2]_2(\mu\text{-}N_2).0.5dme$ shows an essentially linear W-N-N-W arrangement with a long N-N bond, 1.292(16)Å.[4] Molecular orbital calculations have been reported by Powell and Hall[5] on four dinitrogen-bridged transition metal dimers, with N-N bond lengths ranging from 1.12 to 1.30Å. The calculated Mulliken populations of the $\mu\text{-}N_2$ $1\pi_g$ orbitals increase with increasing N-N bond length: this trend was attributed to the presence of unoccupied $d\pi$ orbitals, which stabilise the $1\pi_g$ MO. Dinitrogen-bridged complexes of trans-$[ReCl(N_2)(PMe_2Ph)_4]$ with $NbCl_5$ and $TaCl_5$ (1:1 adducts), and $ZrCl_4$ (2:1 adduct) have been characterised.[6] Nitrogen-15 chemical shifts were compared for three types of dinitrogen bridge: the trends were interpreted by means of a simple model of frontier orbitals for paramagnetic circulations, in terms of delocalised π orbitals, and by periodicities in the transition series (optical spectroscopy). The chemical shifts were said to reflect the bonding and, to some extent, the reactivity of the dinitrogen ligand. A series of complexes containing a terminal dinitrogen ligand have been studied by ^{15}N n.m.r. spectroscopy.[7] The nitrogen shielding shows a periodic variation with the central metal, the trend being more sensitive for the metal-bound N_α atom than for N_β.

The nature and reactivity of the metal-nitrogen bond in dinitrogen complexes has been investigated by means of the oxidation potential of a series of complexes $[M(N_2)_2\{(p\text{-}XC_6H_4)_2PCH_2CH_2P(C_6H_4X\text{-}p)_2\}_2]$, M = Mo or W.[8] The results are consistent with through-metal conjugation, between the phosphorus atom and N_2, which enhances the strength of the M-N_2 bond. The product of reaction of $[Mo(N_2)_2(PMePh_2)_4]$ with $Ph_2PCH_2CH_2SMe$ has been characterised by X-ray methods as (1).[9]



(1)

5.1.2 Bonds to Hydrogen

Secondary amides with electron-withdrawing substituents exchange predominantly by the imidic acid mechanism. This conclusion applies to N-formylglycine in which the contribution from the alternative N-protonation mechanism is less than 1% of the total.[10] Decreasing the solvent polarity tends to favour the imidic acid route:[11] Perrin and Lollo discuss the implications of this for protein chemistry for which the assumed mechanism of acid-catalysed proton exchange has been N-protonation. Reactions of the fluorinated amines $(CF_3)_2NH$, $CF_3N(OCF_3)H$, $CF_3N[OCF(CF_3)_2]H$, CF_3NHF, and SF_5NHF with HF and AsF_5 has been shown to generate the corresponding substituted ammonium AsF_6^- salts;[12] these were found to be compounds having dissociation pressures ranging from ca. 5torr to ca. 50torr, at 22°C.

It has been proposed that NO_2ClO_4 is an essential intermediate in the thermal decomposition of NH_4ClO_4 at 500K.[13] Support for this comes from (i) the detection of nitrates in partially decomposed NH_4ClO_4, (ii) the influence of nitrate salts on the induction period, and (iii) an analysis of the rate of decomposition of NO_2ClO_4 itself.

5.1.3 Bonds to Gallium

The structure of gaseous $Me_3N.GaH_3$ has been determined by electron diffraction:[14] the N-Ga bond was found to be 2.124(7)Å, in good agreement with the earlier microwave study.

5.1.4 Bonds to Carbon or Silicon

Lentz[15] has described a greatly improved synthesis of trifluoromethyl isocyanide: it employs four, key, high-yield reactions, (2)-(5), and depends finally on the dehalogenation of N-trifluoromethyl carbimidedihalides. The unstable CF_3NC was produced in high purity and in quantities of ca. 10g. Although

$$CF_3N{=}CF_2 + HF \rightarrow (CF_3)_2NH \qquad \ldots(2)$$

$$(CF_3)_2NH + BX_3 \rightarrow (CF_3)_2NBX_2 + HX \qquad \ldots(3)$$

$$(CF_3)_2NBX_2 \rightarrow CF_3N{=}CX_2 + BF_3 \qquad \ldots(4)$$

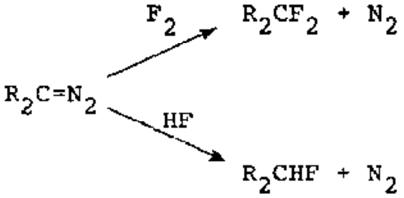
$$CF_3N{=}CX_2 + Mg \rightarrow CF_3N{\equiv}C + MgX_2 \qquad \ldots(5)$$

this compound has a rather limited stability in the liquid state, owing to the facile isomerisation to CF_3CN, the gas phase rearrangement requires temperatures above 750K, according to Bock et al.[16] who have monitored the decomposition by photoelectron spectroscopy. The isomerisation energies for three other isocyanides, RNC, R = Me, ^tBu, Ph, have been estimated to be -30, -27, and -28 kcal mol^{-1}, respectively.[17]

The photochemical reactions of several singlet arenecarbonitriles with aliphatic amines have been investigated:[18] in low polarity solvents aminyl radicals are formed, whereas in more polar media both aminyl and alkyl radicals result. It was suggested that aminyl radical formation is characteristic of relatively non-polar hetero-excimers in which H-bonding may favour N-H transfer.

The He photoelectron spectrum of NCNCS has been analysed and assigned with the help of MO calculations and by comparison with the spectra of NCNCO and HNCS. The molecule is bent at the central N atom at which the bond angle was estimated to be 155±5°.[19] The ions H_2CN^+, $HCNH^+$, CNH_2^+, and H_2CNH^+ have been generated in the gas phase and identified by means of their unimolecular and collisionally-induced dissociation characteristics.[20] The heats of formation of the aminomethylidene cation (CNH_2^+) and aminomethylene cation radical ($HCNH_2^{+\cdot}$) were determined to be 265(±9) and 258(±1) kcal mol^{-1}.

An improved synthesis of perfluoronitrosoalkanes has been reported by Marsden and Shreeve.[21] It involves the one-pot reaction of the perfluorocycloalkene with NOCl or N_2O_4, in the presence of KF in MeCN; yields are approximately 80%. Reactions of the nitroso compounds with (i) glass (thermal decomposition) - gave the nitro analogues, (ii) C_2F_4 - gave oxazetidines, and (iii) N_2F_4 (in metal apparatus) - gave the NF_2 derivatives. Direct fluorination with 1-5% F_2 of arylhydrazones in MeOH at ca. 0°C has been shown to produce a mixture of mono- or gem di-fluoro products:[22] diazo compounds were thought to function as intermediates, Scheme 1.



Scheme 1

The addition of sodium or potassium alkoxides, particularly potassium tert-butoxide, to the lithium salts of either 1,2-diaminoethane or 1,3-diaminopropane afford alkyne isomerisation agents.[23] According to Abrams these agents effect triple bond migration to the end of a methylene chain under milder conditions and in higher yield than do previously reported catalysts. Gaseous trimethyleneimine, $HN\text{-}\overline{CH_2\text{-}CH_2\text{-}CH_2}$, exhibits ^1H n.m.r. spectra characteristic of a system undergoing slow inversion at nitrogen in the temperature range 30° to 150°C.[24] Two conformers are in equilibrium at 30°C in 1:ca.3 ratio and the free energy of interconversion was estimated to be 17.9 kcal mol^{-1}.

The crystal structure of $N(SiH_3)_3$ at 115K has been determined by X-ray crystallography.[25] The deviations from molecular C_{3h} symmetry are negligible and there are no short intermolecular contacts. The heavy atoms show large vibrational amplitudes parallel to the C_3 axis, however the mean Si-N bond length (1.730(5)Å) is not significantly different from that in the gas phase (1.735(2)Å). Stable crystalline adducts of SiF_4 with a number of aminocyclophosphazenes have been reported:[26] adduct stoichiometries were found to range from 1:1 to 1:3. It was concluded from vibrational spectroscopic evidence that N-Si bond formation had occurred, with ring and/or exocyclic nitrogens functioning as donor atoms.

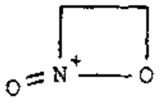
5.1.5 Bonds to Oxygen

The equilibrium constant of reaction (6) has been determined

$$NO_2 + NO_3 + M \rightleftharpoons N_2O_5 + M \qquad \ldots(6)$$

directly for the first time, using i.r. and differential u.v.-visible absorption spectroscopy, to be $(3.44 \pm 0.81) \times 10^{-11} cm^3$ molecule^{-1} at 298K.[27] The quantum yield for NO_3 production by u.v. photolysis of N_2O_5 has been measured directly by Johnston et al.[28] The average value was 0.89 ± 0.15, although at low N_2O_5 concentrations and at low gas pressures the yield approached 1.0. Rate constants for the gas-phase reactions of NO_3 radicals with a series of organic compounds at 298K have been measured by Atkinson et al.[29] These quantities are of interest in connection with atmospheric pollution by NO_3 radicals. Smith and coworkers[30] have studied qualitative and quantitative aspects of the reaction between NO_2/N_2O_4 and (hexane-)soot by FT i.r. The rapid reaction near room temperature yields several surface species, including $C\text{-}NO_2$, C-ONO, and $C\text{-}N\text{-}NO_2$. Plausible reaction mechanisms were proposed and discussed. The gas-phase reaction between NO_2 and $SOCl_2$ has been reinvestigated; the products formed initially were identified as NOCl, NO_2Cl, and SO_2.[31] The reaction was shown to be first order in $SOCl_2$ and second order in NO_2. At least three different solid products were found to be deposited: their ionic constituents were identified as NO^+, NO_2^+, SO_3Cl^-, $S_2O_6Cl^-$, and $S_2O_7^{2-}$.

An international study of the reactions of acetyl nitrate with cyclic olefins has provided strong evidence for a mechanism which does not involve the formation of a β-nitrocarbocation.[32] This alternative mechanism involves an initial [2+2] addition of NO_2^+ to the C=C bond: the authors also presented the results of calculations on 3 species, (2) to (4), relevant to the $C_2H_4\text{-}NO_2^+$ energy surface.



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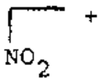

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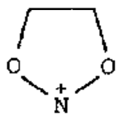


(4)

The reaction of low concentrations of $^{15}NH_3OH^+$ with HNO_3 has been shown to produce singly labelled N_2O, containing equal amounts of ^{15}NNO and $N^{15}NO$.[33] As the hydroxylaminium concentration was increased the proportion of $^{15}N_2O$ formed also increased. This behaviour was explained by Stedman et al. in terms of the concentrations of nitrous acid present. Evidence has been obtained which indicates that the decomposition of the trioxodinitrate ion in neutral solution involves reaction (7), rather than the previously accepted reaction (8), as the limiting step.[34] The presumed fate of $(HONO)^{\overline{\cdot}}$, reactions (9) and (10), is

$$HN_2O_3^- \rightarrow NO + (HONO)^{\overline{\cdot}} \qquad ...(7)$$

$$HN_2O_3^- \rightarrow HNO + NO_2^- \qquad ...(8)$$

$$(HONO)^{\overline{\cdot}} + HN_2O_3^- \rightarrow HONO + (HN_2O_3)^{2-} \qquad ...(9)$$

$$(HN_2O_3)^{2-} + NO \rightarrow [ONN(OH)NO_2]^{2-} \rightarrow NO_2^- + N_2O + OH^- \qquad ...(10)$$

consistent with earlier labelling experiments.

The persistence of both O- and C-centred free radicals in gas-phase cigarette smoke, for periods of 5 minutes or more, is said to demand a steady state description: according to Pryor and coworkers,[35] the radicals are both produced and destroyed in a series of reactions, (11) to (17), involving NO_x, i.e. either NO + NO_2. They have provided evidence for this hypothesis in a study using the e.s.r. spin-trapping technique. Dessaux et al.[36] have described a range of conditions under which gaseous NO_x may

$$NO + \tfrac{1}{2}O_2 \xrightarrow{slow} NO_2 \qquad ...(11)$$

$$NO_2 + \rangle C{=}C\langle \rightarrow O_2N-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot\,(\equiv R\cdot) \qquad ...(12)$$

$$R\cdot + O_2 \rightarrow RO_2^{\cdot} \qquad ...(13)$$

$$RO_2^{\cdot} + NO \rightarrow RO\cdot + NO_2 \qquad ...(14)$$

$$RO_2^{\cdot} + NO_2 \rightarrow RO_2NO_2 \qquad ...(15)$$

$$RO\cdot + NO_x \rightarrow RONO_x \qquad ...(16)$$

$$R\cdot + NO_x \rightarrow RNO_x \qquad ...(17)$$

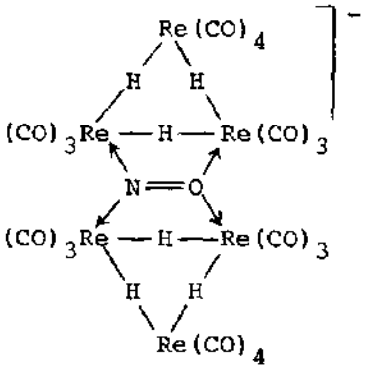
$$NO_x + N \rightarrow N_2 + {}^{x}/_{2}O_2 \qquad ...(18)$$

be decomposed, equation (18), using active nitrogen, generated at atmospheric pressure with a microwave discharge. Activated, carbon-supported alkali metals catalyse the reduction of NO_x by C and CO above 500K;[37] tetraethyl lead does not poison the catalyst.

A mass spectrometric study of the reaction between NH_3 and NO on vanadium oxide catalysts, in the temperature range 300-400°C, is said to be consistent with the production of significant quantities of nitrosamine.[38] The same study found no direct evidence for the formation of N_2H, a species which is implicated in one currently favoured mechanism for the NH_3/NO reaction. Raman spectroscopic data for the solid nitric oxide dimer $(^{16}O^{14}N)_2$ and for two isotopically substituted species, $(^{16}O^{15}N)_2$ and $(^{18}O^{15}N)_2$, have been recorded and analysed.[39] The data have necessitated revised assignments of the fundamentals as well as revised calculations of force constants for cis-N_2O_2. Irradiation at 220-320nm causes cis-N_2O_2, at 13 to 20K in an Ar matrix, to photodissociate to N_2O and oxygen atoms.[40] Among the reactions of oxygen atoms generated in this way those with NO or cis-N_2O_2 were found to produce NO_2, asym-N_2O_3, and sym-N_2O_3 (probably two conformers). Sulphur atoms generated by u.v. photolysis of OCS were found to react with NO and cis-N_2O_2 giving SNO and SN_2O_2, apparently as S(O)N·NO and ONSNO. The heats of combustion and vapourisation of trans-di-tert-butyl hyponitrite have been used to calculate ΔH_f^o to be -41.3 ± 2.9 kcal mol^{-1}.[41] From additivity relationship the authors estimated ΔH_f^o (trans-HON=NOH) to be 3.1 ± 3.1 kcal mol^{-1}, a value in good agreement with published MO calculations.

E.s.r. studies have shown that u.v. irradiation of titanium oxide, grafted on to porous Vycor glass, in the presence of N_2O leads to the formation of N_2O^- anion radicals:[42] on addition of O_2 at 77K the signal due to N_2O^- disappears and is replaced by that for O_2^-. Nitrous oxide selectively oxidises CH_4, to MeOH and HCHO, over molybdenum-on-silica in the presence of water vapour.[43]

The reaction between $NOBF_4$ and $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ in CH_2Cl_2 produces the novel anionic species, $[\{Re_3(\mu\text{-}H)_3(CO)_{10}\}_2(\mu_4\text{-}\eta^2\text{-}NO)]^-$, (5), containing a nitrosyl ligand uniting two triangular clusters.[44] Johnson et al.[45] have described the reaction of $NOBF_4$ with $[HRu_3(CO)_{11}]^-$ to a μ_2-NH_2



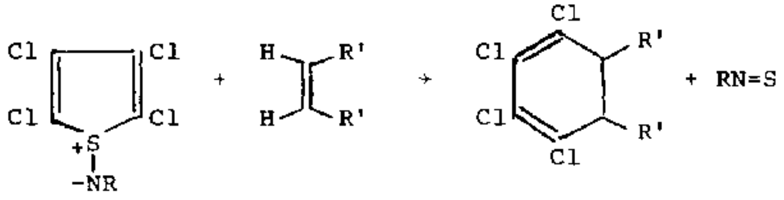
(5)

complex, $[HRu_3(CO)_{10}NH_2]$. Hydrogen was reported to react with a μ_2-bridging NO ligand in $[HRu_3(CO)_{10}NO]$ to form the same μ_2-NH_2 complex as well as $[H_2Ru_3(CO)_9NH]$, containing a μ_3-NH group.

The ^{15}N chemical shift of bent nitrosyl ligands bonded to cobalt are strongly deshielded, by 500-800 ppm., relative to comparable linear nitrosyls.[46] Nitrogen-15 n.m.r. evidence has been presented, by Mason and coworkers,[47] for the rapid intramolecular interconversion in solution of bent and linear nitrosyl ligands in $[RuCl(NO)_2(PPh_3)_2]BF_4$.

5.1.6 Bonds to Sulphur, Selenium or Tellurium

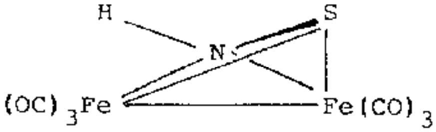
Thiophene S,N-ylides react readily with electron-rich dienophiles yielding adducts formed by the extrusion of acyl- and sulphonyl-thionitroso compounds, equation (19).[48] In the absence of a trapping reagent, e.g. mono- or di-ene, the highly reactive thionitroso compounds, RNS, give a mixture of products. Herberhold and Bühlmeyer[49] have described the synthesis of the



...(19)

R = CO_2Et, CO_2Ph, or $SO_2C_6H_4Me$-p : R' - various.

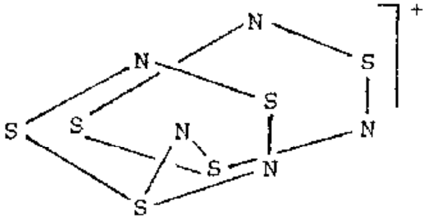
binuclear complex (6) in which the six-electron sulphur imide group has been stabilised by the $Fe_2(CO)_6$ moiety. The reaction of $(Ph_3P)_2(CO)_2RuCl_2$ with $S_2N_2.2AlCl_3$ generates



(6)

$[(Ph_3P)_2(CO)_2(S_2N_2)RuCl]^+AlCl_4^-$ in which c-S_2N_2 functions as an N donor to Ru.[50]

Studies of NH_3 or methylamines with SO_2 in Ar and N_2 matrices have been reported by Sass and Ault.[51] The $SO_2.2NH_3$ adduct was observed spectroscopically for the first time and i.r. spectroscopic assignments were given for the methylamine:SO_2 1:1 adducts. The reaction of $S_2N^+AsF_6^-$ and S_4N_4 in SO_2 yields $(S_3N_2)_2N^+AsF_6^-$ in good yield.[52] This cation (7) is the first example of a mono-bridged bicyclic sulphur-nitrogen cation: the



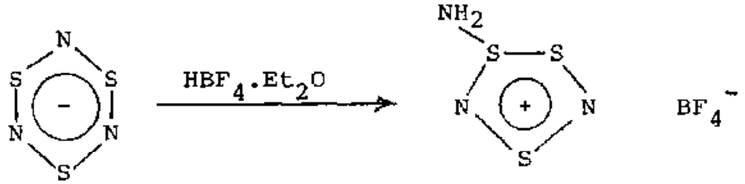
(7)

structure was determined by single crystal X-ray methods and reveals a cation structure with essentially eclipsed S_3N_2 rings. The cation disproportionates slowly in solution in SO_2, according to equation (20), and reacts with azide ion to give polysulphur

$$2(S_3N_2)_2NAsF_6 \xrightarrow{SO_2} 2S_4N_3AsF_6 + S_4N_4 \qquad \ldots(20)$$

nitride. The radical ion commonly encountered in the chemistry of sulphur-nitrogen cations has been identified in solution as $S_3N_2^{+\cdot}$ as a result of isotopic (^{15}N, ^{33}S) labelling experiments.[53] The symmetry was described as C_{2v} and the $^2A_2$ ground state of this π radical is such that the unpaired electron is in an orbital with

30% N and 70% S p orbital character. Protonation of $S_3N_3^-$ by HBF_4-Et_2O has been shown to produce the ring-contracted S-amino thiodithiazyl cation (8), equation (21), which was isolated and



(8) ...(21)

characterised by X-ray methods as the BF_4^- salt.[54]

The gas-phase core binding energies of NSF, NSF_3 and several compounds of the type NSF_2R and F_2SNR have been determined.[55] Qualitative interpretation of the data shows that $N(p\pi)\rightarrow S(d\pi)$ bonding is probably more important in the NSF_2R compounds and in NSF_3, and that the N atom of NSF_3 is more negatively charged than that of NSF. The HOMOs of NSF and NSF_3 have principally N 2p character and are stabilised by interaction with a higher lying S 3d orbital. Zirz and Ahlrichs[56] have reported the results of their calculations on the electronic structures of SN^+, NSF, NSF_3, $HNSF_x^+$ (x = 1 or 3), and $MeNSF^+$.

Reactions of SF_4=NF with oxidising agents (e.g. $ClOSO_2F$) or F^- ion sources (e.g. $CF_3(CO)F$) give cis-$SF_4(OSO_2F)NFCl$ and $SF_5NF(COCF_3)$, respectively.[57] The intermediate species with F^- ion sources is believed to be SF_5NF. SF_4=NF reacts with F_2C=NF in two distinct stages, reaction (22), depending on whether KF

$$SF_4{=}NF + F_2C{=}NF \xrightarrow{KF} F_5S{-}NF.CF{=}NF \xrightarrow{CsF} F_5S{-}N{=}NCF_3 \qquad ...(22)$$

or the more active CsF is used as catalyst. The reaction of HCN with $Xe(OMF_5)_2$, M = Se or Te, yields $F_5M{-}N{=}C{=}O$, reaction (23), presumably via $F_5MOXeCN$ and F_5MOCN.[58] This route provides the first synthesis of the explosively unstable, selenium(VI) isocyanate. As a result of the smaller SeNC angle (117°) the

$$Xe(OMF_5)_2 + HCN \rightarrow HOMF_5 + F_5MNCO + Xe \qquad ...(23)$$

structure could not be established by i.r. spectroscopy but rather by electron diffraction.

5.1.7 Bonds to Nitrogen

Schmidt's "Hydrazine and its derivatives" has been reviewed by Sisler:[59] Smith's book on hydrazine and related compounds will be mainly of interest to organic chemists.[60] Hydrazine is quantitatively oxidised to N_2 by periodate in weakly acidic solution.[61] The kinetic measurements were successfully accounted for by considering five-component reactions. Quantitative aspects of the photo-oxidation of N_2H_4 in HNO_3 and $HClO_4$ media by the uranyl ion have been investigated;[62] they are of possible interest to those concerned with reprocessing nuclear fuel.

1,2-Disubstituted hydrazines react with $O_2\cdot^-$ in aprotic media and in the gas phase to produce the anion radical of the 1,2-disubstituted azocompound.[63] The latter is cleanly oxidised to the pure azo compound when exposed to O_2. The combined reactions offer a catalytic process with turnover numbers >200, reaction (24). Dilworth and coworkers[64] have

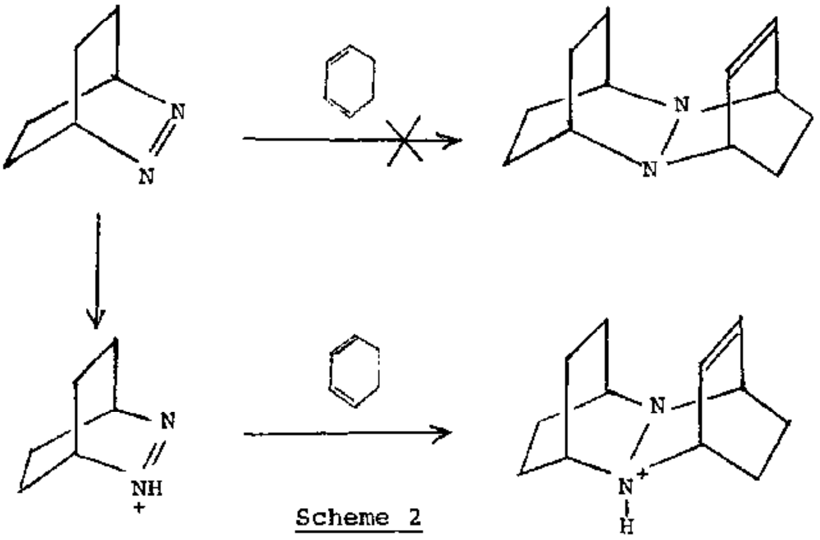
$$\mathrm{RNH{\cdot}NHR} + O_2 \xrightarrow{O_2\cdot^-} \mathrm{RN{=}NR} + H_2O_2 \qquad \ldots(24)$$

$$(\mathrm{R = Me\ or\ Ph})$$

reported the use of $(Me_3Si)_2NN(SiMe_3)_2$ as a source of dinitrogen for metal complexes; thus reaction with $NbCl_5$ in THF gives high yields (ca. 80%) of $[NbCl_3(THF)_3N_2]$. The hydrazine derivative can also function as a simple reducing agent and will reduce $[MoCl_4L_2\}$ to $MoCl_3L_3$, L = MeCN or THF.

Nelson et al.[65] have shown that protonation of bicyclic azo compounds can enhance their dienophilic character, Scheme 2.

A binuclear tungsten complex containing the previously unreported μ-η^2,η^2-$NHNH^{2-}$ has been isolated by Schrock and coworkers.[66] The complex $[W(NPh)Me_3]_2(\mu\text{-}\eta^1,\eta^1\text{-}NH_2NH_2)(\mu\text{-}\eta^2,\eta^2\text{-}NHNH)$ was formed in the reaction of $[W(NPh)Me_4]$ with N_2H_4. The parent 1,1-diazene, $H_2N{=}N$, has been produced in low temperature matrices (<90K) by irradiation of carbamoyl azide.[67] This diazene is blue, whereas the 1,2-isomer is yellow, and decomposes quantitatively when photolysed at 80K to H_2 and N_2. A silylated triazene, stable up to 150°C, has been prepared by reaction (25):[68] the new compound shows proton migration between the outer nitrogens, $\Delta G^{\ddagger} = 78\,kJ\,mol^{-1}$ at 55°C. The acid-

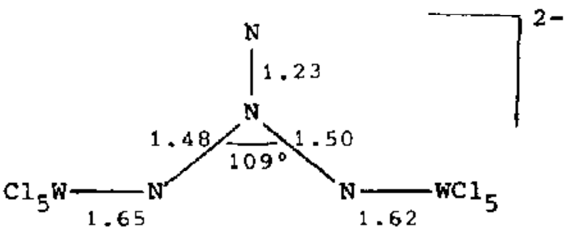


Scheme 2

$$ {}^{t}Bu_3Si\text{-}N{=}N{=}N \xrightarrow[\text{2. MeOH}]{\text{1. } {}^{t}Bu_3SiNa} {}^{t}Bu_3Si\text{-}N{=}N\text{-}NH\text{-}Si{}^{t}Bu_3 \qquad \ldots(25) $$

catalysed decomposition of 1,3-di-^{n}butyl-3-methyltriazene in aqueous buffer has been investigated.[69] The data were said to support the view that a fast, reversible protonation of the triazene is followed by a rate-determining heterolysis to $^{n}BuN_2^{+}$ and $^{n}BuMeNH$. Evidence for similar, specific acid catalysis of other triazenes was presented. Dehnicke et al.[70] have reported the crystal structure at -40°C of a μ-isotetrazenido(4-) complex of W(VI), formed by reaction (26). The geometry of the bridging

$$ 2Ph_4AsCl + WNCl_3 + WN_3Cl_5 \rightarrow (Ph_4As)_2[Cl_5W(\mu\text{-}N_4)WCl_5] \qquad \ldots(26) $$



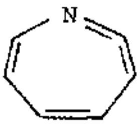
ligand is nearly symmetrical (see above) however the refinement for C and N atoms in the structure used only isotropic temperature factors.

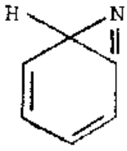
Accurate structural data on covalent azides are scarce owing to the explosive nature of such compounds. Christe et al.[71] have determined the geometric structure of gaseous CF_3N_3 from a combined analysis of electron diffraction intensities and microwave spectroscopy. The molecule adopts a staggered conformation and bond lengths and angles for CF_3N_3 and some other azides are collected in Table 1. A study of the quantum yields, ϕ, for the disappearance of PhN_3 in MeCN solution has indicated a chain decomposition mechanism:[72] thus ϕ increases from 0.5 to 3000 as the concentration increases to 0.2M. The branching chain mechanism may involve not only phenylnitrene but also 1,4-tetraazadiene or triaza-species. A new photochemical study of PhN_3 by laser-flash photolysis in inert or nucleophilic solvents indicates that there is a relatively long-lived precursor to the triplet phenylnitrene.[73] Nucleophilic solvents react with this singlet state intermediate, probably the dehydroazepine, (9),

Table 1. Principal Geometric Parameters (Å and deg.) of some Azides, XN_3, studied in the Gas Phase.

	HN_3[b]	CH_3N_3[c]	Me_3SiN_3[d]	ClN_3[e]	NCN_3[f]	CF_3N_3[g]
$X-N_\alpha$	1.015(15)	1.468(5)	1.734(7)	1.745(5)	1.355(2)	1.425(5)
$N_\alpha-N_\beta$	1.243(5)	1.216(4)	1.198(8)	1.252(10)	1.261(2)	1.252(5)
$N_\beta-N_\omega$	1.134(2)	1.130(5)	1.150(11)	1.133(10)	1.121(2)	1.118(3)
$XN_\alpha N_\beta$	108.8(4.0)	116.8(0.3)	128.0(1.6)	108.7(0.5)	114.5(0.2)	112.4(0.2)
$N_\alpha N_\beta N_\omega$	171.3(5.0)	180^h	180^h	171.9(0.5)	169.2(1.6)	169.6(3.4)
τ[a]		35.0(7.0)	24.0(5.0)			0.0

[a] Torsional angle of group X around X-N bond. τ = 0° corresponds to staggered position. [b] r_s values, [c] r_a values, [d] r_a values, [e] r_s/r_o values, [f] r_α values, [g] r_{av} values. [h] Estimated value.

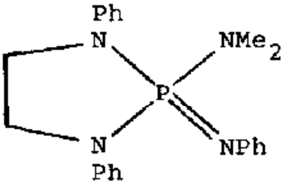

(9)


(10)

although it is in equilibrium with the singlet nitrene most likely forming the azirine, (10), first. The photochemistry of other aryl azides was also investigated.

5.1.8 Bonds to Phosphorus

The crystal and molecular structure of $PF_2(NH_2)$ have been determined at 95K in order to resolve the conflicting structures deduced earlier from microwave spectroscopy and electron diffraction.[74] The coordination of the nitrogen was shown to be pyramidal and the torsion angle calculated to be 74°: the N-P distance is 1.639Å. The gas phase molecular structure of $PF_3(NH_2)_2$ at 50°C has been determined by electron diffraction.[75] As had been predicted the π-donor NH_2 groups are placed equatorially with the donor orbitals in the equatorial plane, thus maximising π overlap with the P atom. Evidence for some P=N character was inferred from the bond length, 1.65Å, and the restricted rotation about this bond. Iminodiazophospholane, (11), has been shown by X-ray methods to have the structure shown,



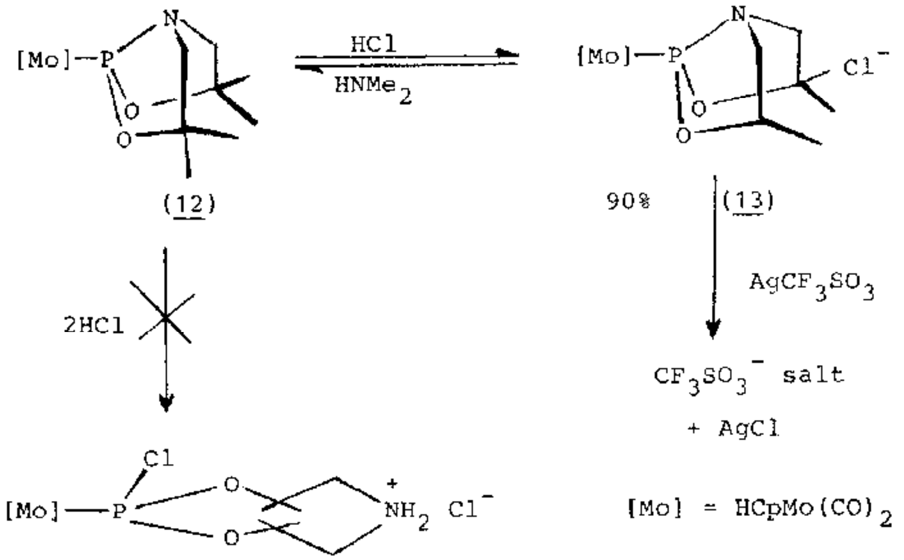
(11)

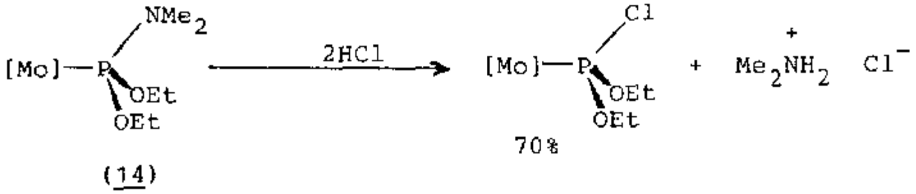
with a very short P=N(Ph) bond, 1.539Å.[76]

Riess et al.[77] have shown that the phosphorammonium salt (13) is formed by N-protonation of the coordinated bicyclic phosphine in complex (12). By contrast the P-N bond in (14) is cleaved by HCl under comparable conditions.

5.1.9 Bonds to Halogens

Nitrogen trifluoride has been shown to form a type I clathrate hydrate;[78] dissociation pressure 16.5atm. at 0°C. It was inferred that NF_3 molecules can be incorporated in both small and large cages and also that reorientation of the molecules about the C_3 axis was taking place at 1.6K. The addition of ONF_3 to trifluoroethenes in the presence of catalytic amounts of a Lewis acid produces new compounds containing the N,N-difluorohydroxyl-





amino group, equation (27).[79] The known ONF_2^+ cation was thought to function as the active intermediate. There is a rapid

$$\begin{aligned} F_2C{=}CFR_f + ONF_2^+\ AsF_6^- &\rightarrow [F_2C{-}CFR_f{-}ONF_2]^+\ AsF_6^- \\ &\qquad\qquad \Big\downarrow ONF_3 \\ &\quad CF_3CFR_fONF_2 + ONF_2^+\ AsF_6^- \qquad \ldots(27) \end{aligned}$$

conversion of NO to ONF by ONF_3.[80] A free-radical mechanism involving $F_2NO\cdot$ was proposed, equations (28) and (29).

$$NO + ONF_3 \rightarrow ONF + F_2NO \qquad \ldots(28)$$

$F_2NO\cdot + NO \rightarrow 2ONF$ ...(29)

The low-temperature i.r. spectra of thiazyl fluoride show no indication of an ionised form in the solid state.[81] The relatively unstable adducts with BF_3, PF_5, and AsF_5 were, however, characterised by this means. The structure of gaseous $(ClNSF_4)_2$ has been investigated by electron diffraction: the 4-membered SNSN-ring is planar with the out-of-plane Cl atoms trans.[82] The extremely short N-Cl bond lengths, 1.638(10)Å, were rationalised in terms of the large, 122°, SNCl bond angles.

DesMarteau and coworkers[83] have succeeded in preparing $CF_2{=}NBr$ by the fluoride ion-promoted bromination of FC≡N, reaction (30).

$$FCN + MF[\rightarrow F_2C{=}N^-M^+] \xrightarrow[22°C]{Br_2} F_2C{=}NBr + MBr \qquad ...(30)$$

M = K,Rb,Cs.

Further reaction of $CF_2{=}NBr$ occurs with the formation of the known CF_3NBr_2. The caesium fluoride-promoted bromination of $CF_2{=}NCl$ has been found to proceed according to reaction (31):[84] this

$$CF_2{=}NCl \xrightarrow{Br_2/CsF} CF_3NBrCl + CF_3NBr_2 \qquad ...(31)$$

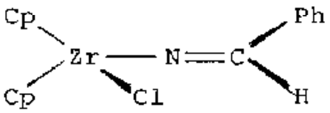
$$CF_3NCl_2 \xrightarrow{Br_2/CsF} CF_3NBrCl \xrightarrow{Br_2/CsF} CF_3NBr_2 \qquad ...(32)$$

represents the first example of a stable compound containing the NBrCl group. The formation of this product can be understood in terms of the bromination of CF_3NCl; however, the NBr_2 compound was shown to arise from the bromination, perhaps with $CsF.Br_2$, of the NBrCl compound. Thus the conversions in (32) are claimed to support this view.

Solutions of NI_3.py in pyridine have been investigated by Raman spectroscopy: it was concluded that chains of NI_4 tetrahedra are present even in the presence of excess base.[85]

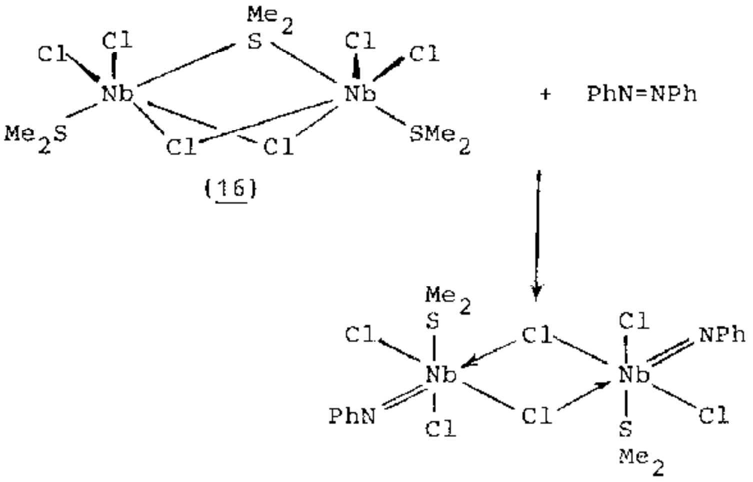
5.1.10 Bonds to Transition Metals

An unusually short Zr-N bond (2.013(5)Å) has been reported for (15): since the NC bond is 1.259(7)Å and the ZrNC angle is 170.5°



(15)

the authors[86] refer to the compound as an organometallic heteroallene. The dinuclear niobium complex (16) reacts readily with azobenzene, equation (33), to afford the metal imide (17) as red crystals.[87]



(16)

(17)

...(33)

The chemical and electrochemical oxidation of $[Ru(tpy)(bpy)(NH_2CHRR')]^{2+}$, with R = R' = Me, has revealed two consecutive 2-electron processes.[88] The first of these is irreversible and yields the corresponding imine species, reaction (34): the second produces (reversibly) a complex containing the N-alkylideneamide ligand, reaction (35). The X-ray structure of

$$[Ru(tpy)(bpy)(NH_2CHMe_2)]^{2+} \xrightarrow{-2e^-} [Ru(tpy)(bpy)(NH{=}CMe_2)]^{2+} + 2H^+ \quad ...(34)$$

$$[Ru(tpy)(bpy)(NH{=}CMe_2)]^{2+} \underset{+2e^-}{\overset{-2e^-}{\rightleftharpoons}} [Ru(tpy)(bpy)(NCMe_2)]^{3+} + H^+ \quad ...(35)$$

the $4e^-$ oxidation product, as the perchlorate monohydrate, shows a linear $Ru{=}N{=}CMe_2$ linkage with Ru-N distance 1.831(10)Å. The ^{15}N chemical shifts of some stable hydrazido(2-)-complexes as well as of imido- and nitrido- complexes have been investigated;[89] they are potentially valuable in connection with studies of the reduction processes of transition metal dinitrogen complexes.

5.2 PHOSPHORUS

5.2.1 Phosphorus, Polyphosphines and Phosphides

No other species are involved in the P_4-$2P_2$ equilibrium up to 1470K according to recent photoelectron spectroscopy and, in agreement, MNDO calculations show deep troughs in the hypersurface at P_4 and P_2.[90] In continuation of this work, calculations point to a high energy of activation (ca. 100 kcal.) for dimerisation to P_8 and there is similarly no evidence for the addition of P_2 to P_4 to give P_6.[91]

There are analogies to the disproportionation of P_4 to phosphine [P(-3)] and hypophosphite [P(+1)] in the presence of hydroxide in related reactions with softer bases such as CN^-, Ph_3Sn^- and alkali metal phosphites, phosphonites and phosphinites.[92] The overall reaction is represented in equation (36) and specifically with

$$n+1/4\ P_4 + 2X^- \rightarrow PX_2 + P_n^- \qquad \ldots(36)$$

X = CN^-, $P(CN)_2^-$ and a polyphosphide are obtained from respectively the P(+1) and P(-3) components. Similarly, with a phosphorus:phosphinite ratio of 1:2.4, the products are the salt $M[O{\cdot}PR_2{:}P{\cdot}PR_2{:}O]$ and the polyphosphide M_3P_7 in a 3:1 ratio. The disproportionation product, $Li[OPPh_2{:}P{\cdot}PPh_2{:}O]$, has been investigated by single crystal X-ray diffraction. Reaction with base can, however, take place without disproportionation (equation 37) as shown by the formation of $M[O{\cdot}PR_2{:}P{\cdot}P{:}PR_2{:}O]$,

$$\tfrac{1}{2}P_4 + 2X^- \rightarrow P_2X_2^{2-} \qquad \ldots(37)$$

where M = Li or Na and R = Et or Ph, from a phosphorus: phosphinite reaction where the ratio is increased to 1:4. Phosphorus disproportionation again occurs in the P_4-$LiCH_2PPh_2$(tetramethylethylenediamine) reaction, but the oxidation product is an unidentified red oil.[93] The reduction product is the polyphosphide, $[Li(tmeda)]_3P_7$ whose structure shows the expected P_7 cage with the lithium ions coordinated to two nitrogens of the substituted ethylenediamine molecule and two of the di-coordinated phosphorus atoms of the cage.

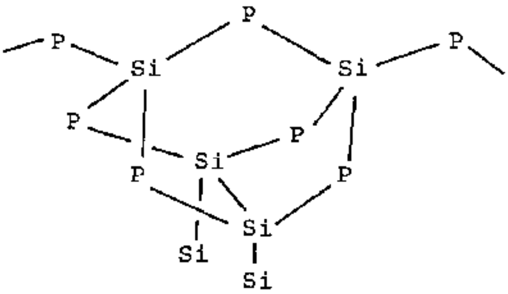
Black semi-conducting K_4P_6 can be obtained by heating a 2:3 mixture of the elements to 870K.[94] The compound occurs in two modifications, the α-form stable below 870K and the β stable above 870K, and both have been investigated by single crystal X-ray diffraction. The structures are defect variants of the hexagonal AlB_2 type; i.e. $K_4P_6\square_2$, and contain P_6 rings. The P-P distances, 2.150Å in the α-form and 2.155Å in the β, are shorter than normal single bonds and represent a situation where one π-bond is delocalised over six bonds. Thermal decomposition gives K_3P_7 and this also results in reactions with benzophenone; KCl is eliminated on reaction with Me_3SnCl giving a mixture of $P_7(SnMe_3)_3$ and $P(SnMe_3)_3$.

Related tetraphosphides have also been isolated either from direct combination of the elements or by decomposition of the appropriate diphosphide.[95] The compounds obtained include Eu_3P_4, Sr_3P_4 and Ba_3P_4; single crystal studies indicated the presence of P_4^{6-} chains in which the central P-P distance (2.32Å) is longer than the peripheral bonds (2.23Å).

Knudson effusion methods have been used to measure the vapour pressures of the europium phosphides EuP_7, EuP_3, EuP_2 and Eu_3P_4,[96] and a variety of methods has been used to show that of the binary cadmium phosphides, CdP_2 is stable below 870K and Cd_3P_2 above this temperature.[97]

A redetermination of the ZnP_2 structure shows that it is isostructural with the corresponding arsenide with both zinc and phosphorus atoms in tetrahedral coordination.[98] The former to four phosphorus atoms at 2.39Å(mean) and phosphorus to two zinc and two phosphorus atoms (2.20Å). The phosphorus atoms are, in fact, arranged in semispiral chains parallel to the c axis which are interconnected by zinc atoms.

The compound K_2SiP_2, obtained from a high temperature reaction between the elements in a 2.2:1:2.2 ratio, crystallise in the Ibam space group and has a structure based on SiP_4 tetrahedra, which share common edges to give chains of condensed Si_2P_2 rings.[99] The Si-P distances are all equal (2.272Å) with P-Si-P angles of 95.6, 120.0 and 113.7°; the Si-P-Si angles are 84.4°. Also obtained from the elements heated ultimately to 1050°C is the new Zintl phase, $Ba_3Si_4P_6$, shown by X-ray diffraction to contain Si_4P_5 (18) cages interconnected by phosphorus atoms and Si-Si bridges into a corrugated two dimensional network.[100] The cage structure is similar to that in P_4S_5 if phosphorus atoms occupy the silicon positions; P-Si distances range between 2.243 and 2.316Å.



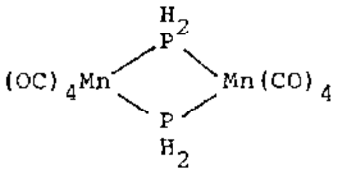
(18)

The ternary compounds ALi_3X_2, where A = Y, La or Nd and X = P, As, Sb or Bi, have structures from X-ray and neutron diffraction data based on that of $CaAl_2Si_2$.[101] Here two lithium atoms occupy the aluminium sites in the distorted tetrahedral holes in the X atom lattice while the lanthanoid atom and the third lithium populate the slightly distorted octahedral holes of the X atom lattice. AEuX ternaries, where A = Cu, Ag or Au and X = P, As, Sb or Bi, have also been prepared from the elements and have a modified Ni_2In structure.[102]

Ab initio effective potential calculations at both the SCF and CI levels have been reported for MX_3, MX_4^+, MX_4^-, MX_5^+ amd MX_6^-, where M = P, X = H or Cl and M = As, X = H.[103] The Lewis acidity of MX_5 is also discussed and the activation energies for Berry pseudo-rotation in PH_5 and AsH_5 evaluated as 2.0 and 2.5 $kcal.mol^{-1}$ respectively.

Structures for the two phosphine complexes $[(OC)_4MnPH_2]_2$ and $[(OC)_4MnPH_2]_3$ show the presence of respectively a planar, centrosymmetric four membered Mn_2P_2 ring (19) and a six membered Mn_3P_3 (20) in the twist conformation.[104] The related $(CpNiPH_2)_2$ complex is structurally similar to (20) but with a chair type ring.

Recent experiments point to the insertion of hexafluoroisopropylidenimine, $(CF_3)_2C{:}NH$, into the P-H bonds of the methylphosphines,



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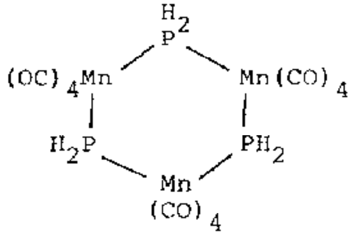
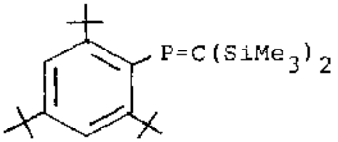


(20)

Me_nPH_{3-n} for n = 0-2.[105] The products are $Me_nPH_{2-n}C(CF_3)_2NH_2$ but with trimethylphosphine itself reaction gives the oxidation product $Me_3P{:}NCH(CF_3)_2$.

A comprehensive review on the history and current states of the problem of double bond formation between the heavier main group elements has appeared.[106] A range of new π-bonded two-coordinate species of the type RM:MR has been synthesised.[107] The compounds include $(Me_3Si)_3CP{:}PC(SiMe_3)_3$ (21), $^tBu_3C_6H_2P{:}PC(SiMe_3)_3$ (22), $^tBu_3C_6H_2P{:}PCH(SiMe_3)_2$ (23), $^tBu_3C_6H_2As{:}AsCH(SiMe_3)_2$ (24), and the mixed species, $^tBu_3C_6H_2P{:}AsCH(SiMe_3)_2$ (25) and $^tBu_3C_6H_2P{:}SbCH(SiMe_3)_2$ (26). Compound (21) results when $(Me_3Si)_3CPCl_2$ is reduced with sodium naphthalenide in THF at -78°C, while a similar reduction of a mixture of $(Me_3Si)_3CPCl_2$ and $^tBu_3C_6H_2PCl_2$ leads to (22) together with the two symmetrical diphosphenes. Compound (21) was also obtained by treating $(Me_3Si)_3CPCl_2$ with $(Me_3Si)_3CLi$, but attempts to produce (22) by a similar reaction of the lithium derivative with a mixture of $^tBu_3C_6H_2PCl_2$ and $(Me_3Si)_3CPCl_2$ were not successful and led instead to the new phospha-alkene (27). The unsymmetrical diphosphene



(27)

(23) and the mixed compounds (25) and (26) were obtained by HCl elimination in the presence of DBU from $^tBu_3C_4H_2PH_2$ and $(Me_3Si)_3CMCl_2$ where M is respectively P, As or Sb. X-ray structures for (21) and (25) show the presence of two independent half molecules in the asymmetric unit of the former with P-P

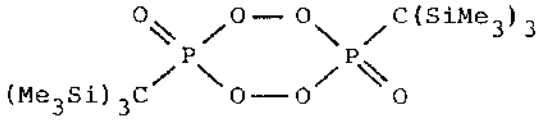
distances of 2.004 and 2.014Å; the geometry about the P=P bond is planar and trans. The P-As bond in (<u>25</u>) is 2.124Å consistent with the presence of a double bond. ^{31}P n.m.r. and electronic spectra have also been measured, the latter showing bands ascribed to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions. A new symmetrical diphosphene, $(Me_3Si)_2CH{\cdot}P{:}P{\cdot}CH(SiMe_3)_2$ results when the germyl phosphine $(Me_3Si)_2CH{\cdot}PHGeCl_3$ is treated with DBU.[108]

Ab initio and extended Hückel calculations have been reported for RN:NR, RP:PR and RR'Si:SiR'R where R = NH_2 showing, inter alia, that π bond orders to peripheral atoms are weak, resulting in low energy barriers to rotation.[109] HeI photoelectron spectra are now available for $^tBu_3C_6H_2P{:}PC_6H_2{}^tBu_3$ and $^tBu_3C_6H_2P{:}PC_6H_2Me_3$[110] together with resonance Raman spectra for the former[111] and $(Me_3Si)_3CP{:}PC(SiMe_3)_3$.[112] The P=P stretching mode is difficult to observe directly in the infrared and values of 610cm^{-1} and 595cm^{-1} respectively derived from resonance Raman data are particularly useful; some degree of mixing with P-C modes is however to be expected.

As well as being susceptible to attack by electrophiles, diphosphenes also react with nucleophiles such as MeLi.[113] The tri-t-butylphenyl derivative, ArP:PAr (<u>28</u>) gives a deep red solution on treatment with MeLi in THF solution containing the $(ArP{\cdot}PArMe)^-$ anion. Further reaction with methanol gives the diphosphine ArHP·PArMe while the two oxides, $ArPH_2O$ and ArMePHO, result from reactions with LiOH. N.m.r. evidence points to the formation of mono- and dicationic species, $ArP{=}\overset{+}{P}ArAg$ and $AgAr\overset{+}{P}{=}\overset{+}{P}ArAg$, where the tri-t-butyl phenyl compound (<u>28</u>) reacts with $Ag(SO_3CF_3)$ in THF solution.[114] Because of the isolobal relationship between H^+ and Ag^+, these compounds are important models for studies on the protonation of the P=P double bond.

In the complexes, (<u>28</u>).$Fe(CO)_4$ and (<u>28</u>).$Ni(CO)_3$, obtained from (<u>28</u>) and $Fe_2(CO)_9$ and $Ni(CO)_4$ respectively, the ligand behaves as an η^1 group and bonds via the phosphorus lone pair.[115] The P-P distance shows a small increase to 2.050Å from that (2.034Å) in the uncomplexed ligand. Complexes in which an $Fe(CO)_4$ group is attached to the phosphorus or arsenic atom can be isolated from the reaction of $Fe_2(CO)_9$ with $^tBu_3C_6H_2As{:}PCH(SiMe_3)_2$ and in the chromium carbonyl complex, $^tBu_3C_6H_2As{:}AsCH(SiMe_3)_2.Cr(CO)_5$ there is again η^1 coordination via the silicon substituted arsenic atom.

Ozonolysis of $(Me_3Si)_3C{\cdot}P{:}P{\cdot}C(SiMe_3)_3$ at -80°C consumes two mols of ozone to give a product which is stable to 40°C.[116] As cleavage of the P-P most probably occurs, a cyclic diperoxide structure (29) is considered to be the most likely.



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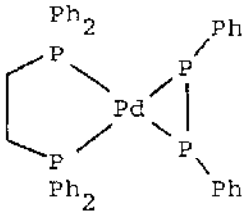
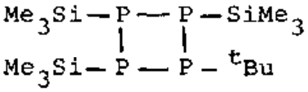


(30)

Contrary to the η^1 type ligand behaviour of the diphosphene above, a complex (30) has been isolated in which the unstable PhP:PPh coordinates as an η^2 species.[117] The compound, which results from treatment of the bis(diphenylphosphanyl)ethane complex, cis-$PdCl_2$(dppe), with Li_2(PhPPPh), contains an almost planar PdP_4 system. The Pd-P distances are 2.366Å and the P-P separation, 2.121Å, points to the retention of a π-component with a bond order of approximately 1.5. Further reaction with $W(CO)_5$.THF leads to attachment of two $W(CO)_5$ groups via the lone pairs of the coordinated phosphene, and an increase in the P-P bond distance to 2.186Å.

A novel nickel cluster compound, formulated on n.m.r. and X-ray evidence as $Ni_5(CO)_6[(Me_3Si)_2CHP:PCH(SiMe_3)_2]_2Cl$, results from the addition of $P[CH(SiMe_3)_2]Cl_2$ to $Na_2[Ni_6(CO)_{12}]$.[118] Each diphosphene ligand interacts with two nickel atoms (mean Ni-P 2.18Å) and the P-P distances in the ligands, 2.085 and 2.098Å, point to retention of the double bond character. A significant feature of the structure is the cis configuration for the coordinated diphosphene; the isolated compounds invariably show trans geometry.

Current knowledge in the general area of phosphorus chain and ring compounds has been reviewed.[119] The cyclo-triphosphine, $(^tBuP)_3$, can be cleaved by halogens to the open chain species, $X(^tBuP)_3X$ where X = Cl, Br or I;[120] possible configurations were discussed and related to n.m.r. data and it was shown that specific diastereomers could be reduced stereospecifically to the corresponding phosphine by $LiAlH_4$. Dilithiation takes place on reaction with butyl-lithium and subsequent treatment with Me_3SiCl leads to $Me_3Si(^tBuP)_3SiMe_3$.[121] A new member of the cyclotetraphosphine series (31) has been isolated from a reaction of ^{t}BuPCl$_2$ and $P_3(SiMe_3)_5$ in THF solution as intensely coloured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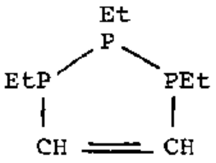

(32)

yellow crystals.[122]

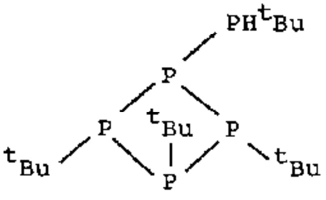
ΔH_o values of 7.8±0.2 and 6.0±0.3 kcal.mol^{-1} obtained from measurements of the equilibria in equations (38) and (39) at 60

$$\tfrac{3}{5}(MeP)_5 \rightleftharpoons (PMe)_3 \qquad \ldots(38)$$

$$\tfrac{4}{5}(MeP)_5 \rightleftharpoons (PMe)_4 \qquad \ldots(39)$$

and 160°C.[123] Fractional distillation of the mixture obtained when $K_2(EtP)_4$ reacts with 1,2-dichloroethylene yields in addition to $(EtP)_3$, the phosphole (32).

Thermolysis of 1,2-di-t-butyldiphosphine, ^{t}BuHP·PH^{t}Bu, gives a complex mixture which includes not only the well known compounds, ^{t}BuPH$_2$, H(^{t}BuP)$_3$H and (^{t}BuP)$_4$, but also two new polyphosphines (33)[124] and (34).[125] The former contains the novel iso-P_5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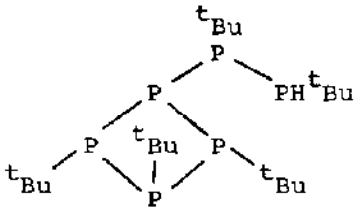
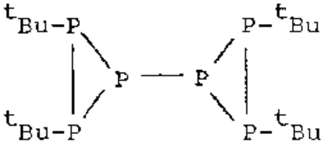

(34)

skeleton; the latter is thought to be formed via compound (33). The new hexaphosphine (35), consisting of two linked three membered rings, has also been reported as the product of coupling between the cyclo-triphosphines (36, X = SnMe$_3$) and (36, X = Cl).[126]

A range of lithium phosphides, including LiP_2H_3, LiP_5H_4, Li_3P_7, Li_2HP_7, LiH_2P_7, LiH_4P_7, LiH_8P_7, LiH_5P_8 and $Li_2H_2P_{14}$, has



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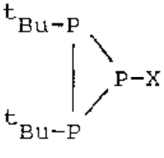
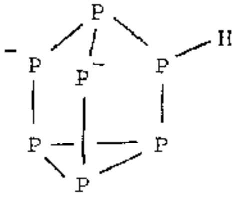
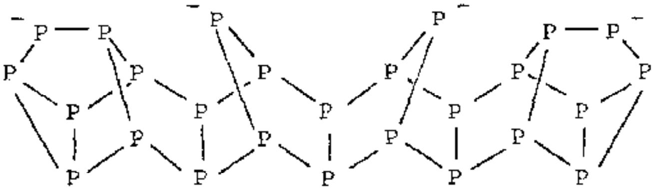


(36)



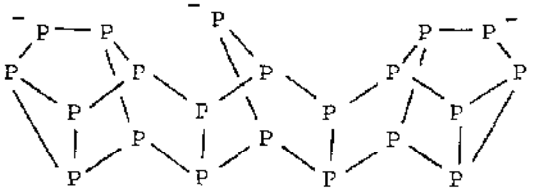
(37)

been identified by ^{31}P n.m.r. spectroscopy as product of the reaction between diphosphine and BuLi in THF solution.[127] One of these compounds, Li_2HP_7, has been isolated and shown by n.m.r. spectroscopy to have structure (37); an alternative preparative route involves the metallation of either LiH_2P_7 or P_7H_3.[128] The dilithium compound however decomposes at room temperature to produce, inter alia, $Li_4P_{26}.16THF$,[129] which from two dimensional n.m.r. spectroscopy is formulated as (38) containing two P_7 and two P_9 units. A further large polyphosphide, Li_4P_{20}, results



(38)

when $LiPH_2$ reacts with white phosphorus,[129] and derivatives of the $P_{21}{}^{3-}$ anion with structure (39) are obtained by treating white phosphorus with a sub-stoichiometric amount of sodium in THF.[130] The compound isolated by crystallisation at -20°C is $Na_3P_{21}.15THF$

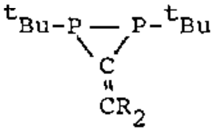


(39)

but other polyphosphides including Na_2P_{16} and Na_2HP_7 are also produced. The lithium salt Li_3P_{21} can be obtained by treating Li_3P_7 with iodine or P_7H_3 with $LiPH_2$.

A range of compounds is also obtained when $RPCl_2$, for R = Me, Et or ^iPr, and white phosphorus mixtures react with magnesium metal again in THF solution;[131] similar compounds result from thermolysis of P_7R_5 in the presence of other phosphines such as P_8R_6 and $(PR)_5$. A number of separation techniques were employed among the compounds isolated were P_9R_5, $P_{10}R_6$, $P_{10}R_4$, $P_{11}R_5$, $P_{12}R_4$, and $P_{13}R_5$.

Substituted methylenediphosphiranes (40, R = H, Me or $4\text{-}ClC_6H_4$) have been obtained for the first time - the methyl and chlorophenyl derivatives are stable - by cyclocondensation between the diphosphine salt $K_2(P^tBu.P^tBu)$ and 1,1-dichlorooolefins.[132] The chlorophenyl derivative from single crystal X-ray data has ca. C_2 symmetry with P-P-C and PCP angles of 52.4 and 75.3° respectively. Full details of the structures of the two diastereomers of the silicon spirocycle (41) are now available with the compounds showing respectively $\bar{4}$ and 2 point symmetry.[133] A novel germanium spirocycle (42) can be isolated from a condensation reaction between two mols of $K_2(P^tBu{\cdot}P^tBu)$ and $GeCl_4$.[134] The dispiro compound (43), containing P_3Si, P_2Si_2 and P_4Si rings with the silicons as spiro atoms, has a structure in which the three rings are almost orthogonal; Si-P bonds vary between 2.233 and 2.317Å.[135]



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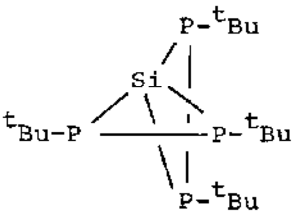

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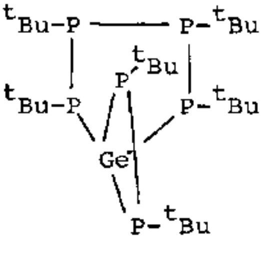

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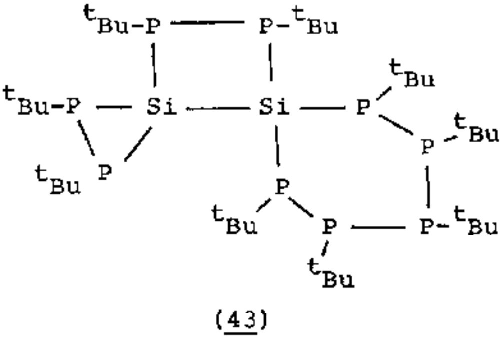


(43)

An unusual complex results when white phosphorus, $Co(BF_4)_2.6H_2O$ and bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$, react in a THF-butanol mixture.[136] The structure (see Figure 1), established by X-ray crystallography, shows the cobalt atom in very distorted octahedral coordination by the ligand $Ph_2PCH_2PPh_2{\cdot}P_4{\cdot}Ph_2PCH_2PPh_2$, which results from the rearrangement of a P_4 molecule into a P_4 chain followed by reaction with two mols of bis(diphenylphosphino)methane. The four unsubstituted phosphorus atoms are attached to the metal atom at distances ranging between 2.281 to 2.305Å and coordination is completed by bonds to phosphorus atoms of the original ligand (2.196, 2.203Å). The central P-P bond in the P_4 chain (2.197Å) is longer than those adjacent (mean 2.17Å) and partial double bond character is assigned to these. The structure is rationalised by considering coordination as involving an η^4 substituted tetraphosphabutadiene group.

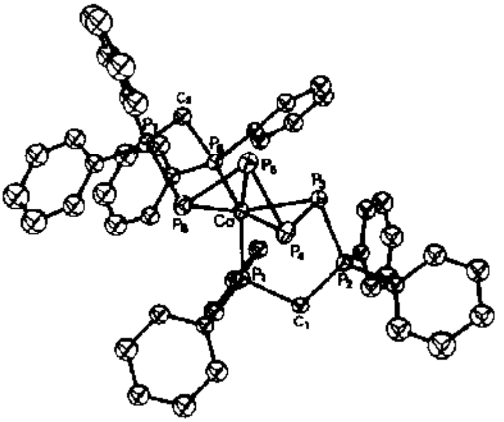
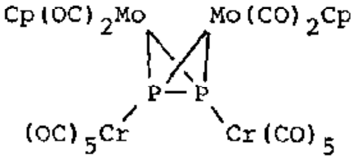


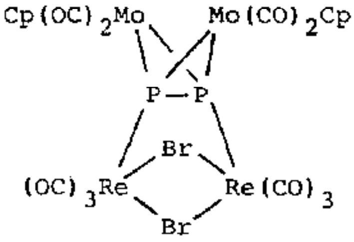
Figure 1. Structure of the $[Co(Ph_2PCH_2PPh_2P_4PPh_2CH_2PPh_2)]^+$ cation (reproduced by permission from J. Am. Chem. Soc., 106 (1984)3667).

Complexes containing coordinated P_2S or P_2Se groups have been synthesised by refluxing a solution of $Co(BF_4)_2.6H_2O$ in ethanol with triphos, $(Ph_2PCH_2)_3CMe$, and either P_4S_3 or P_4Se_3 in benzene.[137] The compounds, which have the stoichiometry $[Co(triphos)P_2X]BF_4.PhH$ where X = S or Se, have been investigated by X-ray methods. Cobalt is in six-fold coordination to three phosphorus atoms of the triphos ligand (Co-P 2.203-2.220Å) and, in a staggered arrangement, to the three atoms in the P_2X group. In the sulphur derivative, the P_2S ligand is disordered about a pseudo-three fold axis giving "Co-P" distances of 2.260, 2.275 and 2.276Å, but while disordering is still present in the selenium analogue, one orientation is preferentially populated giving "Co-P" distances of 2.272 and 2.327Å and a "Co-Se" distance of 2.403Å.

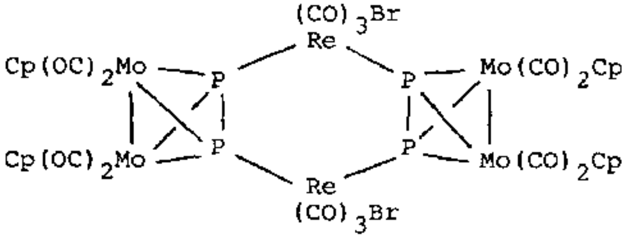
The diphosphorus complex, $Cp_2Mo_2(CO)_4P_2$, on reaction with $Cr(CO)_5(THF)$ or $Re_2(CO)_6Br_2(THF)_2$ gives compounds (<u>44</u>) and (<u>45</u>) respectively, with the latter being converted to (<u>46</u>) in THF solution.[138] X-ray structures are available for both (<u>45</u>) and (<u>46</u>), the latter showing a planar six-membered Re_2P_4 ring and little change in the molecular parameters of the Mo_2P_2 unit on coordination.



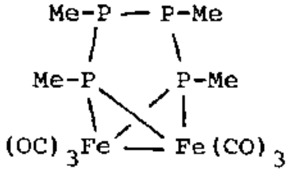
(<u>44</u>)



(<u>45</u>)



(<u>46</u>)



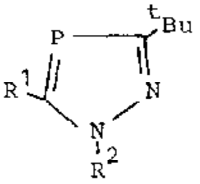
(<u>47</u>)

The triphosphine ring in $(^tBuP)_3Cr(CO)_5$ behaves as a unidentate σ-donor and again there are only small changes in the molecular parameters on coordination.[139] An X-ray structure for compound (<u>47</u>), previously prepared by treating $Fe(CO)_5$ with $(PMe)_5$, shows strong similarities with that of the arsenic analogue $Fe_2(CO)_6(AsMe)_4$.[140] The four Fe-P distances lie between 2.215 and 2.221Å with P-P distances of 2.201, 2.192 and 2.200Å; the nonbonded P---P separation, 2.715Å, indicates a fractional bond between the ends the P_4 chain.

5.2.2 Bonds to Carbon

Coverage in this section follows the previous pattern and is subdivided by oxidation state; within each section multiple bonds between phosphorus and carbon are considered first.

The +3 Oxidation State. The unstable molecules $MeC{\vdots}P$ and $CD_3C{\vdots}P$ have been detected by gas phase i.r. spectroscopy in the pyrolysis products of $EtPCl_2$ and its deuterated analogue.[141] The carbon-phosphorus stretching mode in $MeC{\vdots}P$ occurs at 1558.7 cm^{-1}, and the associated rotational structure has been analysed. 1,3-dipoles such as diazoalkanes, azides, nitrile oxides and nitrilimines undergo cycloaddition with the room temperature stable phospha-alkyne $^tBuC{\equiv}P$.[142] (See reference 155 for related reactions with a phospha-alkene). Diazomethane derivatives, e.g. $R^1R^2CN_2$, where R^1R^2 = H, Me, ^tBu, COPh, CO_2Me, $POPh_2$, etc., lead to diazaphospholes (48) while triazaphospholes (49, R = H, Me, CH_2CN, CO_2Me or $SiMe_3$) are the products of reactions with azides; the nitrile oxide, (mesityl)CNO, and PhC:NNPh lead to respectively



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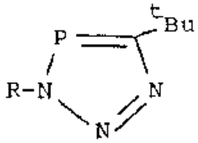

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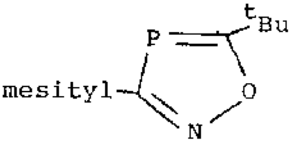

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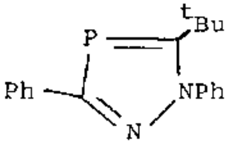
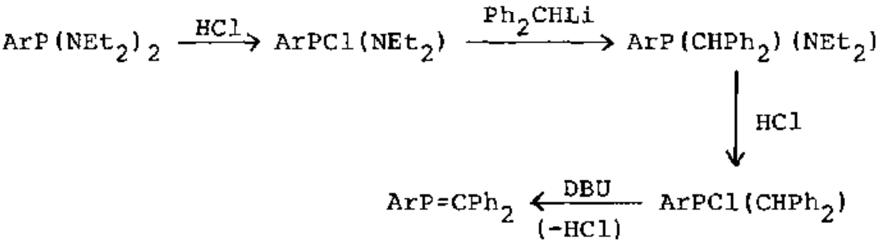


(51)

(50) and (51).

X-ray crystallography has recently shown the presence of a new type of phospha-alkyne coordination in the complex, $Fe_2Pt(Ph_2PCH_2CH_2PPh_2)(CO)_6(^tBuC{\vdots}P)]$.[143] The structure contains a $PtFe_2$ ring with the $P{\vdots}C$ grouping transverse to the Fe-Fe bond; the phosphorus atom is coordinated to all three metal atoms in the ring.

An improved synthesis of the phospha-alkenes, ArP:CPh$_2$ where Ar = mesityl or 2,6-dimethylphenyl, follows the reactions in Scheme 3.[144] The structure of the mesityl compound has been determined



$$\begin{tikzcd}
\mathrm{ArP(NEt_2)_2} \arrow[r, "\mathrm{HCl}"] & \mathrm{ArPCl(NEt_2)} \arrow[r, "\mathrm{Ph_2CHLi}"] & \mathrm{ArP(CHPh_2)(NEt_2)} \arrow[d, "\mathrm{HCl}"] \\
 & \mathrm{ArP{=}CPh_2} & \mathrm{ArPCl(CHPh_2)} \arrow[l, "\mathrm{DBU}", "\mathrm{(-HCl)}"']
\end{tikzcd}$$

Scheme 3

(P=C 1.692Å, mesityl-P-C 107.5°) and HFS calculations point to an important bonding role for phosphorus d orbitals. Previously unknown phospha-alkenes, substituted at carbon by hydrogen and halogen atoms, have been synthesised as shown in equation (40) as a mixture of E and Z isomers,[145] but attempts to convert the product into the isocyanide analogue, $^t\mathrm{Bu_3C_6H_2}\overset{+}{\mathrm{P}}{\equiv}\bar{\mathrm{C}}$, by loss of HX

$$2,4,6\text{-}^t\mathrm{Bu_3C_6H_2PH_2} \xrightarrow[\mathrm{KOH}]{\mathrm{CHX_3}} {}^t\mathrm{Bu_3C_6H_2PH(CX_2H)} \rightarrow {}^t\mathrm{Bu_3C_6H_2P{=}CHX} \quad \ldots(40)$$

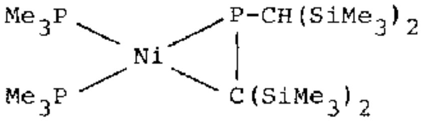
X = Cl or Br.

were unsuccessful. Replacement of CHX$_3$ in equation (40) by CH$_2$Cl$_2$ leads to ^{t}Bu$_3$C$_6$H$_2$P:CH$_2$. The phospha-alkene, ^{t}Bu$_3$C$_6$H$_2$P:CPh(SiMe$_3$), forms an Fe(CO)$_4$ complex on reaction with Fe(CO)$_5$ where the ligand is η^1 bonded and occupies an equatorial site in the trigonal bipyramidal arrangement about iron.

The reaction in equation (41) has been used to prepare three new derivatives where R = (Me$_3$Si)$_2$CH, 2,4,6-^{t}Bu$_3$C$_6$H$_2$ and (Me$_3$Si)$_3$C;

$$\mathrm{ClP{:}C(SiMe_3)_2 + RLi \rightarrow RP{:}C(SiMe_3)_2 + LiCl} \quad \ldots(41)$$

the tri-t-butylphenyl derivative is a solid which X-ray crystallography shows is planar about the P=C bond (1.665Å, C=P-C -10.7°).[146] A curious complex in which the phospha-alkene group behaves as an η^2 system has been generated as one of the products of a complex reaction between $[(Me_3Si)_2CH]_2PNa$ and $(Me_3P)_2NiCl_2$. X-ray diffraction shows structure (52) in which the coordination about nickel is close to square planar; nickel distances to phosphorus and carbon in the three membered ring are 2.239 and

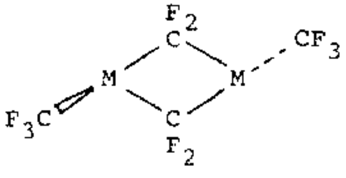


(52)

2.020Å. The P-C(ring) distance, 1.773Å, is midway between the single and double bond values.

Thermolysis of the stannanes, $Me_3SnM(CF_3)_2$ where M = P or As, at 300-340°C leads to the heteroalkenes $CF_3M{:}CF_2$, which can be isolated by quenching the vapour at liquid nitrogen temperature and identified by ^{19}F n.m.r. spectroscopy at -110°C.[147] The compounds readily dimerise giving (53) to (55), the former with trans-CF_3 groups is the most abundant isomer.

Ethynylphospha-alkenes, $RC{\vdots}C{\cdot}P{:}C(SiMe_3)_{2-n}Ph_n$ where R = Me_3Si or Ph and n = 0 or 1, can be obtained in high yield by treating $ClP{:}C(SiMe_3)_{2-n}Ph_n$ with the appropriate alkynyl Grignard reagent.[148] The compounds dimerise to give the diphosphetanes (56, R,R' = Me_3Si or Ph), confirmed by a structure determination



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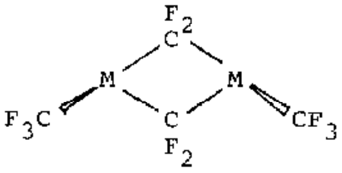

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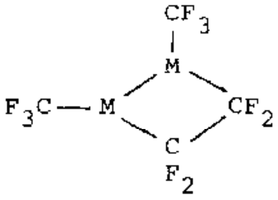

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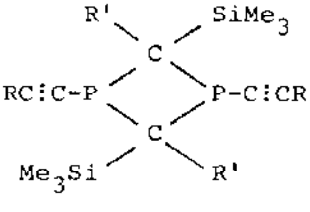

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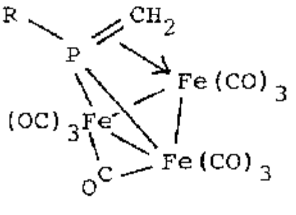

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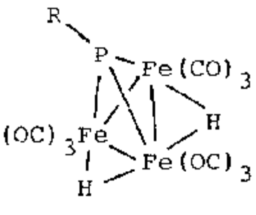
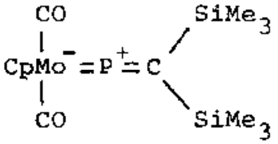


(58)

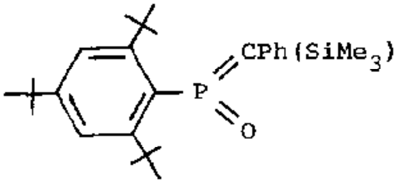
for R = $SiMe_3$ and R' = Ph.

Although phospha-alkenes of the type $RP{:}CH_2$ are apparently unstable, one such species with R = $4\text{-}MeOC_6H_4$ has been stabilised in the iron cluster compound (57) as a μ_3-η^2 bridging group.[149] The compound results from deprotonation of (58) with sodium amide, followed by reaction with diiodomethane. A member of a new class of compounds containing a two coordinate phosphorus atom doubly bonded to both carbon and a transition metal (59) has been characterised as the product of the reaction between $ClP{:}C(SiMe_3)_2$ and $K[Mo(CO)_3Cp]$ in THF solution in the presence of sodium hydride.[150] The Mo-P distance is short (2.174Å) and the P-C distance (1.649Å) is shortened over those in uncoordinated phospha-alkenes. The Mo-P-C system is almost linear and the electronic structure can be discussed in terms of a phosphavinylidene contribution.

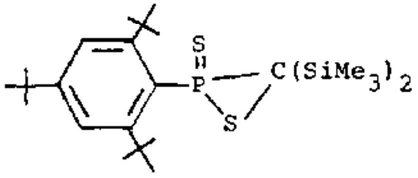


(59)

Phospha-alkenes have been oxidised by ozone[151] and sulphur[152] to give respectively (60) and (61). Compound (60), which is the first stable methyleneoxophosphorane, results from the ozonation of $^tBu_3C_6H_2P{:}CPh(SiMe_3)$ at -78°C; it has almost planar geometry at the phosphorus atom with P-O and P-C distances of 1.458 and 1.657Å respectivel and, rather surprisingly, reacts only slowly with alcohols giving phosphinic acid esters. The disulphide (61) is probably produced via $Me_3C_6H_2P(:S):C(SiMe_3)_2$ and this primary oxidation product can be isolated by treating (61) with tributylphosphine. An X-ray structure for the monosulphide shows P=S and P=C distances of 1.925 and 1.647Å compared with values of



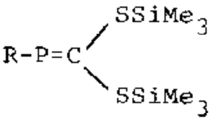
(60)



(61)

1.932 and 1.795Å for the related distances in (61).

Carbon disulphide at -30°C can insert into the P-Si bonds of disilylphosphines, $RP(SiMe_3)_2$ where R = Me,[153] ^tBu,[154] Ph or mesityl, to give phospha-alkenes (62). Two intermediates, (63) and (64), were detected in the preparation of (62, R = mesityl) and the structure of (62, R = Ph) has been determined. In contrast, the methyl compound is unstable and readily dimerises to (65). This molecule with ca. C_s symmetry in the solid state shows endocyclic P-C distances of 1.88 and 1.91Å and P-C-P and C-P-C ring angles of 90 and 86° respectively.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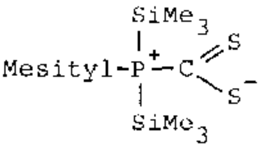
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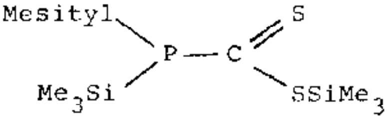
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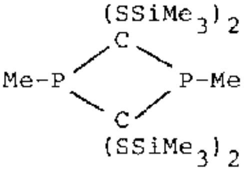
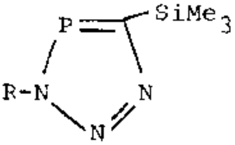

(65)

As discussed already for phospha-alkynes,[142] the phospha-alkene, $ClP{:}C(SiMe_3)_2$, undergoes cycloaddition reactions with azides, diazo compounds ($R^1R^2CN_2$) and a nitrile oxide giving compounds (66)-(68) respectively.[155] Related reactions of $ClP{:}CPh(SiMe_3)$ with $RCHN_2$, where R = H, CO_2Et, COPh, $(MeO)_2P(O)$, MeOPhP(O) or Ph_2PO, yield diazaphospholes (69),[156] compounds which are also produced from the phospha-allyl chloride $(Me_2NCR{:}P{\cdot}CR{:}NMe_2)^+Cl^-$ and substituted hydrazines $R'N_2H_3$.[157]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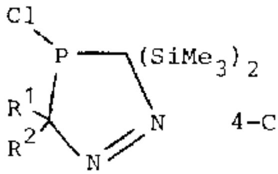
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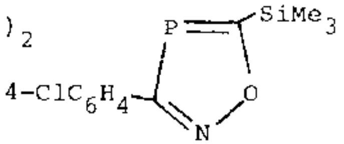
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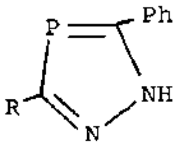

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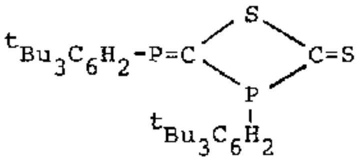


(70)

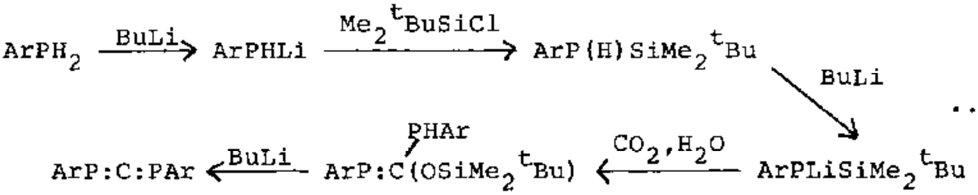
The silicon derivative $(Me_3Si)_2NP{:}CHSiMe_3$ reacts differently with MeLi and ^tBuLi, the former giving the bis(phosphino)methane $Me_2P{\cdot}CH(SiMe_3){\cdot}PMe[CH(SiMe_3)_2]$ in a complex reaction while the latter yields $^tBu_2P{\cdot}CH(SiMe_3)_2$.[158]

Evidence has been presented for the existence of a phosphathioketene, $^tBu_3C_6H_2P{:}C{:}S$ during the reaction between $^tBu_3C_6H_2P(SiMe_3)_2$ and thiophosgene in dioxan;[159] a red solid identified as the dimer (70) by X-ray crystallography precipitates on addition of acetonitrile. The compound is assumed to result from an unsymmetrical [2+2] cyclocondensation. Further evidence for the formation of a reactive RP:C:S species is the isolation of RP:C(SH)PHR' on irradiation of (70) in the presence of a primary phosphine $R'PH_2$.

Methods have been reported in 1984 for the preparation of the previously unknown phospha-[160] and diphospha-allenes.[160-162] The former results from the reaction in equation (42) of the phosphaketone ArP:C:O, where Ar = 2,4,6-$^tBu_3C_6H_2$, a versatile intermediate for the synthesis of species containing P=C systems. The phosphaketone also reacts with a silylphosphine, equation (43), to produce a symmetrical diphospha-allene;[160] this compound can also be synthesised by the methods outlined in equations (44)[161]

$$ArP{:}C{:}O + Ph_3P{:}CPh_2 \longrightarrow ArP{:}C{:}CPh_2 + Ph_3PO \qquad \ldots(42)$$

$$ArP{:}C{:}O + ArPLi(SiMe_3) \longrightarrow ArP{:}C{:}PAr + Me_3SiOLi \qquad \ldots(43)$$

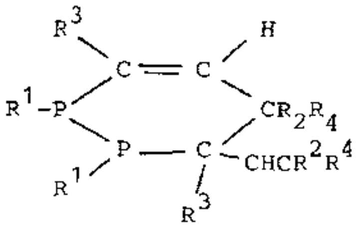


$$ArPH_2 \xrightarrow{BuLi} ArPHLi \xrightarrow{Me_2{}^tBuSiCl} ArP(H)SiMe_2{}^tBu \xrightarrow{BuLi} ArPLiSiMe_2{}^tBu$$
$$ArPLiSiMe_2{}^tBu \xrightarrow{CO_2,H_2O} ArP{:}\overset{PHAr}{C}(OSiMe_2{}^tBu) \xrightarrow{BuLi} ArP{:}C{:}PAr \qquad \ldots(44)$$

$$ArP{:}CH{\cdot}PClAr \xrightarrow{^tBuOK} ArP{:}C{:}PAr \qquad \ldots(45)$$

and (45).[162] In all cases the Ar group is the sterically demanding 2,4,6-tri-t-butylphenyl group. The reactant in equation (45) is one of a recently prepared series of compounds, i.e. ArP:CH·P(X)Ar where X = Cl, Br, I, H or Ar.[162] The central P-C bonds in ArP:C:PAr are short (1.635 and 1.630Å) and the P-C-P angle of 172.6° is a consequence of the presence of the large phosphorus substituents which are almost orthogonal with respect to the P-P axis.[163]

A new phosphabutadiene, 2,4,6-$^{t}Bu_3C_6H_2P{:}C(OSiMe_3){\cdot}CH{:}CHPh$, has been isolated from the reaction between $^{t}Bu_3C_6H_2P(SiMe_3)_2$ and PhCH:CHCOCl, but if the phosphorus atom carries a less bulky substituent, the product is a substituted 1,2-diphosphinine (71).[164]



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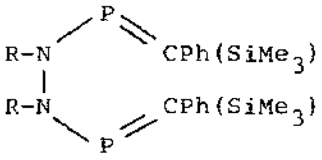

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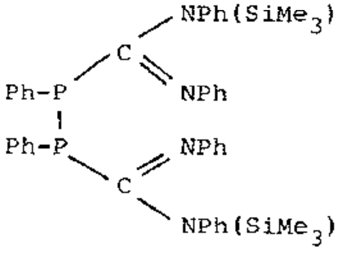

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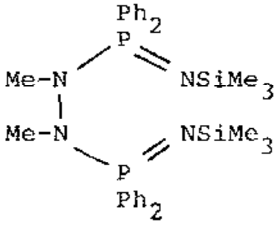
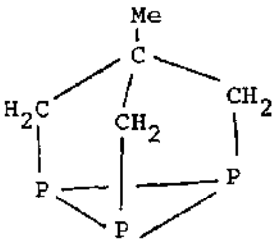


(74)

A range of new phosphorus hexadienes, (72)-(74), has been synthesised for investigations into pericyclic reactions.[165]

Electron diffraction for the crowded molecule, $(Me_3Si)_3CPH_2$, gives Si-C, Si-Me and P-C separations as 1.941, 1.883 and 1.808Å respectively; steric strain in the $(Me_3Si)_3C$ group is relieved by reducing the Me-Si-Me angles to 104.3°, by tilting the Me_3Si groups away from each other and by twisting the Me_3Si groups away the fully staggered conformation.[166]

The methods used previously for the arsenic and antimony analogues, i.e. reaction between $MeC(CH_2Br)_3$ and a mixed sodium potassium phosphide in monoglyme, have been used to prepare compound (75), which behaves as an η^1 ligand in the $Cr(CO)_5$ complex.[167] Good yields of the tetranuclear cobalt complex, $Co_4(\mu_3\text{-}PPh)_4(PPh_3)_4$, result on treatment of $CoCl_2.2PPh_3$ with $PhP(SiMe_3)_2$ in THF; each cobalt atom in the compound is surrounded by a distorted tetrahedron of three μ_3-P atoms and one



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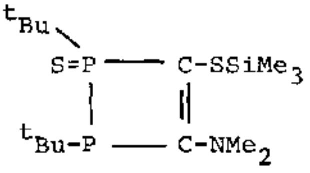


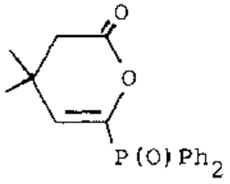
(76)

monodentate PPh_3 group.[168] The corresponding reaction with nickel chloride is incomplete but in the presence of acetyl chloride two new complexes, $Ni_8Cl_4(PPh)_6(PPh_3)_4$ and $Ni_8(CO)_4(PPh)_6(PPh_3)_4$ could be isolated.

Silylphosphines, $Li[PR(SiMe_3)]$ where R = Me, ^tBu, Ph, mesityl or Me_3Si, react even at -78°C with N,N-dimethylthiocarbamoyl chloride to give initially the mixed species, $RP(SiMe_3)[C(S)NMe_2]$, but while the mesityl derivative reorganises to the two symmetrical products, $RP(SiMe_3)_2$ and $RP[C(S)NMe_2]$, the t-butyl analogue loses Me_2NSiMe_3 to give the diphosphetene (76).[169] This unusual compound contains a P-P bond (2.219Å) between a four coordinate P(V) atom and a three coordinate P(III) atom, endocyclic angles at these atoms are respectively 79 and 74°.[170]

Alkane elimination occurs on heating the $Et_2PH.MEt_3$ complexes, where M = Ga or In, leading to cyclic trimers $(Et_2PMEt_2)_3$, which have been characterised by mass, i.r., and n.m.r. spectroscopy.[171] A series of mercury(II) halide complexes, $HgX_2(R_2PH)_n$ for X = Cl, Br or I, R = ^tBu or ^cHex and n = 1 or 2, which can be deprotonated to $XHgPR_2$ phospho-mercury derivatives by triethylamine in THF, have been prepared and characterised.[172] The latter compounds are also accessible via reactions of HgX_2 with $LiPR_2$. Metal carbonyl complexes containing coordinated phosphines, such as Me_2PSMe, $(CF_3)_2PSMe$ and the selenium analogues, can be obtained on reaction with $M(CO)_4$(norbornadiene) where M = Cr, Mo or W.[173]

Bifunctional acid chlorides, $ClC(O)CR_2C(O)Cl$, where CR_2 = $(CH_2)_{1-6}$, CHMe or CMe_2, in ether solution are reagents for converting the silylphosphine Ph_2PSiMe_3 to acylphosphines $Ph_2P{\cdot}C(O)CR_2C(O){\cdot}PPh_2$.[174] A number of these products can be oxidised by molecular oxygen to the corresponding P($\overline{V}$) species but with medium chain length compounds, $Ph_2P(O)H$ can be lost and intramolecular cyclisation gives the unsaturated lactone (77) instead.



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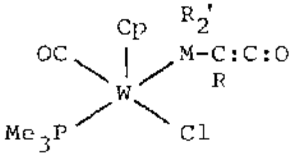

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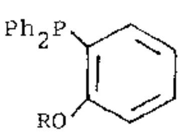


(79)

Phosphorus and arsenic substituted ketenes, $R_2'MCR{:}C{:}O$, have been synthesised and stabilised (78) by reactions of $R_2'MCl$, where R' = Me or Ph and M = P or As, with the ketenyl complex $CpW(CO)(Me_3P)(RC{:}C{:}O)$.[175] Structures have been reported for two N-phenylthiocarbamoylphosphines, $R_2PC(S)NHPh$ for R = Ph or ^{c}Hex,[176] and for the Pd(II) and Pt(II) complexes, $M[S_2CP^cHex_2]_2$, of the substituted dithioformate ligand.[177] Ligand coordination is via a sulphur and a phosphorus atom to give a cis planar arrangement with Pt-S and Pt-P distances of 2.328 and 2.276Å respectively. The phosphino-dimethylthioformamide, $Ph_2PC(S)NMe_2$, on treatment with sulphur in benzene yields the thiophosphoryl derivative $Ph_2P(S)C(S)NMe_2$; the phosphoryl analogue results from an Arbusov reaction between Ph_2POMe and $Me_2NC(S)Cl$.[178]

Pentamethyl-cyclopentadiene substituted phosphorus compounds are formed on treatment of phosphorus(III) halides with Me_5C_5Li in ether and among the many compounds isolated are $R_2P(C_5Me_5)$, where R = Me, Ph, Cl, Br or NMe_2; R_2 = $(CH_2)_2$, $O(CH_2)_2O$, $S(CH_2)_2S$ or $NMe(CH_2)_2NMe$; R/R = Me/Cl, ^{t}Bu/Cl or Ph/Cl, and $RP(C_5Me_5)_2$ where R = Cl or Br.[179]

Hexamethyldisilazane converts the substituted triphenylphosphine (79, R = H) to the trimethylsilylderivative (R = $SiMe_3$), a useful intermediate for reactions with a range of phosphorus halides.[180] Products such as $Ph_2PC_6H_4OPRCl$ (R = Cl or Ph), $Ph_2PC_6H_4OPF_2Ph_2$ and

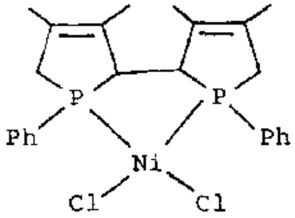
$(Ph_2PC_6H_4OPBu_3)Br$ can be obtained by reaction with $RPCl_2$, Ph_2PF_3 and $(Bu_3PF)Br$ respectively. Compound (79, R = H) also gives a hydrobromide salt with P-H and O-H bond lengths of 1.42 and 1.00Å respectively; both groups form strong hydrogen bonds (H...Br 2.41 and 2.09Å respectively) to the bromide anion.

Crystal structures have been determined for both PPh_2^- and $AsPh_2^-$ as the lithium di(12-crown-4) salts showing P-C distances of 1.804 and 1.811Å and a C-P-C angle of 105.2°.[181] The As-C distance is 1.972Å with a slightly wider C-As-C angle of 108.6°; in both cases the lithium is coordinated to eight oxygens with ca. D_{4d} symmetry.

In addition to yielding $Ph_2PCH_2PCl_2$, the reaction of dichloromethane with $Li[CH(PPh_2)_2]$ as its tetramethylethylenediamine complex also produces the cis and trans isomers of the ethenediylbis(phosphine), $Ph_2P{\cdot}CH{:}CH{\cdot}PPh_2$.[182]

Thermolysis of the substituted phosphole (80) at 140-170°C in alcohol in the presence of anhydrous nickel chloride gives red crystals of the complex (81), containing the previously unknown diphospholene.[183]

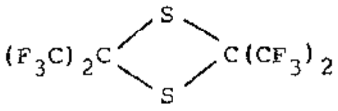
(80)



(81)

The best preparative route to the phenylcyanophosphide ion, $PhPCN^-$, is by treating $(PhP)_5$ with either ammonium or phosphonium cyanides, th ough the anion can also be obtained via the $P(CN)_2^-$-PhLi and $PhP(CN)_2$-CN^- reactions.[184] The anion in the $(Ph_3PNPPh_3)^+$ salt is planar with a C-P-C angle of 102° and, because of the relatively long (1.76Å) P-C and short (1.13) C-N distances, it has been described as a cyanide complex of phenylphosphinidene. Cyanodithiophosphinates, $PhP(CN)S_2^-$, result when sulphur reacts with $PhPCN^-$ and the anion can be alkylated to PhRPCN by a wide range of alkyl halides (RX). The $P(CN)_2^-$ ion can be coordinated to a metal when $M(CO)_5(MeCN)$ for M = Cr, Mo or W reacts with $Na(18\text{-crown-}6)P(CN)_2$ in dichloromethane.[185]

Phosphorus and arsenic tricyanides, $M(CN)_3$, cleave one of the C-S bonds in the hexafluorothioacetone dimer (82) in the presence of catalytic amounts of Et_3N to give (83) by insertion of the CN moiety.[186]



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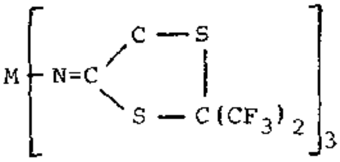

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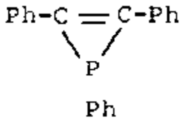
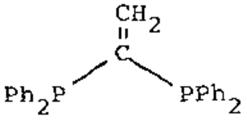


(84)

The structure of triphenylphosphirene (84), released from its $W(CO)_5$ complex by successive treatment with iodine and an excess of 1-methylimidazole, shows ring P-C bonds of 1.82Å and a very small (41.8°) C-P-C angle.[187]

Reaction of the bisphosphine (85) with methyliodide gives a monoquaternised species which on standing in methanol solution is converted to (86) by a [3+3] cyclocondensation reaction.[188] Compound (86) is formulated as a double semi-ylide quaternary salt and the reaction is effectively ylid formation without using a base.



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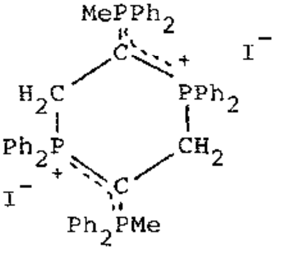

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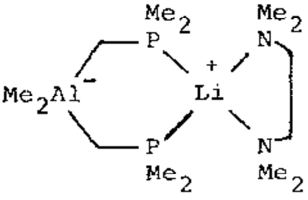


(87)

Treatment of dimeric $[Al(CH_2PMe_2)_3]_2$ with methyllithium in the presence of N,N'-tetramethylethylenediamine causes disproportionation and the formation of polymeric $[Li(PMe_2CH_2)_4Al]_n$ and $[Li(tmeda)][Me_2Al(CH_2PMe_2)_2]$ (87) in place of the expected aluminate.[189] The lithium is in slightly distorted tetrahedral coordination with a P-Li-P angle of 105.7°. $Li[C(PMe_2)_3].2THF$ is dimeric in the solid state with two planar CP_3 groups linked by Li(THF) units.[190]

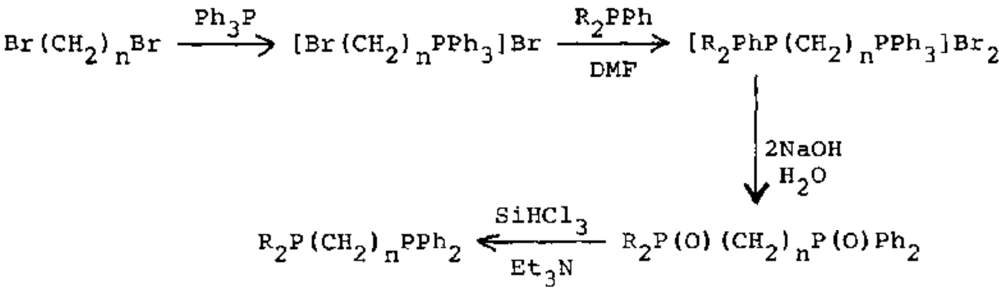
Among the alkyl phosphine complexes investigated this year are those between the Group 6 metal carbonyls and R_3M, $R_3'M$, R_2MMR_2', $R_2MM'R'$ and $R_2'MM'R$ where R = Me, R' = CF_3, M = P or As and M' = S, Se or Te.[191,192] The $2Me_3P.B_2H_4$ adduct forms an air stable 1:1 complex with zinc chloride (structure determined) and a number of other metal complexes, such as $Cu(Ph_3P)I$, were also characterised.[193]

"One pot" syntheses of triaryl-phosphines, -arsines and -stibines have been reported which depend on the initial formation of "M^{3-}" species by treating the element with sodium in liquid ammonia.[194] After addition of PhBr or PhI and irradiation for 60-120 min. good yields of the products Ph_3M are claimed. A highly basic tertiary phosphine, tris(2,4,6-trimethoxyphenyl)-phosphine, has recently been synthesised from $(PhO)_3P$ and $2,4,6\text{-}(MeO)_3C_6H_2Li$.[195] The compound gives a perchlorate salt from NH_4ClO_4 in ethanol, implying the phosphine basicity is higher than that of ammonia (pKa 9.21), and can be quaternised with a variety of alkyl halides. In spite of the bulkiness of the aryl groups, i-propyl bromide also reacts readily. The phosphine forms, as expected, a range of Cu(I) and Ag(I) complexes. Related phosphines were also prepared from $PhPCl_2$ and Ph_2PCl and the trimethoxyphenyl and 2,6-dimethoxyphenyl lithium salts.

4-Substituted triarylphosphines form complexes with both $HgCl_2$ and $Hg(ClO_4)_2$, which have been characterised by i.r. and ^{31}P and ^{199}Hg n.m.r. spectroscopy,[196] and chlorostannane substituted tertiary phosphines, $R^1R^2P(CH_2)_nSnClMe_2$ where R^1R^2 = Bu, ^tBu, ^cHex, Ph, etc. and n = 2 or 3, can be obtained from redistribution reactions between $R^1R^2P(CH_2)_nSnMe_3$ and Me_3SnCl.[197]

A convenient route to unsymmetrical diphosphines, $Ph_2P(CH_2)_nPR_2$ where R = Me or Et and n = 3 or 4, involves the intermediate formation of phosphonium salts and is outlined in Scheme 4.[198]

Vibrational spectra have been reported for the cyanoethyl-



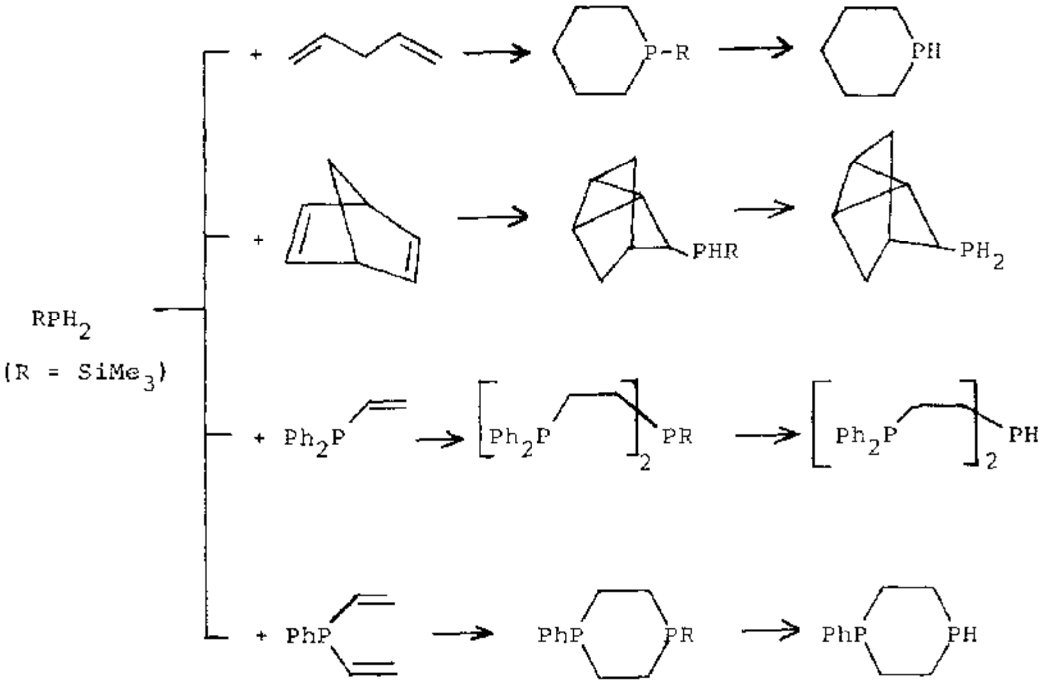
$$Br(CH_2)_nBr \xrightarrow{Ph_3P} [Br(CH_2)_nPPh_3]Br \xrightarrow[DMF]{R_2PPh} [R_2PhP(CH_2)_nPPh_3]Br_2$$

$$\xrightarrow[H_2O]{2NaOH} R_2P(O)(CH_2)_nP(O)Ph_2 \xrightarrow[Et_3N]{SiHCl_3} R_2P(CH_2)_nPPh_2$$

Scheme 4

phosphine, $P(CH_2CH_2CN)_3$, its oxygen, sulphur and selenium oxidation products and a range of Hg(II), Pd(II), Pt(II) and Cu(I) complexes.[199]

Reactions of olefins with phosphines in the presence of AIBN have been exploited in the formation of a range of new compounds.[200,201] For example, the trimethylsilylphosphine reactions summarised in Scheme 5 give initially a range of new silyl phosphines which can be hydrolysed to novel phosphines.[200] Similar addition reactions, summerised in equations (46) and (47),



Scheme 5

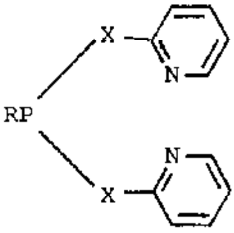
take place with dimethyl and diethyl phosphines to produce new tri- and tetra-dentate phosphine ligands.[201]

$$MeP(CH_2CH{:}CH_2)_2 + 2R_2PH \rightarrow MeP(CH_2CH_2CH_2PR_2)_2 \qquad ...(46)$$

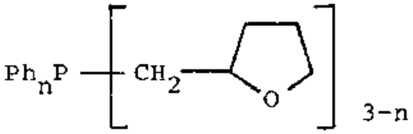
$$P(CH_2CH{:}CH_2)_3 + 3R_2PH \rightarrow P(CH_2CH_2CH_2PR_2)_3 \qquad ...(47)$$

A series of substituted 1,3-diphosphapropanes, including $H_2PCH_2PH_2$, $RPHCH_2PH_2$, $RPHCH_2PHR$, and R_2PCH_2PHR where R = ^iPr, ^tBu

or CH_2Ph, has been synthesised and characterised[202] and the related methylene bridged tetraphospha-alkanes, $^{i}Pr_2PCH_2\cdot P^{i}Pr\cdot (CH_2)_n\cdot P^{i}Pr\cdot CH_2P^{i}Pr$, where n = 3, 6 or 10, can be obtained by alkylating lithium phosphides such as $^{i}Pr_2PCH_2P^{i}PrLi$ and $Li^{i}PrPCH_2P^{i}PrLi$.[203] New potentially tridentate ligands containing pyridine groups (88) are produced when $RPCl_2$, where R = Me or ^{t}Bu, react with either 2-hydroxy- or 2-amino-pyridine;[204] the ligands form chromium and molybdenum carbonyl complexes in which (88, X = O) behaves as a tridentate group but (88, X = NH) is only bidentate as a result of hydrogen bonding to the pyridyl groups of a neighbouring molecule.[205] Related compounds (89, n = 1 or 2 and (90) result respectively from reactions between either $PhPLi_2$ or Ph_2PLi and tetrahydrofurfuryl chloride and $RPCl_2$, where R = Me, ^{t}Bu or Ph, with two mols of furfuryl-lithium.[204] These also form chromium and molybdenum carbonyl complexes and, although reactions can be complicated, $Mo(CO)_6.Ph_2PCH_2C_4H_7O$ has been isolated with (89, n = 2) and $Cr(CO)_4.[MeP(C_4H_3O)_2]_2$ with (90, R = Me). The latter shows both ligands attached to the metal via phosphorus atoms at distances of 2.309Å. The ligand (89, n = 1) is probably the most versatile behaving as mono-, bi-, and tri-dentate; it is also an active methanol homologation catalyst.



(88, X = O or NH)



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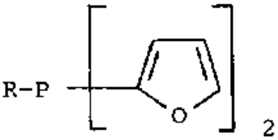
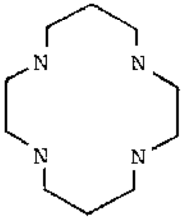


(90)

Two new macrocyclic ligands have been synthesised in high yields from cyclam (91) by one step processes with respectively two mols of $MeP(NMe_2)_2$ in toluene to give (92), and Ph_2PH in the presence of an excess of aqueous formaldehyde to give (93).[206] X-ray structures are available for (92) and (93). The macrocycle (94) can also be prepared in a one step process from $Li_2(PhPCH_2CH_2PPh)$ and $S(CH_2CH_2Cl)_2$.[207] All five of the possible diastereoisomers have been isolated and cobalt and nickel complexes prepared from the α-,[207] β-[207] and γ-[208] forms. Three of the possible diastereoisomers of the related heterocycle (95), obtained as described above but with bis(3-chloropropyl)sulphide in place of the 2-chloroethyl derivative, can be isolated and an X-ray structure is available for the nickel complex of the β-form, $[Ni_2Br_2L](BPh_4)_2.MeOH$.[209]



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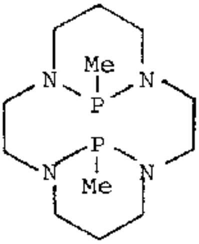

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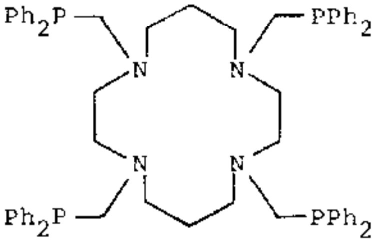

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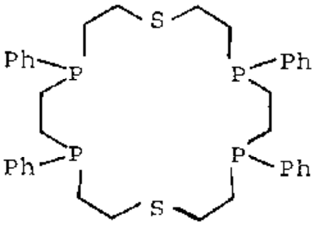

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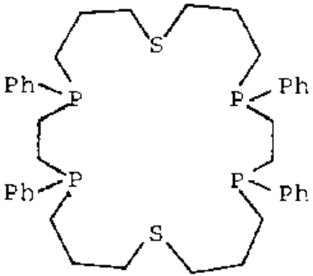
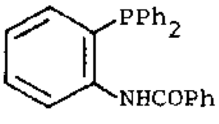


(95)

N-H oxidative addition occurs in reactions of the ligand (96) with iridium(I) species such as $IrClL_2$, where L_2 = $2Ph_3P$ or dppe, giving mixtures of (97) and (98) as products.[210] Related platinum complexes can also be prepared. The phosphorus analogue of 2,2'-bipyridyl (99) forms a hydrochloride in which the nitrogen atom is the basic centre, but metal-phosphorus bonding is present in the initial complexes formed with $M(CO)_5.THF$ where M = Cr or Mo.[211] Carbon monoxide is, however, readily lost to give



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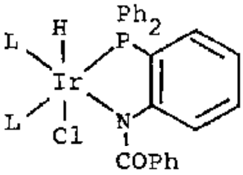

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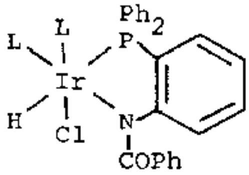

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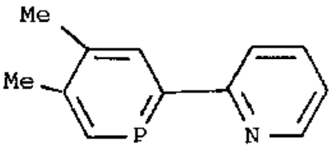

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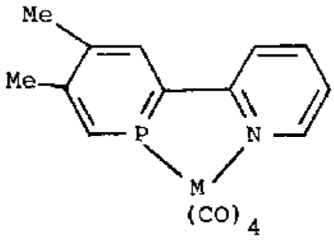
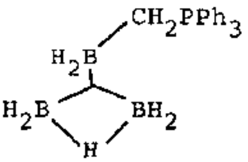


(100)

the chelates (100) where, for the chromium derivative, the phosphorine shows good ligating power (Cr-P 2.280Å); the N-Cr-CO unit is similar to that in $py.Cr(CO)_5$ showing no apparent cooperativity between the two types of ring.

Further details have been published on the chelating properties of ethylenediphosphinetetraacetic acid, an interesting ligand containing both hard and soft donor centres.[212]

The +5 Oxidation State. Treatment of $Ph_3P:CH_2$ in toluene with Ph_2SbCl leads to transylidation and isolation of $Ph_3P:C(SbPh_2)_2$; the by-product is Ph_3PMeCl.[213] Sb-C distances in the new ylid are 2.110 and 2.136Å and the conformation is similar to that in the phosphorus analogue. The methylene ylid, $Ph_3P:CH_2$, forms a gold(I) cyanide complex which oxidatively adds halogen to give $Au(CN)X_2(CH_2:PPh_3)$; the compound contains a stable gold-ylidic carbon bond.[214] B_3H_7.THF reacts in THF solution with ylids of the type $Ph_3P:CHR$, where R = H, Me or Ph, to give 1:1 adducts such as (101)[215] while the novel ylid $Ph_2P{\cdot}NR{\cdot}PPh_2:CH_2$ has been



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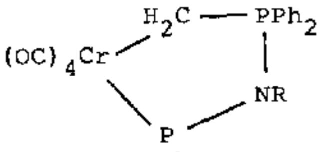
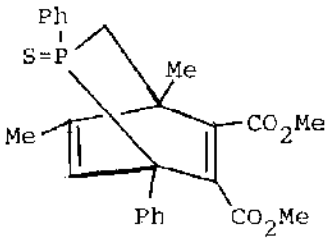


(102)

stabilised in complex (102), obtained when $(Ph_2P)_2NR$ reacts with $(OC)_5Cr(CH_2SOMe_2)$.[216] Complexes were also obtained when mixtures of $M(CO)_6$, for M = Cr, Mo or W, and $Ph_3P{:}CHCN$ were irradiated but coordination via the nitrogen atom was suggested by i.r. and n.m.r. spectroscopy and confirmed by a single crystal X-ray study on $(OC)_5Cr(NCCH{:}PPh_3)$.[217] The ylid $(Me_2N)_3P{:}CH_2$ (=L) forms complexes of the type ML_2Cl_n where M = Cu, Ag, Au, Zn, Cd or Hg.[218]

Evidence for the three coordinate, phosphorus(V) species $PhP({:}S){:}CH_2$ has been obtained from the thermolysis of (103), when the products isolated with trapping agents such as methanol and 2,3-dimethylbutadiene are respectively PhMeP(S)(OMe) and (104).[219]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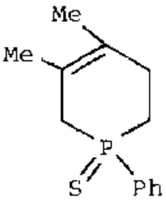
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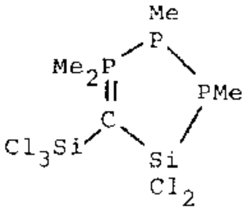
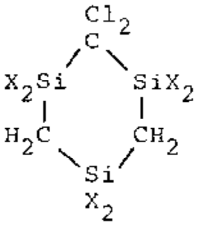

(105)

P-Si bond cleavage occurs on heating mixtures of $(Cl_3Si)_2C{:}PMe_2Cl$ and $MeP(SiMe_3)_2$ to 130°C for 15h giving products containing $(Cl_3Si)_2C{:}PMe_2{\cdot}PMe_2{:}C(SiCl_3)_2$ together with $(Cl_3Si)_2CHPMe_2$, P_5Me_5 and the unusual five membered ring compound (105).[220] Ylid formation is also reported from reactions of Me_2PSiMe_3 with the trisilahexane derivatives (106, X = F or Cl) and (107); after initial Si-P bond cleavage and elimination of a trimethylsilyl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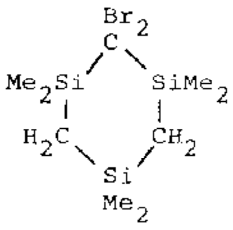
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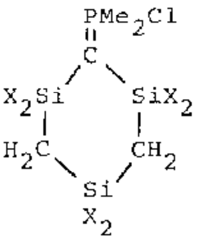
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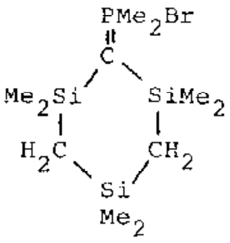

(109)

halide, rearrangement gives (108, X = F or Cl) and (109) respectively.[221] Single crystal X-ray data for (108, X = Cl) and

(109) show P=C bond lengths of 1.686 and 1.646Å respectively. Treatment of (108, X = Cl) with PCl_3 leads to ylidic carbon-silicon bond cleavage forming $(Cl_2P)_2C{:}PMe_2Cl$, a compound also obtained in the reaction of $(Cl_3Si)_2C{:}PMe_2Cl$ with PCl_3.[222] 1,3-Disilapropane derivatives containing a CCl_2 group also give ylids on treatment with two mols of Me_2PSiMe_3, the initial product, $(\equiv Si)_2C{:}PMe_2PMe_2$, being converted to $(\equiv Si)_2C{\cdot}PMe_2Cl$ on reaction with further disilapropane.[223]

The lithium derivative, $Ph_2PCLi(SiMe_3)_2$, obtained from $Ph_2PCH_2SiMe_3$ by successive treatment with BuLi, Me_3SiCl and a further mol of BuLi, reacts with a wide range of halides RCl, including Ph_2PCl, $^tBu_2PCl$, MeI, EtBr, PhCOCl and (mesityl)COCl, to give substituted methylene phosphoranes, $R_2PR{:}C(SiMe_3)_2$.[224] This provides a preparative route not only to P-alkyl and P-phosphino derivatives but also for the first time to the P-acyl products. With dihalides $R'X_2$, the original lithium compound yields diylids, such as $(Me_3Si)_2C{:}PPh_2{\cdot}R'{\cdot}PPh_2{:}C(SiMe_3)_2$ where R = $(CH_2)_{1-3}$, PhP, ^tBuP, etc. Structures have been determined for $Ph_2(mesityl)P{:}C(SiMe_3)_2$ and the diylid $[(Me_3Si)_2C{:}PPh_2]_2CH_2$.

Bisylids can be obtained following equation (48),[225] and mixed

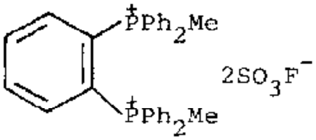
$$3LiCCl(SiMe_3)_2 + RPCl_2 \longrightarrow (Me_3Si)_2C{:}PR{:}C(SiMe_3)_2 + 3LiCl + Cl_2C(SiMe_3)_2 \qquad ...(48)$$

methylphenylcarbodiphosphoranes follow from reactions (49) and

$$(Ph_3PCH_2Br)Br \xrightarrow{PMe_3} (Me_3P{\cdot}CH_2PPh_3)Br_2 \xrightarrow{NaNH_2} Me_3P{:}C{:}PPh_3 \qquad ...(49)$$

$$(Ph_3PCH_2Br)Br \xrightarrow[NH_4PF_6]{Me_2PhP} (Me_2PhPCH_2PPh_3)(PF_6)_2 \xrightarrow{NaNH_2} Me_2PhP{:}C{:}PPh_3 \qquad ...(50)$$

(50).[226] The bisphosphonium salt (110) on reaction with $Et_3P{:}CHMe$ unexpectedly yields $MePh_2P{:}C{:}PPh_3$, a further member of the mixed ylid series. On deprotonation phosphonium cations containing both i-propyl and cyclo-propyl groups give ylids with an open chain i-propylide group e.g. (111) rather than those (112)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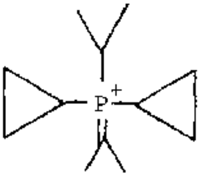
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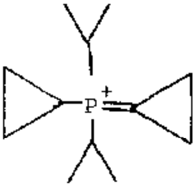
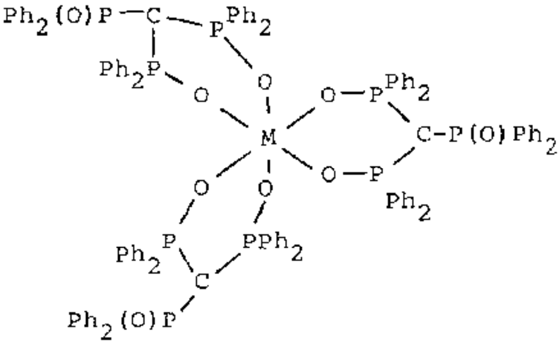

(112)

with a cyclo-propylide function.[227]

A number of complexes (113, M = Sc, Y, Lu or Pr) have been isolated containing the mesomerically stabilised phosphinoylmethanide anion $C(PPh_2O)_3^-$, which are non-fluxional on the n.m.r. time scale.[228] The structure of the yttrium derivative has been determined.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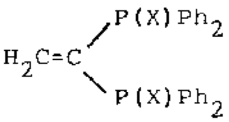

(114)

Diaryloxytriphenylphosphoranes, $Ph_3P(OC_6H_4X)_2$, are the products from reactions of triphenylphosphine and phenols in the presence of di-i-propylazodicarboxylate, $({}^iPrO_2CN)_2$ in THF or chloroform solution at 0°C.[229] 1,1-Substituted ethylenes (114, X = O or S) can be obtained by oxidation of the phosphorus(III) species with NO and S_8 respectively.[230] Detailed ^1H and ^{31}P n.m.r. data have been collected for a series of bridged diphosphines, $[RR^1P(X)]_2Y$, where R,R^1 = alkyl, X = S or lone pair, and Y = O, S or absent.[231]

Electron diffraction data for $(CF_3)_3PO$ give the following values: P-C 1.897, P-O 1.476Å, O-P-C 114.2, C-P-C 104.3 and P-C-F 110.4°.[232] The structure is basically tetrahedral but the trifluoromethyl groups are tilted away from the P=O bond; a surprising feature is the increase in the P-C bond length of ca. o.1Å compared with that in Me_3PO. Vibrational data leading to force constants have been collected and analysed for Me_2PHO[233] and the cations Me_3MCl^+ for M = N, P, As or Sb.[234]

5.2.3 Bonds to Halogens

The +3 Oxidation State. Six bands, as predicted, are observed in the p.e. spectra of OPCl and SPCl, previously reported from high temperature reactions of $PXCl_3$ with silver;[235] ionisation energies for the sulphur compound are ca. 1eV lower than the OPCl values. P.e. spectra of the trihydrides and trihalides of the Group 5 elements have been assigned and compared with calculations using the SCC-X_α method.[236]

The O-bonded thioacetate, $PF_2OC(S)Me$, is the initial product when $PBrF_2$ and $MeC(O)SSnBu_3$ react but treatment of the trihalide with $MeC(S)OSiH_3$ gives the S-bonded isomer.[237] Both compounds however equilibrate at room temperature to a mixture containing 80% of O-bonded compound. N.m.r., vibrational and mass spectrometric data were collected. Low temperature X-ray investigations for PF_2NH_2[238] and PF_2NHMe[239] show extensive hydrogen bonding in the former with different P-F bond lengths (1.590, 1.608Å), the P-N bond length is 1.638Å. Molecules of the methylamine derivative have a conformation similar to that of the major (trans) form in the gas phase with again two different P-F distances (1.587, 1.600Å). The P-N distance here is however substantially shorter (1.617Å), than in PF_2NH_2 and the nitrogen atom plays no part in the hydrogen bonding system. The bond shortening is consistent with the presence of $p(N) \rightarrow d(P)$ π-bonding.

Factors such as displacement reactions on phosphorus, catalysis and autocatalysis by HF and/or the fluorophosphorane product etc., may influence the disproportionation reactions in equations (51) and (52). These have been investigated and a mechanism proposed

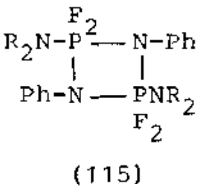
$$2RPF_2 \rightarrow \tfrac{1}{2}(RP)_n + RPF_4 \qquad \ldots(51)$$

$$2R_2PF \rightarrow R_2PPR_2 + R_2PF_3 \qquad \ldots(52)$$

which involves the initial formation of a phosphinophosphonium salt $(RPFZ{\cdot}PRZ)^+LF^-$, where Z = R or F and L = $RPZF_3$.[240]

Substituted diazadiphosphetidines (115) are obtained from Staudinger reactions between PhN_3 and a range of aminodifluorophosphines, R_2NPF_2.[241]

Further data are now available on the ligand behaviour of the related $MeN(PF_2)_2$.[242] At room temperature in acetonitrile, the product from $Mo(CO)_3(MeCN)_3$ is $[MeN(PF_2)_2]_2Mo(CO)_3$ which contains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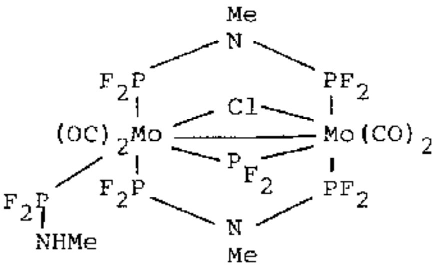
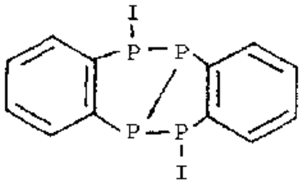

(116)

both mono- and bi-dentate ligands while a dinuclear species $[MeN(PF_2)_2]_4Mo_2(CO)_3$ is obtained in refluxing MeCN. A novel quadruply bridged compound (116), originally produced in the presence of hydrogen chloride, is obtained more readily by treating $[MeN(PF_2)_2]_3Mo_2(CO)_5$ with Et_3NHCl; the structure follows from an X-ray investigation.

A new bicyclic P-C system (117) has been formed by treating o-phenylenebis(dichlorophosphine) with lithium iodide in benzene;[243] from X-ray diffraction, the compound contains two P_3C_2 rings with a common P-P bond (2.215Å), P-P distances to those carrying iodine atoms are 2.207 and 2.211Å. Treatment of the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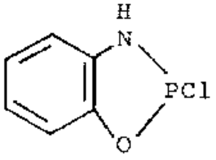
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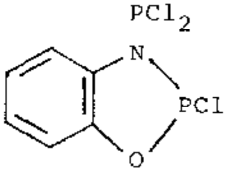
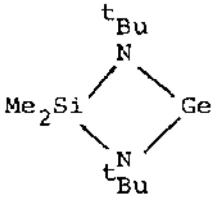

(119)

oxazaphospholine (118) with PCl_3 gives (119) which can be oxidised at both phosphorus atoms by elemental sulphur.[244]

Either in the presence or absence of the solvent toluene, reaction between PCl_3 and the cyclic germylene (120) leads to (121) by insertion of the heterocycle into each of the P-Cl bonds.[245] The compound has ca. C_{3h} symmetry with the Ge, Cl and Si atoms lying in a plane, but the symmetry is reduced as the phosphorus atom lies at the apex of a flat pyramid (Ge-P-Ge 115.0°, Ge-P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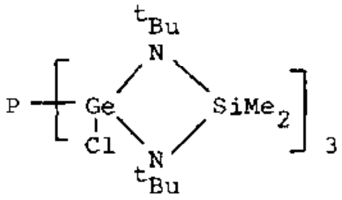

(121)

2.310Å). The unusual geometry results from steric requirements of the bulky substituents. Corresponding reactions between PCl_3 and $Me_2Si(N^tBu)_2M$, where M = Sn or Pb, lead to respectively $Me_2Si(N^tBu)_2SnCl_2$ and liberation of $PbCl_2$ with formation of $Me_2Si(N^tBu)_2PCl$.

The +5 Oxidation State. New ab initio calculations on the Berry pseudorotation in PF_5 have established a transition state with C_{4v} symmetry, which has hitherto been assumed, and when correlation effects and basis enlargement are included, the barrier is calculated as 16 $kJ.mol^{-1}$.[246]

A trigonal bipyramidal structure with equatorial amido groups (C_{2v} symmetry) follows from electron diffraction studies on $PF_3(NH_2)_2$.[247] The N-P-N angle is opened to 127.4° and the axial fluorine atoms are bent slightly toward the equatorial fluorine (F_e-P-F_e 89.5°); bonds to the equatorial and axial fluorines are 1.560 and 1.619Å respectively.

I.r. spectra of the 1:1 adducts of NSF with PF_5 and AsF_5 have been interpreted in terms of ionisation to give $NS^+ MF_6^-$;[248] in each case a sharp peak at ca. $1440cm^{-1}$ was assigned to ν(NS). X-ray data for the adduct between $POF_3.SbF_5$ and SbF_5 show a cis bridged structure.[249]

I.r. and Raman data have been collected for the condensed fluorophosphates $K_2P_2O_5F_2$ and $P_2O_3F_4$;[250] reaction of the latter with boric acid in difluorophosphoric acid gives $B(O_2PF_2)_4^-$ which was characterised by ^{11}B, ^{19}F and ^{31}P n.m.r. spectroscopy.[251] Boron trihalides with HPO_2F_2 initially lead to the same compound but further reaction gives a second product tentatively identified as $BF(PO_2F_2)_3^-$.

The best preparative route to the betaine $py.PO_2F$ is via sulphur-oxygen exchange with $py.PS_2F$ in liquid sulphur dioxide.[252] The compound can also be detected in the fluorination of $py.PO_2Cl$

with $AsCl_3$ but not with either NaF or $NaSO_2F$ and is present in the product obtained by the reaction of $POCl_2F$ and P_4O_{10} with an excess of pyridine.

A new method for the synthesis of HPF_5^- uses Olah's reagent, $Et_3N.5HF$, with either $P(OR)_3$ where R = Et or Ph, $P(NEt_2)_3$ or PCl_3.[253] Fluorine exchange between the related $PhPF_5^-$ anion and $PhPF_4$ is first order in both compounds and retardation in the presence of donors such as acetonitrile supports formation of a fluorine bridged intermediate.[254] In the di-benzo-36-crown-12 adduct with two mols of $NaPF_6$ each sodium is coordinated to five oxygen atoms and two fluorines of a PF_6 group.[255]

The use of COF_2,[256] SF_4[257] (see also ref.294), and XeF_2[258] as fluorinating agents has been reported during 1984. The first compound is useful in replacing P-H bonds, see equation (53), but oxidative addition occurs with R_3P, $(RO)_3P$ and $Ph_2P(CH_2)_2PPh_3$.[256]

$$(RO)_2P(O)H + COF_2 + Et_3N \longrightarrow (RO)_2P(O)F + CO + Et_3NHF \qquad ...(53)$$

R = Et or Bu

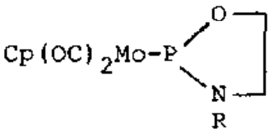
With the mixed phosphinoarsine, $Ph_2P(CH_2)_2AsPh_2$, oxidation occurs only at phosphorus to give $Ph_2F_2P(CH_2)_2AsPh_2$. Sulphur tetrafluoride at -78°C will convert 2,4,6-$^tBu_3C_6H_2P(SiMe_3)_2$ to $^tBu_3C_6H_2PF_4$, which has a fixed ligand arrangement at ca. -50°C,[257] and, XeF_2 has been used to convert the complex, $Ir(CO)Cl_2(PEt_3)_2$-(PCl_4), to the corresponding PF_4 containing species.

I.r. and Raman spectra of PCl_5 have been reinvestigated.[259] Complex formation between R_nPCl_{5-n}, where R = Me, n = 1,2 and R = Et, n = 1-3, and the bases Cl^-, pyridine, 2,2'-bipyridyl and 1,10-phenanthroline has led to the isolation of compounds such as $R_4N[PMeCl_5]$, $[MePCl_3py]Cl.py$, $[MePCl_3(bipy)]^+Cl^-$, $[MePCl_3(phen)]^+Cl^-$ and the corresponding P-ethyl derivatives.[260] In contrast, the di- and tri-alkyl chlorophosphoranes exhibit no acceptor properties. Related investigations with the bromides $PBr_3(cat)$, where cat = $O_2C_6H_4$, $PBr(cat)_2$ and $PhPBr_4$ has led to the products $[PBr_2(cat)py_2]Br_3$, $[PBr_2(cat)(bipy)]_2Br_3Br$, $PBr(cat)_2.py$, $[P(cat)_2(bipy)]_2Br_3Br$ and $[P(cat)_2(phen)]_2Br_3Br$.[261]

The black complex, $POCl_3.ReCl_5$, is O-bonded with P=O and O...Re distances of 1.46 and 2.14Å respectively.[262] Reaction of $POCl_3$ with four mols of N,N-dimethylurea in liquid sulphur dioxide solution gives a viscous liquid which hydrolyses to produce salts of dimethylbiuretophosphate, $Me_2NC(O)NHC(O)NHPO_3^-$.[263] The chlorine atoms in methylphosphonic dichloride, $MePOCl_2$ can be replaced on treatment with silver carboxylates to give $MePO[OC(O)R]_2$ where R = 2-, 3-, 4-FC_6H_4, 2,6-$F_2C_6H_3$ or 2,3,5,6-F_4C_6H.[264,265] The products decompose slowly to give $[MeP(O)O]_n$ and $[RC(O)]_2O$.

5.2.4 Bonds to Nitrogen

The +3 Oxidation State. Phenyl azide reacts with chlorophosphenium salts, $[R_2NPCl]^+[AlCl_4]^-$ where R = Me or ^{i}Pr, to give related iminium derivatives $[R_2NPCl(:NPh)]^+[AlCl_4]^-$.[266] However, if Me_3SiN_3 is used instead, the Staudinger reaction above is in competition with Me_3SiCl elimination, and the product is unexpectedly a stable phosphenium-iminophosphonium compound, $[R_2NP{\cdot}N{:}PCl(NR_2)][AlCl_4]_2$. It is possible that reaction proceeds via formation of $[R_2NPN_3]^+$ which then reacts with the starting material $[R_2NPCl]^+$ to eliminate nitrogen. A coordinated phosphenium ion is present in compound (122), formed when $NaMoCp(CO)_2$ reacts with (123), R = Me, Et, ^{t}Bu or Ph, X = F or Cl); an X-ray study shows planar coordination about phosphorus in



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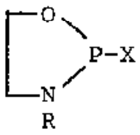

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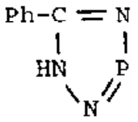
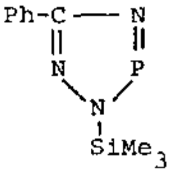


(124)

(122), R = ^{t}Bu).[267]

A new two coordinate phosphorus compound (124) results when $ClP(NMe_2)_2$ is treated with the Schiff base $PhCH{:}N{\cdot}N{:}CPhNH_2$; further reaction of (124) with trimethylchlorosilane leads to (125).[268]



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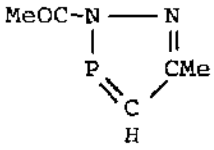

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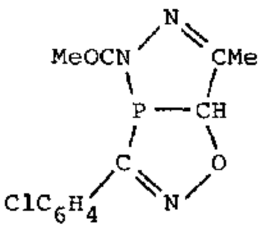
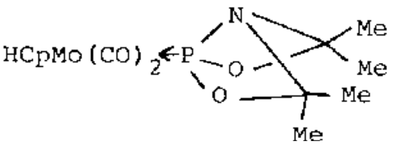


(127)

Cycloaddition of 4-ClC_6H_4CNO to the P=C bond of (126) gives (127) in which each five membered ring is in the envelope conformation. The P-C distance in (127) is 1.849Å.[269]

Attempted protonation of nitrogen atoms directly bonded to phosphorus to give phosphorammonium salts has invariably led to P-N bond cleavage but such a protonated compound of unexpectedly high stability has recently been prepared by simply passing hydrogen chloride into a solution of the molybdenum complex (128).[270] By contrast, the related non-cyclic aminophosphine complex (129) reacts with HCl to give a $P(OEt)_2Cl$ complex with elimination of Me_2NH_2Cl.



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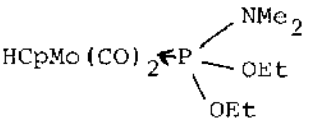
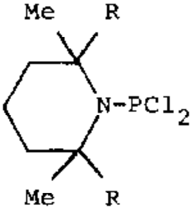


(129)

Potential prototropism in systems containing P-NH-P units has been investigated by an X-ray structural study of $(Ph_2P)_2NH$, its bis(borane) adduct, together with $[(PhO)_2P(O)]_2NH$ and $(PhO)_2P(O){\cdot}NH{\cdot}P(O)Et_2$.[271] All four compounds, in fact, contain an N-H group; the first compound with C_2 molecular symmetry has P-N distances of 1.692Å and a P-N-P angle of 118.9°. The N-H separation is 0.977Å. The bis(borane) structure is similar (P-N 1.679 and 1.695Å) but with an increased (131.6°) P-N-P angle. The final two compounds maintain the N-H grouping but both show weak hydrogen bonding.

Following the success previously reported in isolating bis(dialkylamino)phosphines, $(R_2N)_2PH$ when R is a bulky group, attempts have been reported to isolate the related R_2NPH_2 compounds.[272] Reduction of a cyclohexyl substituted compound R_2NPCl_2 with $LiAlH_4$ gave the desired phosphine in good yield but purification by distillation was not possible. A range of metal carbonyl complexes could however be isolated. Reduction of the tetra-substituted piperidine derivative (130, R = Me) also gave the corresponding phosphine but there was no evidence for successful reduction using the 2,6-dimethylpiperidine derivative (130, R = H), thus emphasising the requirement for a large R_2N group for stability.

The following silver(I) complexes with the aminophosphines $P(NMe_2)_3$ (≡L), $P(NMeCH_2)_3CMe$(≡L') and $P(\overline{NCH_2CH_2})_3$ (≡L") have been isolated: $[AgL_2]^+$, $[AgL_3]^+$, $[AgL_2X]$ where X = Cl, Br, I or CN, $[AgL'_3]^+$ and $[AgL"_4]^+$.[273] Four coordinated complexes cannot be formed with L', presumably for steric reasons, as this coordination type is possible with the smaller ligand L". The structure of $[AgL_2]BPh_4$ is unusual in showing a non-linear P-Ag-P system (167°).



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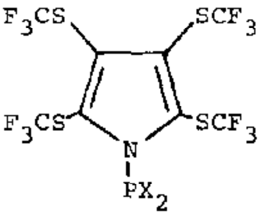
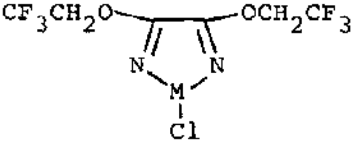


(131)

Reaction between phosphorus trihalides and 2,3,4,5-tetrakis-(trifluoromethylthio)pyrrolyl silver yields the monosubstituted compounds (131, X = Cl, Br or I), but the chlorine derivative can react further to give di- and tri-substitution if the potassium pyrrolyl is used.[274] Related trisubstituted compounds can be obtained from $AsCl_3$ and $SbCl_3$ and the halogens in $Ph_{3-n}PCl_n$, where n = 1 or 2, $(EtO)_2PCl$ and one halogen in each of $POCl_3$ or $PSCl_3$ can similarly be substituted.

Compounds of the type (132, M = P or As) result when the diiminoethane $CF_3CH_2OC(:NH)C(:NH)OCH_2CF_3$, obtained from trifluoroethanol and cyanogen, is cyclised on treatment with PCl_3 or $AsCl_3$ in the presence of triethylamine.[275] Reaction of (132, X = P) with magnesium than leads to the diphosphine (133).



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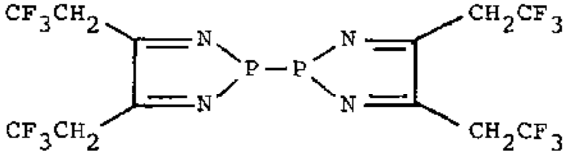
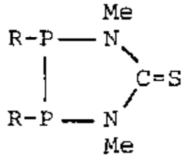


(133)

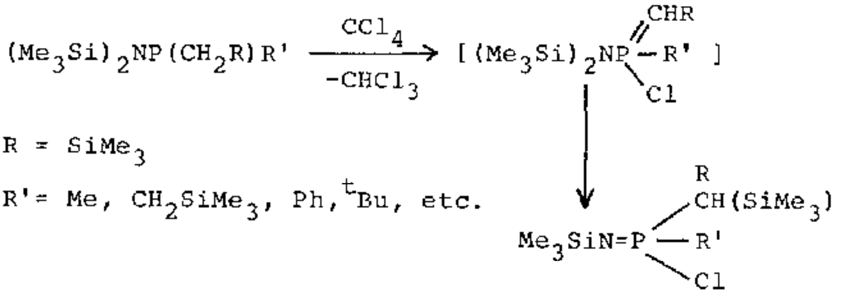
Two new diazadiphospholidine derivatives (134, R = Me or Ph) result from the reaction of $RPCl_2$ with N,N'-dimethylthiourea; full spectroscopic data and a crystal structure of the phenyl compound are available.[276] A crystal structure determination on $Ph_2PNH-SiPh_3$ shows the phosphorus lone pairs lying trans to the



(134)

N-H bond to minimise both steric and electronic repulsions; the P-N bond length is 1.703Å.[277]

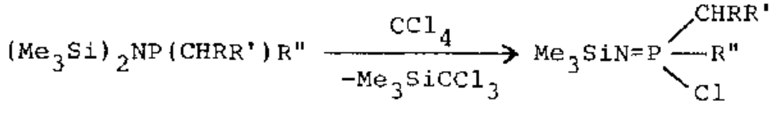
Reactions have been reported for a range of silylaminophosphines, including $(Me_3Si)_2NPHR$, for R = $N(SiMe_3)_2$, ^tBu, ^iPr or Ph,[278] and $(Me_3Si)_2NPRR'$ for R,R' = Me, Et, ^iPr, ^tBu, CH_2SiMe_3, CH_2Ph, Ph, NMe_2, OMe, OCH_2CF_3.[279] The Staudinger reaction between Me_3SiN_3 and the first set of compounds gives two, not readily interconvertible, isomeric products, i.e. $(Me_3Si)_2NHPHR{:}NSiMe_3$ and $(Me_3Si)_2NPRNHSiMe_3$, with the P-H isomeric form being favoured by bulky R groups.[278] The original phosphines can be converted to the corresponding phosphonium salts with methyl iodide but further methyl iodide leads to desilylation and formation of $[(Me_3Si)HNPRMe_2]^+I^-$. They are also oxidised on treatment with $^tBuO_2SiMe_3$ to $Me_3SiN{:}PHR(OSiMe_3)$. Reactions of the second series of compounds, $(Me_3Si)_2NPRR'$, with CCl_4 have been studied where, as shown in equations (54) and (55), loss of either $CHCl_3$ or



R = $SiMe_3$

R'= Me, CH_2SiMe_3, Ph, ^tBu, etc.

...(54)



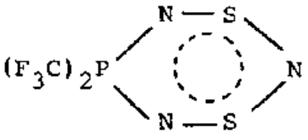
...(55)

R = R' = Me

R" = ^iPr, ^tBu or Ph

Me_3SiCCl_3 is possible.[279]

Depending on the nature of the groups attached to silicon, either N-silylamides, $Ph_2P{\cdot}NSiR_3{\cdot}PPh_2$, or the isomeric phosphinophosphinesilylamides, $Ph_2P{\cdot}PPh_2{:}NSiR_3$, can be prepared by treating the lithium derivative, $Ph_2P{\cdot}NLi{\cdot}PPh_2$, with a chlorosilane, R_3SiCl.[280] A new PN_3S_2 heterocycle (135) has been produced by the reaction of $(CF_3)_2PN(SiMe_3)_2$ with $S_3N_2Cl_2$ but on standing the compound is converted with an eight membered $P_2N_4S_2$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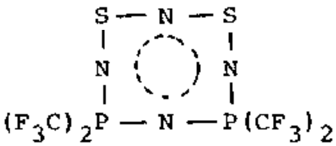

(136)

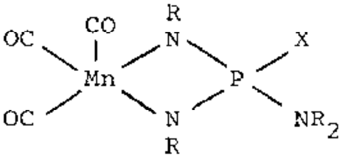
species (136).[281] Related reactions between $^tBu_2MX$, where M = P, As, Sb or Bi and X = Cl or Br, and K_2SN_2 in acetonitrile at -40°C give the substituted sulphur diimides $S(NM^tBu_2)_2$.[282]

The +5 Oxidation State. As recent calculations have indicated that the λ^3-phosphinonitrene, $H_2P\text{-}N$, is better formulated as the triply bonded $H_2P{\equiv}N$ species, attempts have been made to generate such species by photolysis of the hindered azidophosphine $(^iPr_2N)_2PN_3$.[283] This seems to have been achieved as in trapping experiments $(R_2N)_2P(OMe){:}NH$, $(R_2N)_2PCl{:}NSiMe_3$ and $(R_2N)_2P(NH_2){:}O$ can be obtained in near quantitative yields from reactions in the presence of MeOH, Me_3SiCl and H_2O respectively. The products arise from 1,2 addition of the trapping agent to the triple bond in $(^iPr_2N)_2P{\vdots}N$ (see also reference 306).

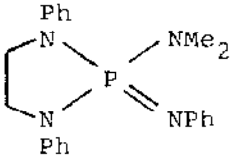
Sterically protected, stable metaphosphonimidates, 2,4,6-$^tBu_3C_6H_2P(X){:}N^tBu$ where X = O, S or Se, have been synthesised for the first time by treating the iminophosphine $^tBu_3C_6H_2P{:}N^tBu$ with, respectively, ozone, sulphur or selenium.[284] Support for the monomeric formulation is from cryoscopy, n.m.r. spectroscopy and the results of chemical reactions when, for example, methanol and water add smoothly to give the phosphonic amides, $^tBu_3C_6H_2P(X)(OR)(NH^tBu)$ where R = Me or H respectively.

The double ylids, $^tBu(Me_3Si)NP(X){:}N^tBu$ where X = S or Se, form platinum complexes in which the P=X bond is coordinated side-on to the metal.[285] This leads to Pt-P and Pt-S distances of 2.285 and

2.378Å and angles at the S, Pt and P atoms of the three membered ring of 61.3, 52.8 and 65.9° respectively. A 16-electron manganese carbonyl complex (137, X = Br) has been isolated when $Mn(CO)_5Br$ reacts with a different type of double ylid, $(Me_3Si)_2NP(:NSiMe_3)_2$.[286] The bromine can be replaced on reaction with PhOLi and an X-ray structure of (137, X = OPh) shows manganese in distorted square pyramidal geometry.



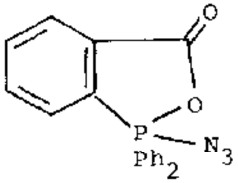
(137, R = $SiMe_3$)



(138)

The phosphorus atom in the iminodiazaphospholane (138) is in highly distorted tetrahedral geometry with N-P-N angles varying between 91.8 and 121.7°.[287] All the P-N distances are short; those to the three coordinate nitrogens range between 1.62 and 1.67Å but that to the NPh group is 1.539Å.

Irradiation of the azide, $[(Me_2N)_3PN_3]PF_6$, leads to the iminophosphonium salt, $[(Me_2N)_2P{:}NNMe_2]PF_6$ but the importance of the anion is shown by the formation of $(Me_2N)_3PNH$ if the corresponding bromide salt is irradiated.[288] The formation of a transient nitrene $[(Me_2N)_3P{:}N]X$ is postulated to account for the different courses of the two reactions. Three new phosphorus($\overline{V}$) azides, (139)-(141) have been synthesised and together with the previously known analogue (142) have been photolysed.[289] Unexpectedly, the product from compound (139) is the isocyanate



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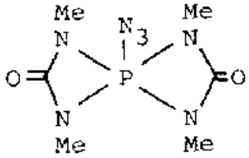

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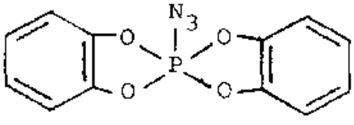

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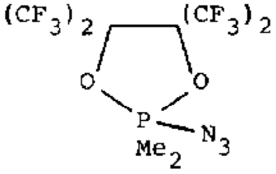

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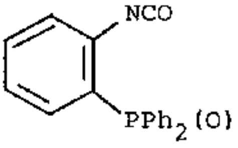

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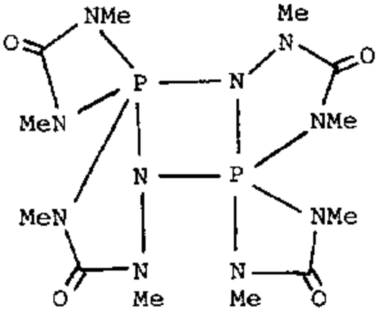

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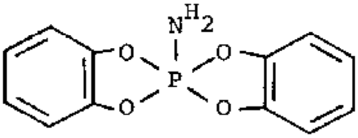

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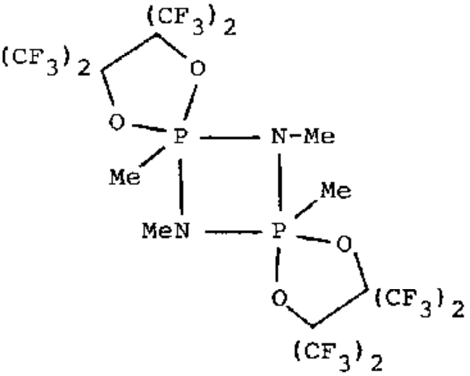
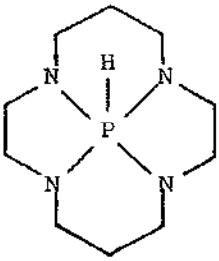


(146)

(143) while (140) gives an unusual spirocyclic product (144), the first phosphorus compound containing bonds to five nitrogen atoms. Photolysis of (141), which contains non-migrating groups, gives only the aminophosphorane (145) but the cyclic derivative (146) in two stereoisomeric forms is the product from (142). The conclusion from this work is that a Curtis type rearrangement can occur with azides bonded to a five coordinate phosphorus atom and the reaction most likely proceeds via preliminary formation of transient phosphorane nitrenes.

X-ray crystallography has shown that the tetracyclic cyclam phosphorane (147) with diborane at 0°C in toluene gives an adduct (148) of the open tautomeric form with BH_3 groups attached to both phosphorus and nitrogen.[290] Structures have also been determined for two tetraazadiphosphacyclohexanes obtained as shown in equations (56) and (57). The rings are in respectively chair and twist conformations;[291] a twist conformation is also reported



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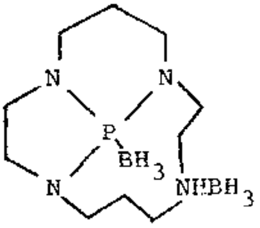

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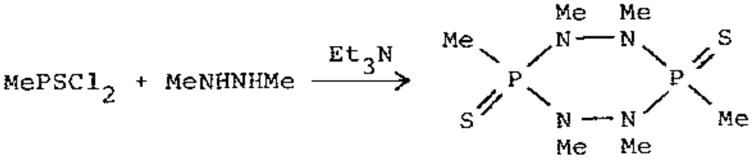

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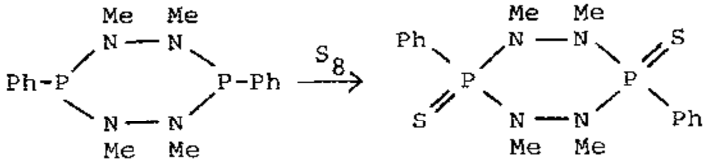
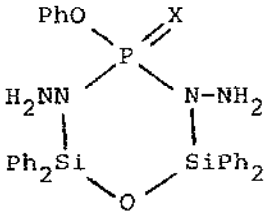


...(57)

for the related EtO(S)P(NHNH)$_2$P(S)OEt.[292]

Condensation reactions between 1,4-dichlorotetraphenyldisiloxane and the dihydrazido-phosphoric and thiophosphoric esters, (PhO)(X)P(NHNH$_2$)$_2$ where X = O or S, lead to new P-N-Si-O heterocycles such as (149)-(151)[293] while the 8-, 9- and 10-membered ring analogues can be obtained from corresponding



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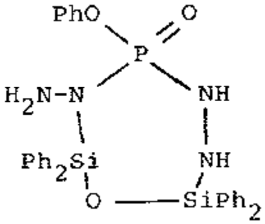

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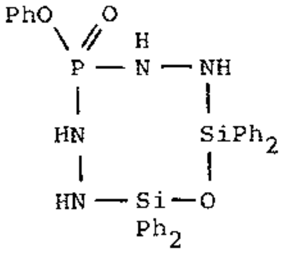
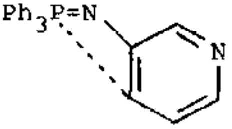


(151)

reactions with $ClSiMe_2 \cdot OSiMe_2 \cdot OSiMe_2Cl$.

Sulphur tetrafluoride at -80°C in ether converts $^tBuP(NHMe)_2$ to $^tBuPF_2(NHMe)_2$ and from a multinuclear low temperature n.m.r. investigation the compound consists of two isomers resulting from different orientations of the NHMe groups.[294] Reaction of $PhPOCl_2$ with methylamine yields $PhPO(NHMe)_2$, which with methyl or phenyl dichlorophosphine leads to N-H substitution and formation of $PhPO[NMe(PClR)]_2$.[295]

Crystal structures for the two pyridyl substituted iminophosphoranes (152) and (153) show respectively short P...C (3.198) and P...N (2.945Å) intramolecular interactions together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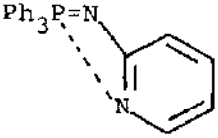

(153)

with P-N and N-C distances at the imino-nitrogen indicating multiple bond character.[296] The electronic consequences and the molecular conformations were discussed in detail.[297]

A series of phosphazenes has been prepared by reaction between triethylphosphite and an amide in the presence of carbon tetrachloride as shown in equation (58).[298] Trichlorophosphazeno-

$$(EtO)_3P + CCl_4 + RNH_2 \xrightarrow[-Et_3NHCl]{Et_3N} (EtO)_3P{:}NR + CHCl_3 \qquad ...(58)$$

$R = CN, COPh, SO_2Ph, P(O)(OEt)_2$

phosphoryl chloride, $Cl_3P{:}N \cdot POCl_2$, is readily synthesised from potassium trimetaphosphimate and PCl_5 at ca. 435K,[299] and a range of alkoxy- and aryloxy derivatives[300,301] together with derivatives of the related imidodiphosphate system,[301] $(RO)_xCl_{2-x}P(O)NHP(O)Cl_{2-y}(OEt)_y$, have been prepared and characterised by ^{31}P and ^{15}N n.m.r. spectroscopy. Multinuclear n.m.r. investigations are reported for $(Me_2N)_3PX$, where X = Se, Te or BH_3,[302] and for a series of 1-piperidyltrifluorophosphoranes where the piperidyl group carries a methyl substituent to impart chirality.[303]

Structures for tri(pyrrolidino)phosphine selenide and -telluride, $[(CH_2)_4N]_3P{:}X$ for X = Se or Te, show that as in similar compounds, one P-N bond is anti-periplanar and synclinal to the other two; P-Se and P-Te distances are 2.105 and 2.355Å respectively.[304]

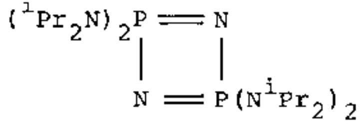
Equations (59)-(61) show the methods used to produce a number of new molybdenum phosphaniminato complexes.[305]

$$(MoNCl_4)_2 \xrightarrow{PPh_3} MoCl_5(NPPh_3)(PPh_3) \qquad \ldots(59)$$

$$MoNCl_3 \xrightarrow{PPh_3} MoCl_3(NPPh_3)(PPh_3) \xrightarrow{PPh_4Cl} PPh_4[MoCl_4(NPPh_3)(PPh_3)] \qquad \ldots(60)$$

$$PPh_4[MoNCl_4] \xrightarrow[PCl_5]{PCl_3} PPh_4[MoCl_5(NPCl_3)] \qquad \ldots(61)$$

Photolysis of $({}^{i}Pr_2N)_2PN_3$ in the presence of trapping agents has already been mentioned,[283] but surprisingly in the absence of such agents the intermediate , ${}^{i}Pr_2NPN$, dimerises to (154) the first example of a cyclic diphosphazene.[306] The compound can be recrystallised from chloroform as an air stable disolvate, containing a planar four membered ring. From endocyclic P-N distances of 1.648 and 1.651Å the formal unsaturation is strongly delocalised. P-N-P and N-P-N angles are 85.0 and 95.0° respectively with exocyclic P-N separations of 1.645Å.



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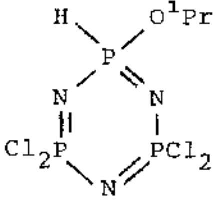

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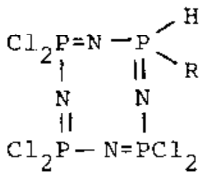
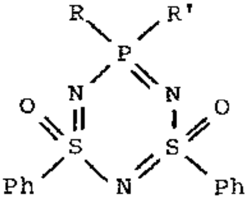


(156)

Alkyl-lithium reactions with chlorocyclophosphazenes are little understood but recent work has shown that the products from the reactions of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ with MeLi followed by i-propanol are the hydrido species (155)[307] and (156, R = O^{i}Pr and Me) respectively.[308] Related reactions using ^{t}BuLi and ^{i}PrOH with P-N-S heterocycles, e.g. (157, R = R' = Cl), also give a hydride product (157, R = H, R' = ^{t}Bu) together with the chloride (157, R = Cl, R' = ^{t}Bu).[307] Novel bi(cyclotetraphosphazenes) (158, R = Me or Et) on the other hand are the products when $N_4P_4Cl_8$ is treated with MeLi in THF followed by, respectively, MeI or EtI.[308]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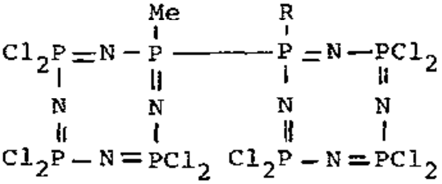
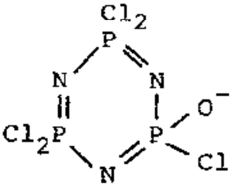

(158)

Hydrolysis of $N_3P_3Cl_6$ with water in acetonitrile in the presence of either Ph_4AsCl or the 18-crown-6 complex of KCl leads to salts of the anions, (159) and (160), the latter in both cis and trans isomeric forms.[309] The mixed P-N-S heterocycle, [$(NPCl_2)_2NSOCl$], similarly gives two isomeric forms of (161) with the disubstitution product (162) obtained when an excess of water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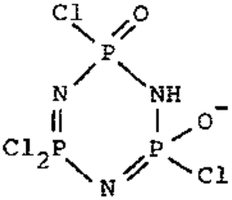
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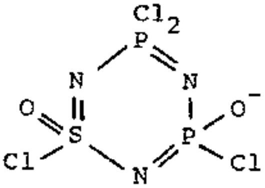
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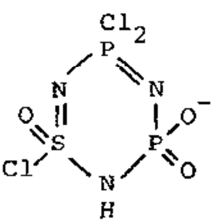
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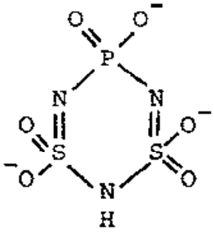
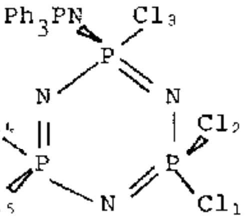

(163)

is used. The related heterocycle, $[NPCl_2(NSOCl)_2]$, is completely hydrolysed with aqueous solutions of NH_4HCO_3 or NaOAc to the anion (163) where the hydrogen atom is located on the nitrogen distant from phosphorus.[310] The ring has a chair conformation with P-N distances of 1.63 and 1.70Å; S-N distances range between 1.58 and 1.67Å.

Aziridine substituted phosphazenes continue to command interest in view of their antitumor activity. A high dilution technique has been used to synthesise the pure geminal isomer, $N_3P_3(NC_2H_4)_4(NH_2)_2$, which under normal preparative conditions is obtained as a mixture of two conformers together with $N_3P_3(NC_2H_4)_5NH_2$.[311] Substitution of the chlorine atoms in (164) follows the order given by the numerical subscripts to give compounds in the series, $N_3P_3(NPPh_3)Cl_{5-n}(NC_2H_4)_n$ for n = 1-5.[312] They can be separated by column chromatography. The penta-aziridine compound contains a planar ring with distances varying between 1.576 and 1.610Å; P-N(aziridine) distances are 1.677 to 1.722Å. The Ph_3PN conformation is unusual bringing one of the phenyl groups into close proximity to the gem aziridine group and is markedly different from those in previously investigated compounds. Aziridine reactions with the spirocyclic derivatives, $N_3P_3Cl_4[NH(CH_2)_{3\text{ or }4}NH]$, have been investigated.[213]



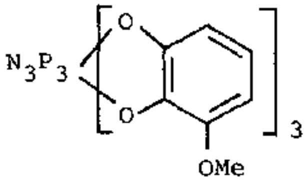
(164)

As an alternative to the Kirsanov reaction for converting amidophosphazenes to the corresponding $N{:}PPh_3$ derivatives, treatment with an excess of Ph_3PCCl_4 in an acetonitrile-trimethylamine mixture has been successful in the formation of gem-$N_3P_3Cl_4(N{:}PPh_3)_2$ and $N_3P_3Cl_3NMe_2(NPPh_3)_2$.[314]

I.r. and n.m.r. spectroscopy points to bonding via ring nitrogen atoms in the majority of the stable, solid SiF_4 adducts with aminocyclophosphazenes.[315] Among the compounds isolated were $N_3P_3(NMe_2)_4Cl_2.SiF_4$, $2[N_3P_3(NMe_2)_6].3SiF_4$,

$2[N_3P_3(NHMe)_6].3SiF_4$, $N_4P_4(NHMe)_8.3SiF_4$, $N_4P_4(NMe_2)_8.3SiF_4$ and $N_4P_4(NH^tBu)_8.2SiF_4$. In the adducts of the spirocyclic ethylenediamine derivatives, $N_3P_3(NHCH_2CH_2NH)Cl_4.SiF_4$ and $N_3P_3(NHCH_2CH_2NH)(NMe_2)_4.3SiF_4$, the exocyclic nitrogen atoms are also involved in the bonding. ^{31}P n.m.r. spectra have been measured for the cis and trans isomers of the mixed chloro-phenoxy-triphosphazenes[316] and ESCA data have been obtained for the spirocyclic (165) and its 1,2-dichloroethane clathrate.[317] ^{35}Cl n.q.r. data for $N_3P_3Cl_4Ph_2$ and $N_3P_3Cl_4(NMe_2)_2$ are also available.[318]

A predominantly non-geminal path is followed in the substitution of $N_3P_3Cl_6$ with sodium p-cresoxide, although small quantities of geminal isomers can be detected at the di- and tri-stages.[319] The yields of each isomer are almost the same as those in the reinvestigated reaction with sodium phenoxide itself and the greater yield of the cis over the trans disubstituted isomer is rationalised by invoking a through space interaction between an oxygen p orbital of an aryloxy group already present and a phosphorus 3d orbital. The $N_3P_3Cl_4Me$ group in (166, X = Y = H; X = H, Y = F, OMe or NMe_2; X = NMe_2, NEt_2, Me, ^tBu, Ph, OMe, F or Cl, Y = H) has a similar electron withdrawing power to the cyanide group from a series of spectroscopic investigations to evaluate the Hammett and Taft parameters.[320]



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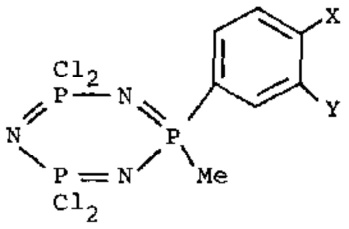
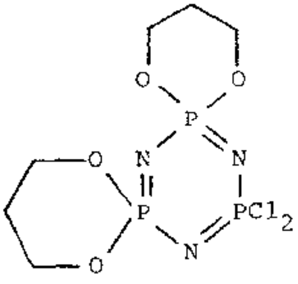


(166)

Two isomeric $N_3P_3Cl_2[O(CH_2)_3O]_2$ derivatives have been isolated from reactions between $N_3P_3Cl_6$ and 1,3-dihydroxypropane which n.m.r. spectroscopy suggests are the dispiro (167) and spiroansa (168) substitution products.[321] This assignment was confirmed by X-ray structures for both compounds showing chair conformations for the phosphate rings in (167) and chair and boat-chair conformations for the six and eight membered rings respectively in (168). The P-N-P angle in the ansa system of (168) is reduced to



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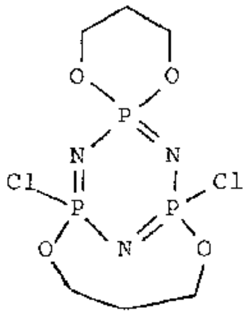
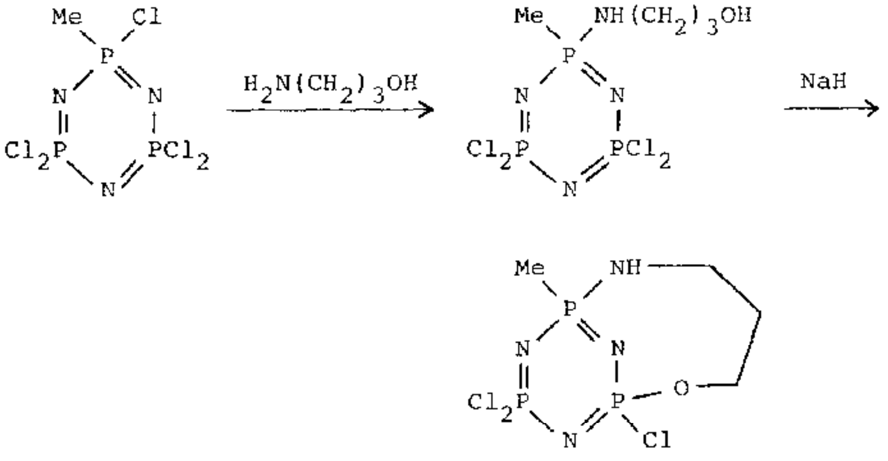


(168)

112.7°. A second anso compound (169) results from the reactions outlined in equation (62).[322] In the final step, a highly dilute

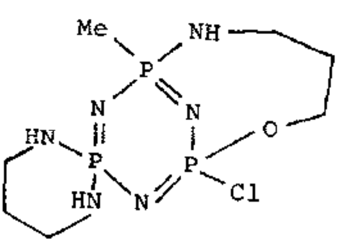


...(62)

(169)

solution of the precursor in dry THF reacts with an excess of sodium hydride over 50h at room temperature.

The ansa compound (169) reacts with 1,3-diaminopropane to give (170), which with 1,6-diaminohexane leads to the bridged compound (171).[323] Three dispiro derivatives have been isolated from reactions between $N_3P_3Cl_6$ and N-methylethanolamine,[324] and n.m.r. data together with an X-ray structure for the dispiro product obtained. The latter shows a cis arrangement of exocyclic nitrogen atoms with dihedral angles of 89.1 and 89.9° between the planar N_3P_3 and spiro rings. Exocyclic P–N distances are 1.635 and 1.624 with P–O values of 1.587 and 1.582Å; endocyclic P–N



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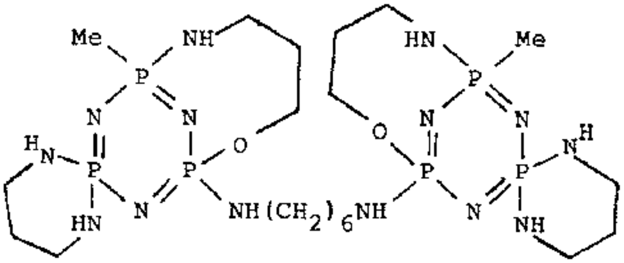
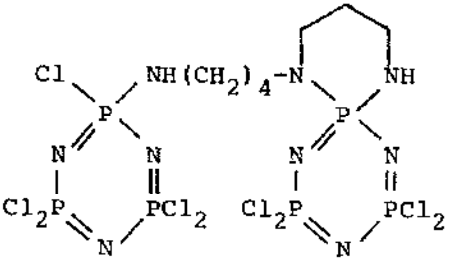


(171)

distances vary between 1.565 and 1.602Å. The O-P-N angles in spirocyclic ring are 95.9 and 96.2°.

The reaction between $N_3P_3Cl_6$ and $H_2N(CH_2)_{3or4}NH_2$ has been reinvestigated and the structure of the dihydrated $N_3P_3[NH(CH_2)_3NH]_3$ determined.[325] Reactions with more complex alkylamines, spermidine $H_2N(CH_2)_3NH(CH_2)_4NH_2$,[326] and spermine $H_2N(CH_2)_3NH(CH_2)_4NH(CH_2)_3NH_2$,[327] yield (172) and (173) respectively with an X-ray structure confirming the identity of the latter. CNDO/2 calculations have been used to probe the electronic and/or geometrical factors involved in determining the conformations adopted by spirocyclic phosphazene.[328]



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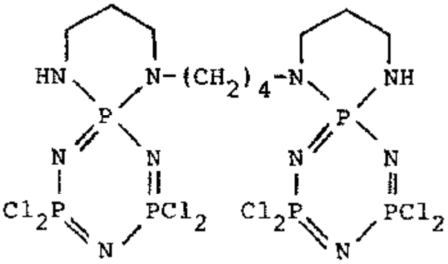
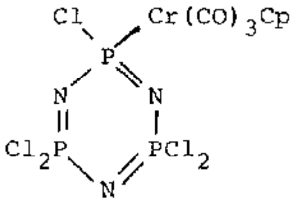


(173)

A number of cyclophosphazenes carrying metal containing substituents have been reported during 1984 from reactions with metal carbonyls[329] and substituted metallocenes.[330,331] On treatment with $Bu_4N[Cr(CO)_3Cp]$, one chlorine atom is substituted in $N_3P_3Cl_6$ to produce (174), while the related molybdenum and tungsten anions yield products (175, M = Mo or W) which also carry a P-cyclopentadiene group.[329] Success in these reactions depends on using the tetrabutylammonium cation, the potassium salt, for example, leads to small amounts of the halogen abstraction product, $MCl(CO)_3Cp$. The structures are based on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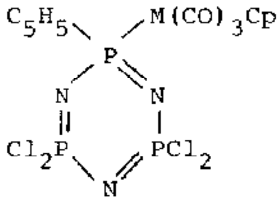
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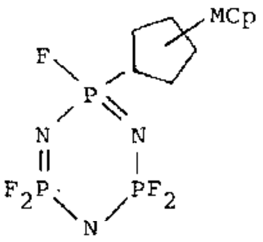
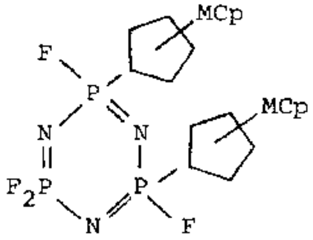

(176)

X-ray investigations of (174) and (175, M = Mo).

Mono- and di-lithiated ferrocene and ruthenocene react with $N_3P_3F_6$ giving a range of substitution products (176)-(179) including compounds in which the metallocene bridges between phosphorus atoms in the same or different cyclophosphazene molecules.[330] Structures for (176, M = Fe) and (178, M = Ru) confirm the assignments. The tetrameric fluoride reacts similarly to give mono- and 2,6-disubstituted compounds analogous to (176) and (177) but both 2,4- and 2,6-transannular bridged species can also be obtained. Initial reactions with $N_3P_3Cl_6$ are similar to those of the trimeric fluoride allowing isolation of the chlorine equivalent of (176), but among others unusual products such as (180), (181, X = H or Cl) and (182) are also obtained. The structure of (182, M = Fe) has been determined. Monolithioferrocene and the tetrameric chloride give what appears to be normal disubstituted compound, $N_4P_4Cl_6(C_5H_4FeCp)_2$, but rather surprisingly its structure (183) is based on the trimeric N_3P_3 nucleus with a large (142.7°) N-P-N angle in the side chain.[331] When a 1:1 mixture of the trimeric and tetrameric chlorophosphazenes is treated with monolithioferrocene, the product is an unusual bicyclic compound (184) containing a P-P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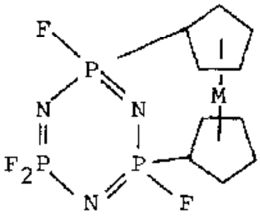
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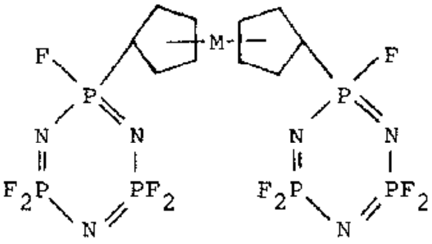
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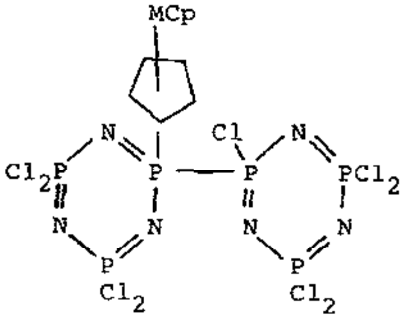

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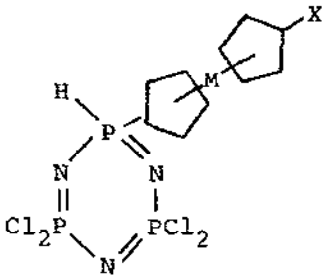

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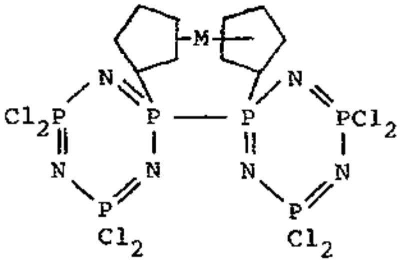

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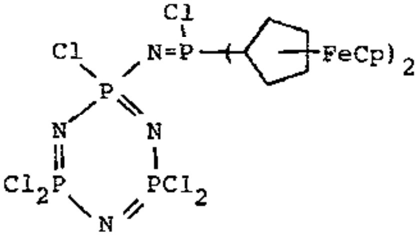

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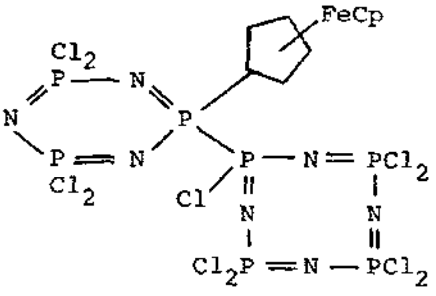
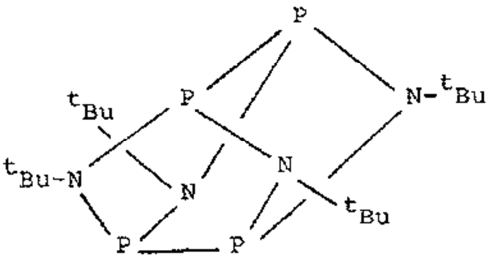


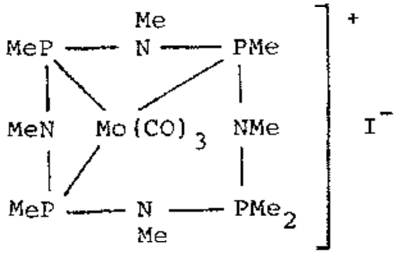
(184)

bond between the six and eight membered rings.

A new eight membered N_4P_4 cage species (185), an analogue of N_4S_4, has been isolated from a reaction of the diazadiphosphetidine $(ClPN^tBu)_2$ with magnesium in THF solution.[332] The molecule has S_4 symmetry with planar nitrogens and a bisbisphenoid arrangement of phosphorus atoms; the P-N bonds alternate in length (1.708, 1.742Å) while the P-P distances (2.330, 2.340Å) are long compared with normal single bonds. The reaction also gives a second, oily product which is possibly an isomeric form of (185).



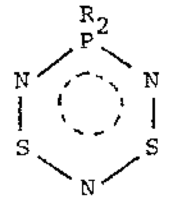
(185)



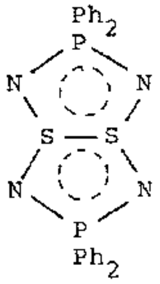
(186)

The η^3-bonded complex (186), obtained from $Mo(CO)_6$ and $[(MePNMe)_4Me]I$, contains a molybdenum atom coordinated to three phosphorus atoms at distances between 2.439 and 2.483Å.[333]

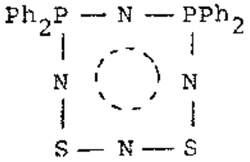
Further properties of the interesting hybrid phosphazene-thiazene derivatives, (187) and the isomeric 1,5- (188) and 1,3-$(Ph_2PN)_2(SN)_2$ (189) species, have been reported. Chlorine is oxidatively added to (187) and (188) on treatment with SO_2Cl_2 giving respectively (190)[334] and (191, X = Cl),[335] but with (189)



(187, R = Me or Ph)



(188)



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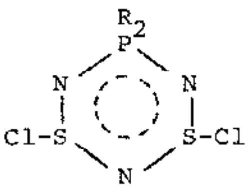

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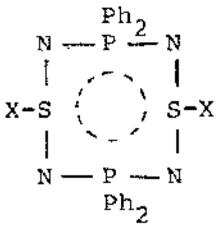

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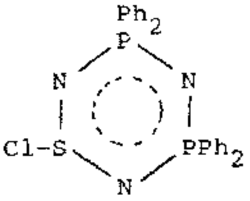
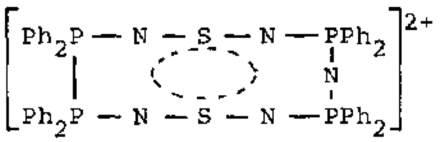


(192)

ring contraction occurs giving (192).[335] Compound (188) with bromine gives (191, X = Br), but again the isomeric (189) reacts differently giving the tribromide salt of the cation (193). Compound (194) is a neutral derivative of (193) which is obtained from a reaction of Ph_3Sb with $[(Ph_2PN)_2NSCl]$ (195, R = R' = Ph).



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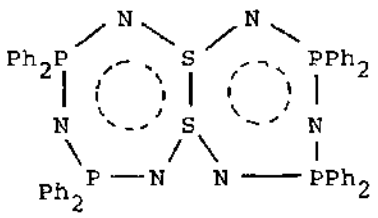

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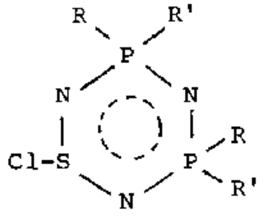


(195)

Crystal structure determinations for (191, X = Br), (193) and (194) put these formulations on a firm basis.

A new route to compounds of the type (195) uses the reaction of a 3:1 mixture of phosphorus(III) chloride with N_4S_4 in acetonitrile solution.[336] The method is particularly successful using Ph_2PCl for (195, R = R' = Ph) but analogues with R = Ph, R' = Cl and R = R' = Cl can be obtained in lower yields using $PhPCl_2$ and PCl_3 respectively. The chlorine atom in (195, R = R' = Ph) can be substituted, inter alia, by I, Ph or NMe_2 on reaction with respectively KI, Ph_2Hg or Me_3SiNMe_2. Corresponding reactions with bromine or iodine, on the other hand, give trihalide salts of the $[(Ph_2PN)_2(SN)]^+$ cation but thermolysis or treatment with Ph_3Sb converts the tribromide into $[(Ph_2PN)_2(NSBr)]$.

5.2.5 Bonds to Oxygen

Lower Oxidation States. Although free phosphinous acid, H_2POH, is unknown its stabilisation as a complex with $W(CO)_5$ has recently been announced.[337] The preparative route involves reduction of $Et_2NPCl_2.W(CO)_5$ to $Et_2NPH_2.W(CO)_5$ by $LiAlH_4$ followed by hydrolysis of the latter in the presence of acetic acid.

An X-ray structure of P_4O_6 single crystals grown from the melt shows the well known cage structure observed previously for the gas phase.[338] Although P-O-P and O-P-O bond angles (mean 127.0 and 99.5° respectively) are close to those in the gas phase, crystal packing effects lead to a mean P-O distance (1.653Å) greater than that (1.638Å) in the vapour. Using Ag_2O, it has been possible to oxidise P_4O_6 to P_4O_7 in a one step process;[339] vibrational spectra and a single crystal X-ray study are reported.

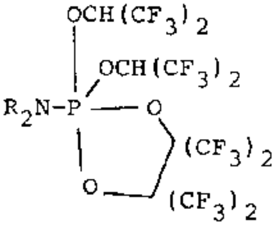
Hexachlorobenzene and sodium diethylphosphite react following the redox process in equation (63) to give a phosphonite diester, which with air and sulphur can be oxidised to the phosphonic and

$$(EtO)_2PONa + C_6Cl_6 \rightarrow C_6Cl_5P(OEt)_2 + (EtO)_2PO_2Na + NaCl \qquad ...(63)$$

$$R_2NPCl_2 + 2LiOCH(CF_3)_2 \rightarrow R_2NP[OCH(CF_3)_2]_2 + 2LiCl \qquad ...(64)$$

R = Me, Et or $SiMe_3$

thiophosphonic diesters respectively.[340] The lithium salt, $LiOCH(CF_3)_2$, reacts with a range of dichloroaminophosphines, equation (64), and further reaction of the phosphite products (R = Me or Et) with hexafluoroacetone yields the phosphorus(V) species (196).[341] The chlorine atom in the substituted dioxaphospholane (197) can be replaced by I, $OCH(CF_3)_2$, $OSiMe_3$ and



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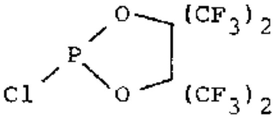

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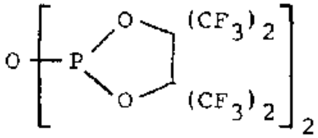
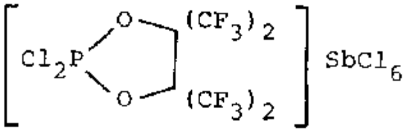


(198)

O_2CCF_3 and the latter on thermal decomposition eliminates trifluoroacetic anhydride to give the oxodiphosphite (198).[342] Compound (197) can be oxidised by $SbCl_5$ or ICl, the former yielding the salt (199) and the latter the corresponding trichlorophosphorane.



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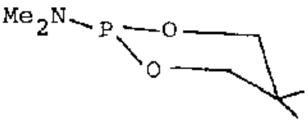
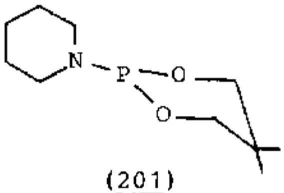


(200)



(201)

Data from a variety of physical techniques points to the presence of amine groups in equatorial positions in the dioxaphosphorinanes (200) and (201);[343] this contrasts with occupation of the axial position in the related methoxy derivatives. In both compounds, the solid state structure shows planar geometry about the nitrogen atom consistent with extensive $N \rightarrow P$ π-bonding; the PO_2C_3 rings have a chair conformation. He(I) photo-electron spectra have been measured for a series of polycyclic phosphite, thiophosphite and arsenite esters.[344]

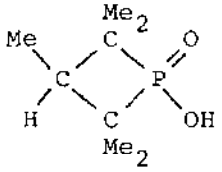
Metal carbonyl complexes with $P(OCH_2CF_3)_3$ ($\equiv$L) including $Ni(CO)L_3$, $Ni(CO)_2L_2$, $CpFeIL_2$ and $(Me_3C_6H_3)Cr(CO)_2L$ have been isolated as relatively stable products of reactions with $Ni(CO)_4$, $CpFe(CO)_2I$ and $(Me_3C_6H_3)Cr(CO)_3$.[345]

Crystal structures have been determined for $NH_4H_2PO_3$[346] and the hydrated calcium phosphite, $Ca(H_2PO_3)_2.H_2O$.[347] The former contains infinite chains of HPO_3^- tetrahedra linked by O-H...O hydrogen bonds (O...O 2.546Å) which are then interconnected by N-H...O hydrogen bonds.

The +5 Oxidation State. Further evidence is now available from negative ion mass spectrometry[348] and kinetic data[349] for the identification of the monomeric, metaphosphate anion, PO_3^-. Mass spectra of a series of phosphate triesters can be rationalised by the initial capture of a thermal electron followed by loss of either a vinyl or aryl group to give the dimethylphosphate anion. Subsequent elimination of dimethylether will then give PO_3^-, which when suitably activated decomposes by loss of an oxygen atom to produce the metaphosphite ion, PO_2^-. Other evidence comes from the smooth unimolecular decomposition of $PhCH(PO_3^{2-})CHBrCOPh$ in methanol solution to give a chalcone PhCH:CHCOPh and bromide ion in addition to the metaphosphate anion. Observation of a three coordinate phosphorus(V)-oxygen compound, $^tBu_3C_6H_3P(:O)(:CPhSiMe_3)$, has already been mentioned.[151]

Acid-base equilibria in D_2O solution of the phosphonic acids, $MePO_3H_2$ and $H_2N(CH_2)_{1-3}PO_3H_2$, have been studied by multinuclear n.m.r. spectroscopy.[350] In the amino-derivatives, the phosphorus chemical shift is markedly affected by amine deprotonation and cyclic conformers from the close contact between amine and phosphonate groups are proposed. ^{31}P n.m.r. shift changes have been used to assess association constants for a variety of Group 1 and 2 cations with, for example, dimethylphosphate monoanion, ethylphosphate dianion, the AMP dianion and the CAMP monoanion.[351] The complexing power of the substituted ethylenediamine, $[CH_2N(CH_2PO_3H_2)_2]_2$, has been investigated and a number of M(II) complexes isolated.[352]

Little is known about the simple chemistry of pentamethylphosphetanic acid (202) but recently its Group 1, strontium, barium, silver and ammonium salts have been isolated.[353] In many respects the free acid is similar to a carboxylic acid and forms hydrogen bonded dimers which persist in CCl_4 solution at concentrations as low as 0.001M. The acid forms adducts with diethylamine[353] and complexes with first row transition elements[354] can be prepared.



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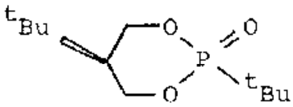

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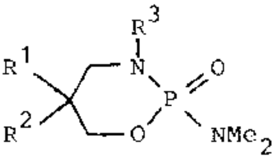
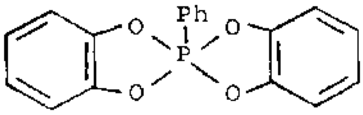


(204)

Structures have been determined for the cis substituted phosphorinane (203)[355] and two oxazaphosphorinanes (204, R^1 = Ph, R^2 = H, and R^3 = NMe_2;[356] and R^1 = R^2 = Me and R^3 = H,[357] showing rings with, respectively, boat, twist and chair conformation. In the 5-phenyl derivative (204), this substituent and the planar NMe_2 group are in cis positions and occupy pseudo-equatorial sites whereas in the last example the NMe_2 group is axial and deviates markedly from planarity.

On partial hydrolysis in the presence of Ph_4PCl, the catechol compound (205) gives a monocatechol adduct of the 2-hydroxyphenylphosphonate anion (206); its structure contains



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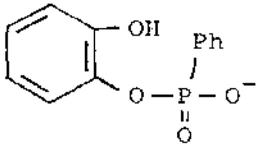
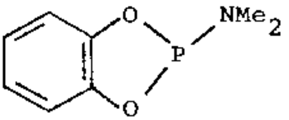
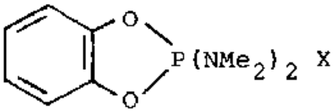


(206)

intramolecular hydrogen bonded seven atom rings which are further linked into chains.[358] Elementary chlorine or bromine convert the phosphorus(III) catecholate (<u>207</u>) to bis(amino)phosphonium salts (<u>208</u>, X = Cl or Br); the reaction proceeds via the expected halogen oxidation product which undergoes ligand exchange with



(<u>207</u>)



(<u>208</u>)

a further molecule of (<u>207</u>).[359] Related morpholine and piperidine derivatives have also been isolated.

Reaction of trimethylphosphate and hexamethylphosphoric triamide in a 2:1 mol. ratio gives the trimetaphosphate, $(Me_4N)_3P_3O_9$, as the major product together with small amounts of the ultraphosphate $(Me_4N)_4(P_3O_8{\cdot}O{\cdot}P_3O_8)$; dimethyl ether and trimethylamine are liberated.[360]

Structures have been determined for two tin addition compounds, $2[(Me_2N)_3PO].Me_2SnCl_2$[361] and the triphenylphosphine oxide of tri-3-thienyl tin bromide.[362] As the former is centrosymmetric the pairs of phosphoryl ligands, methyl groups and chlorine atoms occupy trans positions.

The framework aluminophosphate, $AlPO_4$-15, is correctly formulated as $Al_2(NH_4)(OH)(PO_4)_2.2H_2O$ and is an analogue of $GaPO_4.2H_2O$.[363,364] Its structure contains edge sharing $AlO_4(OH)_2$ and corner sharing $AlO_4(OH)(H_2O)$ octahedra, linked by PO_4 tetrahedra to form channels which are approximately parallel to the b axis. The ammonium cations occupy the channels and are hydrogen bonded to framework oxygens and a water molecule. A second compound, $AlPO_4$-12, $Al_3P_3O_{11}(OH)_2$.en, prepared by adding ethylenediamine to an aluminophosphate gel prior to heat treatment at 200°C, has an open framework structure in contrast to the zeolite-type structure above.[365] It contains $[AlPO_4(OH)]^-$ sheets based on four coordinate phosphorus and aluminium atoms and $[Al_2P_2O_7(OH)]^+$ slabs containing four coordinate phosphorus and five coordinate aluminium. The ethylenediamine is clathrated in the channels that suggest its structure directing role in the synthesis.

A new series of microporous crystalline silico-alumino-phosphates have been synthesised hydrothermally from mixtures of alumina, silica and phosphate in the presence of an amine or a quaternary ammonium salt.[366] As in the case above, the latter behave as templates and are retained in the products. The structure of a synthetic phosphorus substituted molecular sieve, $Na_{13}Al_{24}Si_{13}P_{11}O_{96}.16H_2O$ points to alternation in the occupancy of the tetrahedral sites by aluminium atoms and silicon/phosphorus.[367]

H^+-K^+ exchange on α-titanium phosphate, $Ti(HPO_4)_2.H_2O$, leads to $Ti(KPO_4)_2.3H_2O$ and $Ti(KPO_4)_2.2H_2O$ with interlayer spacings of 10.4 and 9.6Å respectively, but no partially substituted phases could be detected.[368] The structure of half exchanged α-zirconium phosphate, $ZrKH(PO_4)_2$, shows a layer structure similar to that in α-$Zr(HPO_4)_2.H_2O$ but with adjacent layers displaced by ½b.[369] Exchange on high temperature $Na_2Zr(PO_4)_2.nH_2O$ phases has been followed using radioactive sodium.[370]

Metastable alcohol phases of hydrated α-$Zr(HPO_4)_2$ take up bipyridyl or 1,10-phenanthroline to give $Zr(HPO_4)_2(bipy)_{0.25}1.5H_2O$ and $Zr(HPO_4)_2(phen)_{0.5}2H_2O$ with interlayer spacings of 10.9 and 13.6Å respectively.[371] Microcrystalline compounds, formulated as $Zr(R_3NH)_xH_{2-x}(PO_4)_2.yH_2O$ with $x = 0.1$-0.6 and $y = 1$-3, result from hydrothermal reactions between $ZrOCl_2$ and $(R_3NH)H_2PO_4$, where R = Me, Et, Pr, Bu, Pentyl etc.[372] Interlayer spacings range between 9.9Å for R = Me to 16.5Å for R = pentyl.

Layer type vanadyl organophosphonates, similar to the better known zirconium compounds, $Zr(RPO_3)_2$, are obtained by refluxing V_2O_5 with, for example, phenylphosphonic acid in 95% ethanol.[373] The initial product is $VO(PhPO_3).H_2O.EtOH$ which in the atmosphere is converted into the dihydrate; the related p-methoxyphenyl and p-biphenylyl phosphonic acid analogues were also isolated.

Crystals of $(VO)_2H_4P_2O_9$, the precursor of the catalyst $(VO)_2P_2O_7$, have been grown for X-ray diffraction from VO_2 and 85% phosphoric acid.[374] The basic structure consists of vanadyl hydrogen phosphate layers stacked along the c axis and held together by hydrogen bonds; the layers contain pairs of face sharing VO_6 octahedra, four oxygens of which are from phosphate groups. Statistical disordering of the vanadyl oxygen and apical phosphate oxygen between two equivalent sites occurs at room temperature but this is removed on cooling to −130°C.

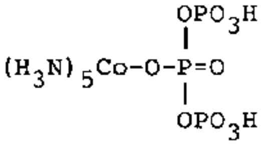
A vanadium(IV) phosphate, $VO(HPO_4).\frac{1}{2}H_2O$, can be synthesised by refluxing $VOPO_4.2H_2O$ with 2-butanol or, more conveniently, by treating V_2O_5 with an excess of concentrated phosphoric acid in ethanol.[375] The compound was characterised by redox titrations, powder X-ray diffraction, etc; its structure is based on layers of hydrogen bonded HPO_4^{2-} anions and pairs of antiferromagnetically coupled U^{4+} cations. Heating above 350°C causes a topotactic dehydration to $(VO)_2P_2O_7$.

Methanephosphonic acid and either potassium or ammonium metavanadates react to give $M(MePVO_5).H_2O$, where M = K or NH_4;[376] the potassium salt contains a polymeric framework based on corner sharing between VO_5 trigonal bipyramids and $MePO_3$ tetrahedra (P-O 1.514-1.528, P-C 1.772Å). The free acid $H(MePVO_5).H_2O$ has also been isolated.

A crystalline layer germanium phosphate, $Ge(HPO_4)_2H_2O$ with an interlayer spacing of 7.75Å has been prepared by refluxing a 10:1 mixture of 85% phosphoric acid and aqueous germanium tetrachloride for 9h.[377] One molecule of water is lost on heating to ca. 320°C with a decreased spacing of 7.34Å (at 400°C). Further water loss between 450 and 700°C gives GeP_2O_7, paralleling the behaviour of the titanium and zirconium phosphates.

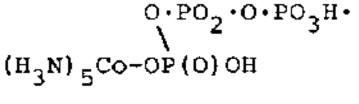
Metal-phosphate complexes continue to be investigated as biological probes serving as structural models for nucleotide complexes or models for the metal ion assisted hydrolysis of ATP. Cobalt in $Co(NH_3)_5.PO_4.3H_2O$ is in slightly distorted octahedral coordination to five nitrogen atoms and an oxygen atom (Co-O 1.945Å) of a unidentate phosphate group.[378] The Co-O-P angle is 129.6° and the structure is completed by an extensive hydrogen bonded network involving all oxygen and nitrogen atoms.

The β- (209) and γ- (210) coordination isomers of the triphosphate complex $[Co(NH_3)_5(H_2P_3O_{10})].H_2O$ have been synthesised from $[Co(NH_3)_5CO_3]NO_3.H_2O$ and $Na_5P_3O_{10}$ in nitric acid solution and separated using an anion exchange column.[379] In addition to ^{31}P



$(H_3N)_5Co{-}O{-}\overset{\displaystyle OPO_3H}{\underset{\displaystyle OPO_3H}{P}}{=}O$

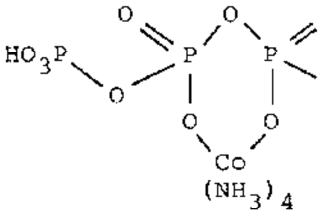
(209)



$(H_3N)_5Co{-}\overset{O\cdot PO_2\cdot O\cdot PO_3H\cdot}{OP(O)OH}$

(210)

n.m.r. data, there are single crystal X-ray structures for both compounds. Hydrolysis[380,381] and isomerisation[380] of the two triphosphate complexes (211) and (212) have been followed by ^{31}P n.m.r. and visible spectroscopy. The βγ-isomer (211) is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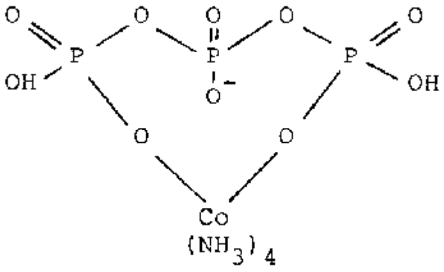
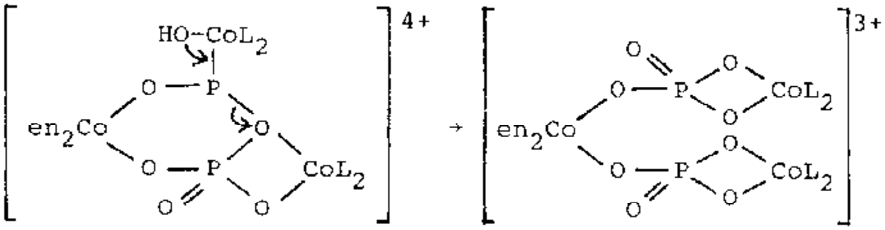

(212)

favoured at 40°C and pH 6.5, shown by hydrolysis rate constants of $3.0 \times 10^{-6} sec^{-1}$ and $6.5 \times 10^{-6} sec^{-1}$ for (211) and (212) respectively. Ring strain, which must vary markedly in the two forms, is not apparently a major factor in determining hydrolysis rates. P-O-P bond cleavage has also been studied by n.m.r. spectroscopy in reactions of $[Coen_2P_2O_7]^-$ with $[CoL_2OH(OH_2)]^{2-}$ where L = propane-1,3-diamine.[382] The data point to the metals acting in concert, equation (65), providing a coordinated nucleophile, OH^-, to assist the leaving group in breaking a central P-O bond and to neutralise the charge on the PO_3 residues.


...(65)

^{31}P n.m.r. data on the hydrolysis of di- and tri-phosphates in the presence of cis-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ have been reported.[383]

Structural studies on two chromium complexes, $[Cr(NH_3)_4HP_2O_7].2H_2O$[384] and the related methylenediphosphate, $[Cr(NH_3)_4(HPO_3 \cdot CH_2 \cdot PO_3H)]Cl$,[385] show in the former a chelating diphosphate group with two intramolecular hydrogen bonds between axial ammonias and phosphate oxygens. The methylenediphosphate group also chelates giving a six membered ring in the half-chair conformation.

Adenosine-5'-(1-thiodiphosphate) can replace the chlorines in $[Cr(H_2O)_4Cl_2]^+$ at 80°C and pH3 to give an αβ-complex[386] and rhodium polyphosphates such as $Rh(H_2O)_4HP_2O_7$, $Rh(H_2O)ADP$, $Rh(H_2O)_nATP$ and a triphosphate complex where the ligand is tridentate have been produced to serve as probes for the behaviour of Mg(II) species in biological systems.[387]

Magnesium and calcium phosphoramidates, $Mg(PO_3NH_2).7H_2O$[388] and $Ca(PO_3NH_2).H_2O$[389] have been obtained from the metal chloride and potassium phosphoramidate in aqueous solution. On heating in air, the calcium salt is initially dehydrated but then gives mono- and di-phosphate while the magnesium analogue yields polyphosphates. The imidodiphosphate, $M_2(O_3PNHPO_3)$, can be observed in each case on heating in dry nitrogen.

Five members if a new series of diphosphate tungsten bronzes, i.e. $BaP_4O_8(WO_3)_{2m}$ for $6 \le m \le 10$, have been prepared by heating mixtures of $BaCO_3$, $(NH_4)_2H_2P_2O_7$ and WO_3 in the ratio 1:4:2m-1 initially to 873K and finally with metallic tungsten in vacuum for several days at 1173-1473K.[390] Two members of a related sodium series, e.g. $Na_xP_4O_8(WO_3)_8$ where x = 1.1-1.5 and $Na_xP_4O_8(WO_3)_{12}$ where x = 1.6-4, were similarly obtained by heating mixtures of Na_2CO_3, $(NH_4)_2HPO_4$ and WO_3 followed by treatment with tungsten at 1173K.[391] Both series have been examined crystallographically, the latter contain frameworks of ReO_3-type slabs connected by PO_4 tetrahedra and distorted hexagonal tunnels containing sodium cations.

The solubility if $MgHPO_4.3H_2O$ in the $Mg(OH)_2$-H_3PO_4-H_2O system can best be described in terms of ion pair formation involving $MgH_2PO_4^+$ and $MgHPO_4$.[392] Cocondensation occurs in heating mixtures of $Ca(H_2PO_4)_2$ and $CaHPO_4$ to form oligomers with the formula $Ca_{n/2}H_2P_nO_{3n+1}$[393] and 140 compositions in the CaO-MgO-P_2O_5 system with $P_2O_5 \leqslant 33.3$ mol% have been investigated at 1000°C.[394]

$Ca_2KH_7(PO_4)_4.2H_2O$ is isomorphous with the ammonium salt from recent X-ray and neutron diffraction data[395] and the $Ca(NH_4)PO_4.7H_2O$ structure has been determined as part of an investigation into highly hydrated phosphate compounds.[396] The latter contains distorted pentagonal pyramidal $Ca(H_2O)_7$ units hydrogen bonded to phosphate tetrahedra giving a layer structure similar to that in struvite, $Mg(NH_4)PO_4.6H_2O$.

Replacement of calcium in hydroxyapatite by barium has been studied by both high temperature solid state reactions and by precipitation from aqueous solution.[397] The former leads to solid solutions over the barium concentration range 60-100 atom%

but there is little barium incorporation in aqueous solution.

X-ray powder data for the mixed apatites, $Mg_xCa_{10-x}(PO_4)_6F_2$ where x = 1-4, point to an increased distortion of the unit cell with increasing magnesium content, e.g. the unit cell volume decreases from 523.1Å^3 for x = 0 to 517.2Å^3 for x = 4, but there appears to be no effect on the P-O bond strengths.[398] The implications for the properties of vertebrate hard tissues are considered. Other compounds of biomineral interest are $CaX(H_2PO_4).4H_2O$ where X = Br or I obtained by adding 85% phosphoric acid to solutions of either $CaBr_2$ or CaI_2;[399] their structures have been determined.

New synthetic methods for $Sn_3(PO_4)_2$ and $Sn_3PO_4F_3$ and the hydrolytic and thermal stability of the latter have been reported.[400] Detailed i.r. and Raman spectra, together with a factor group analysis for the phosphate modes, have been measured for $SnHPO_4$, $PbHPO_4$ and their deuterium analogues.[401] When $SnHPO_4$ is heated between 360 and 590°C the major product is $Sn_2P_2O_7$ not a mixture with SnO_2 as previously reported.

Manganese diphosphate, $Mn_2P_2O_7$, a thortveitite-like compound, is isomorphous with $Sc_2Si_2O_7$ but refinement of the structure indicates a disordered, non-linear (165.9°) P-O-P system.[402] Reactions between phosphoric acid and Mn(III) at 373-573K give, inter alia, $Mn(PO_3)_3$, $MnPO_4.1\frac{1}{2}H_2O$, $MnHP_2O_7$ (three modifications), $MnH_2P_3O_{10}.2H_2O$ and $MnH_2P_3O_{10}$.[403] Related reactions of an excess of phosphoric acid with $M^IH_2PO_4$ and either $Al(OH)_3$ or $Fe(NO_3)_3.9H_2O$ at 170-450°C produced a range of mixed alkali aluminium or alkali iron phosphates, including $M^IM^{III}(H_2P_2O_7)_2$, $M^IM^{III}(HP_3O_{10})$, $M^IM_2^{III}(H_2P_3O_{10})(P_4O_{12})$, $[M^IM^{III}(PO_3)_4]_x$, $M^IM^{III}(P_4O_{12})$, $M_2^IM_2^{III}(P_8O_{20})$ and $M^IM^{III}P_2O_7$.[404] Two solid solutions, γ-$Zn_2Co(PO_4)_2$ and γ-$(Zn_{0.5}Co_{0.5})_3(PO_4)_2$, recently prepared are isomorphous with γ-$Zn_3(PO_4)_2$ and the mineral farringtonite.[405] Dehydration of the double phosphate $Zn_{3-x}Co_x(PO_4)_2.4H_2O$ for $0 < x \leq 1$, obtained from $Zn_2Co(PO_4)_2$ and $Zn_{2.5}Co_{0.5}(PO_4)_2$, can be followed by i.r. spectroscopy showing changes in the cation coordination and distortion of the PO_4 tetrahedra.[406]

Single crystals of $Na_2UO_2P_2O_7$ result when a mixture of the compound is fused with a seven fold excess of $NaPO_3$ at 850°C.[407] The structure contains a three dimensional $UO_2P_2O_7$ framework where uranium bonds to five oxygen atoms of four different P_2O_7 groups (mean U-O 2.38Å) in addition to the oxygens of the UO_2 group.

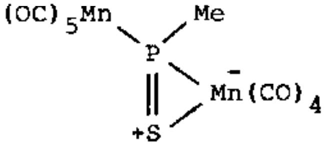
The overall coordination is pentagonal bipyramidal; the P-O-P angle is 135°.

The structure has been determined of the newly prepared trimetaphosphate, $Na_4Cu(P_3O_9)_2.4H_2O$.[408] The hydrated triphosphate, $Li_5P_3O_{10}.5H_2O$, unlike the corresponding sodium and potassium salts, is not dehydrated on heating but decomposes instead to the diphosphate.[409] Reaction between $(NH_4)_5P_3O_{10}$ and aqueous magnesium nitrate solution gives the new mixed salt $Mg_2NH_4P_3O_{10}.8H_2O$;[410] on heating six water molecules are removed more readily than the remainder. A related double salt, $NH_4Al_3(P_3O_{10})_2.16\text{-}18H_2O$, sparingly soluble and X-ray amorphous, can be obtained using aluminium nitrate in place of the magnesium salt; further addition of $(NH_4)_5P_3O_{10}$ leads to products with $Al^{3+}:P_3O_{10}{}^{5-}$ ratios of 1:1 and 1:2.[411] Discrete $H_2P_3O_{10}{}^{3-}$ groups are present in the structures of $K_3H_2P_3O_{10}.H_2O$ and $FeH_2P_3O_{10}$[412] while in $Na_3CuP_3O_{10}.12H_2O$ the triphosphate groups are linked by metal ions into a three dimensional net.[413] An interesting feature of the $Na_3CdP_3O_{10}.12H_2O$ structure is the behaviour of the triphosphate group as a tridentate ligand giving $CdP_3O_{10}(H_2O)_3{}^{3-}$ groups, held together by Na^+ ions and hydrogen bonded water molecules.[414]

Erbium triphosphate, $Er_5(P_3O_{10})_3.20H_2O$, is obtained from $ErCl_3$ and $Li_5P_3O_{10}$ but substitution of $(NH_4)_5P_3O_{10}$ gives a double phosphate, $(NH_4)_3Er_4(P_3O_{10})_3.14H_2O$.[415] $Na_3P_3O_{10}$ on the other hand gives both the hydrated phosphate and the double phosphate showing the ability to form mixed phosphates is $Cs \geq NH_4 > Na > Li$. Similar behaviour is observed with Pr and Gd.

5.2.6 Bonds to Sulphur or Selenium

The thioxophosphine MeP:S can be generated by treating $MePSCl_2$ with magnesium metal and trapped by $Mn_2(CO)_{10}$ as the complex (213).[416] The group is sideways bonded with a P-S distance of



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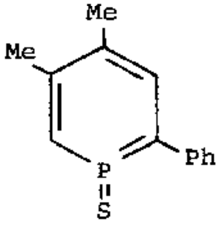

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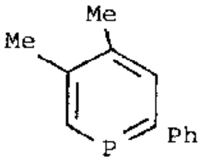

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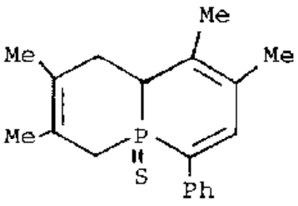
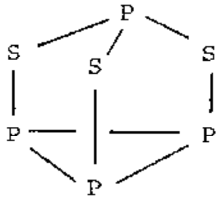


(216)

2.03A. A related species (214) is considered to be formed as an intermediate in the reaction of (215) with sulphur and can be trapped by 2,3-dimethylbutadiene in xylene as (216).[417] A stable aryl dithioxophosphorane, 2,4,6-$^tBu_3C_6H_2P(:S)_2$, has been isolated for the first time as a yellow solid melting at 150-1°C by either the reduction of $ArPH_2$ with S_2Cl_2 in the presence of 2,6-lutidine or by treating $ArP(S)H_2$ with sulphur also in the presence of lutidine.[418]

MNDO calculations are now available for the lower phosphorus sulphides, P_4S_2-P_4S_5, and their derived cations.[419] Calculated heats of formation for the P_4S_3 isomers (217)-(219) are -227.8, -180.5 and -160.8 kJ.mol^{-1} showing greatest stability for the well established form (217). Data for the two P_4S_4 isomers show



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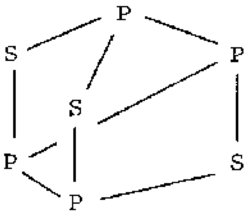

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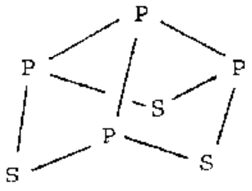
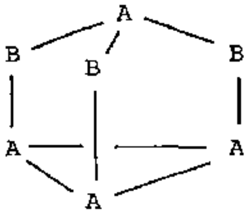


(219)

marginally less stability for the α-form (-294.5) [β-form (-305.3 kJ.mol^{-1})]. Compounds in the series $P_4S_xSe_{3-x}$ (for x = 0-3), $P_yAs_{4-y}S_3$ (for y = 0-4) and $P_yAs_{4-y}Se_3$ contain the same structural unit (220) with a basal triangle of Group 5 atoms and three chalcogens in bridging positions. ^{31}P n.m.r. data[420] have been analysed showing that chemical shifts, which vary from -121 ppm for P_4S_3 itself to -60ppm for PAs_3Se_3, where phosphorus occupies one of the basal positions, depend on a combination of changes in bond angle and electronegativity. There is, in fact, a linear relationship between the observed chemical shift and the



(220)

deviation of both the endo- and exo-cyclic angles from those in the reference compound P_4S_3 (see also ref.482).

New modifications of both $P_4S_3I_2$ and $P_4Se_3I_2$, designated as the α'-forms, have been obtained by treating either P_4S_3 or P_4Se_3 with iodine in the melt.[421] A full structure is available for the selenide - the sulphide is isotypic - which crystallises in the $I\bar{4}2d$ space group. ^{31}P n.m.r. data indicate the same bicyclic structure as in the solid is present in solution. Equilibrium in the P_4S_3-As_4S_3 system, equation (66), lies on the side of the

$$P_4S_3 + 3As_4S_3 \rightleftharpoons 4PAs_3S_3 \qquad \ldots(66)$$

mixed compound as a consequence of greater stability of P-S over As-S bonds.[422] An alternative approach uses the 'topological charge stabilisation' rule, i.e. that stable structures result by substitution of electronegative heteroatoms at sites where the electronic charges are more negative in the homoatomic, isoelectronic, reference compound. The reference species in this case is P_7^{3-} (191, A=B=P), where charge densities from Extended Hückel calculations decrease in the order: (a) bridging positions, (b) the unique apical position, (c) the basal triangle. In PAs_3S_3, the rule would place the most electronegative sulphur atoms in bridging positions, phosphorus with next highest electronegativity in the apical position, and the least electronegative arsenic atoms in the basal triangle.

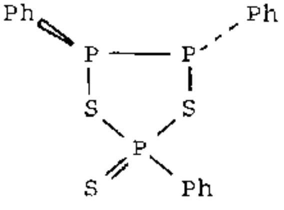
Tetrathiophosphate and trithiophosphite esters can be produced in quantitative yield by the photochemical reaction in equation (67).[423] In competitive reactions with Me_2S_2-Ph_2S_2 mixtures, the

$$P_4S_3 + 6R_2S_2 \rightarrow 3SP(SR)_3 + P(SMe)_3 \qquad \ldots(67)$$

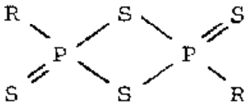
R = Me or Ph

product consists of all eight possible products $S_xP(SPh)_n(SMe)_{3-n}$, where x = 0 or 1 and n = 0-3 but there was preferential attachment of MeS groups at P(V) and PhS groups at P(III).

$(PhP)_3S_3$ can be prepared by treating $PhPCl_2$ with $(Me_3Sn)_2S$ in carbon disulphide solution at -30°C,[424] and because of ambiguities in the previously reported n.m.r. spectrum, the compound has been examined by X-ray diffraction. The structure contains a slightly puckered five-membered ring with a trans orientation of the phenyl groups at P(III) (<u>221</u>). Treatment with sulphur in refluxing CS_2 gives (<u>222</u>, R = Ph), which also contains trans phenyl groups. Major structural parameters are P-S(ring) 2.108, 2.133; P-S(terminal) 1.920Å; P-S-P 86.9; S-P-S 93.1°. The initial product when (mesityl)PCl_2 reacts with $(Me_3Si)_2S$ in toluene is [(mesityl)PS]$_4$, containing a crown conformation, eight membered P_4S_4 ring similar to that in S_8.[425] S-P-S angles vary between 105.8 and 106.6°, P-S-P angles between 95.7 and 97.8° with a mean P-S distance of 2.127Å. Mesityl groups are approximately perpendicular to the plane of the ring but the structure is disordered. On standing, there is decomposition giving (<u>222</u>, R = mesityl) with a structure similar to that of the phenyl derivative described above.



(<u>221</u>)



(<u>222</u>)

New evidence from a range of methods, including d.t.a.-d.s.c., microcalorimetry and dilatometry, points to the previously observed transformation at 450K of triclinic P_4S_{10} to a cubic modification being incorrect.[426] The most likely explanation is decomposition to P_4S_9 which is known to be cubic.

P_4S_{10} can be converted into dichloro- and dibromo-dithiophosphate salts following the reaction in equations (68) and (69).[427] X-ray structures show the presence of simple tetrahedral anions with P-S distances in the chloride of 1.948 and 1.975Å. P-Cl distances are 2.008 and 2.031Å and the angles range between 108.5 (S-P-Cl) and 114.4° (S-P-S). In the bromide

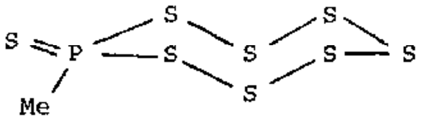
$$P_4S_{10} + 4Ph_3MePCl + 4HCl \xrightarrow{CH_2Cl_2} 4Ph_3MeP^+PS_2Cl_2^- + 2H_2S \quad ...(68)$$

$$P_4S_{10} + 4Ph_4PBr + 4HBr \rightarrow 4Ph_4P^+PS_2Br_2^- + 2H_2S \quad ...(69)$$

which crystallises in the tetrahedral space group $I\bar{4}$, positions in the anion are occupied statistically by sulphur and bromine.

Mixtures of phosphorus(V) oxide sulphides can be obtained by heating various P_4O_{10}-P_4S_{10} mixtures to 525°C.[428] Of the mixed species, $P_4O_6S_4$ is well known but it has now been possible to isolate $P_4O_7S_3$, $P_4O_5S_5$, $P_4O_4S_6$, $P_4O_3S_7$ and P_4OS_9 by either fractional distillation or crystallisation methods. Although $P_4O_2S_8$ was not isolated, it could be identified by ^{31}P n.m.r. spectroscopy.

The heptathiaphosphocane-8-sulphide (223), obtained from $MePS(SSiMe_3)_2$ and S_5Cl_2, contains a crown conformation PS_7 ring with the sulphur and methyl substituents in respectively equatorial and axial positions.[429] Endo- and exo-cyclic P-S distances are 2.10 and 1.94Å respectively with an S-P-S(ring) angle of 111.9°. The structure of $Ph_2P(S)OH$ shows the hydrogen atom located at oxygen and the formation of strong O-H...S hydrogen bonds (3.133Å) which link the molecules into infinite chains.[430] P-O and P-S distances are 1.582 and 1.956Å respectively with an O-P-S angle of 115.4°.



(223)

Compounds of the type $Ph_2P(S)O_2CR$, showing unexpectedly high thermal and hydrolytic stability, can be prepared by treating $Ph_2P(S)Cl$ with either a silver carboxylate, AgO_2CR where R = Me, Et, ^tBu or Ph, or the free carboxylic acid in the presence of a tertiary amine.[431] I.r. and n.m.r. spectra were obtained.

Substituted tin thiophosphinates, $R^1R^2P(S)OSnMe_3$ where R^1R^2 = Me_2, MePh or Ph_2, result from reactions of $R^1R^2P(S)Cl$ and $(Me_3Sn)_2O$;[432] the dimethylthiophosphinate has an infinite chain structure based on planar Me_3Sn groups linked by the oxygen and sulphur atoms of the thiophosphinate group. Changing the mol ratio in the $Me_2P(S)Cl-(Me_3Sn)_2O$ reaction from 1:1 to 2:1 leads to $(Me_2PS)_2O$ and the sulphur analogue, $(Me_2PS)_2S$, can be similarly obtained from $Me_2P(S)Cl$ and $(Me_3Sn)_2S$.[433] In the $POCl_3-(Me_3Sn)_2O$ reaction the product is $Me_3SnO_2PCl_2$ but the corresponding reaction with $(Me_3Sn)_2S$ gives a complicated set of products due to oxygen-sulphur exchange. Treatment of $PSBr_3$ with $(Me_3Sn)_2S$ gives P_4S_9.

Salts of methylthio- and methylseleno-triphenylphosphonium cations can be prepared from reactions of Ph_3PS or Ph_3PSe with methyl-trifluoromethane sulphonate in benzene at room temperature.[434]

New complexes with the general formula $M[S_2P{<}^{O}_{O}{>}R]_n$ where n = 1 and M = Tl(I);[435] n = 2 and M = PhAs,[436] PhSb,[436] Me_2Sn,[437] Et_2Sn, Bu_2Sn and Ph_2Sn; and n = 3 and M = As, Sb or Bi[438] have been reported; among the R groups used are $CMe_2{\cdot}CMe_2$, $CHMe{\cdot}CHMe$, $CH_2{\cdot}CMe_2{\cdot}CH_2$, $CMe_2{\cdot}CH_2{\cdot}CMe_2$ and $CMe_2{\cdot}CH_2{\cdot}CMeH$. The thallium derivatives, obtained from aqueous TlOAc or Tl_2CO_3 and the ammonium dithiophosphate are non-electrolytes. Mass, i.r. and n.m.r. spectra are presented.

Structures of dithiophosphate salts reported in 1985 include $[(EtO)_2PS_2]_2Se$[439] and the related tellurium compound,[440] where the central Group 6 element forms two short (mean 2.209 for Se and 2.420 for Te) and two substantially longer (3.423 for Se and 3.209/3.541Å for Te) intermolecular contacts to sulphur; the central MS_4 unit is planar. There are three crystallographically independent molecules in the unit cell of the Te compound and although most dimensions are similar there are some significant differences. In a series of isomorphous lanthanoid derivatives, $Ln[S_2P(O^iPr)_2]_3.(benzamide)_2$ where Ln = La, Ce, Pr, Sm, Eu or Gd, the central atom is in eight fold, dodecahedral coordination to the six sulphurs of the ligands and two oxygens of the benzamide groups.[441] The heavier lanthanoids produce compounds of the type $\{Ln[S_2(O^iPr)_2]_2(benzamide)_3\}[S_2P(O^iPr)_2]$, for Ln = Gd, Tb, Dy, Er or Yb, in which for the Tb and Er derivatives, the metal is in pentagonal bipyramidal coordination.[442] Four sulphurs from the dithiophosphate groups and an oxygen from one of the benzamide ligands occupy equatorial positions and coordination is completed by two benzamide oxygen atoms in axial positions.

I.r. spectra of a range of metal complexes, including Ni^{2+}, Pd^{2+}, Cd^{2+}, Rh^{3+}, Co^{3+}, As^+ and Cu^+, of the following dithiophosphorus ligands: $Et_2PS_2^-$, $Me(EtO)PS_2^-$ and $(EtO)_2PS_2^-$ have been analysed.[443]

In each case substitution of an alkoxy by an alkyl group causes a decrease in the energy of the two PS_2 stretching modes.

Heating a mixture of arsenic, red-phosphorus and sulphur in a 2:2:5 ratio at 350°C gives the new compound $As_2P_2S_7$ with the structure shown in Figure 2.[444] The molecule is close to C_{2v} and is isostructural with P_4S_7.

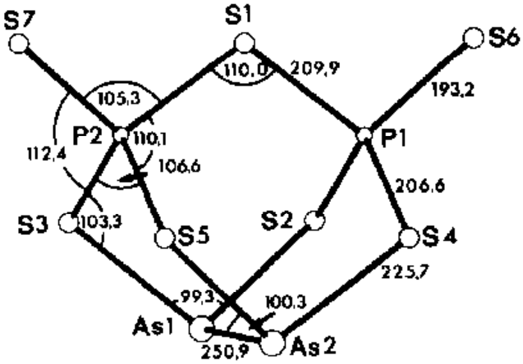


Figure 2. Structure of $As_2P_2S_7$ showing molecular parameters (reproduced by permission from Z. Naturforsch., Teil B, 39(1984)1088).

A new mixed metal layered compound, $Mn_{0.87}Cu_{0.26}PS_3$, prepared from the elements at 750°C for two weeks, has been examined by single crystal X-ray diffraction and EXAFS at the manganese and copper K edges.[445] In addition to the conventional S_3PPS_3 units, the structure contains MnS_6 and $S_3Cu...CuS_3$ entities randomly distributed within the layers.

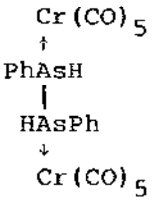
The P-Se distance, 2.094Å, in $(3\text{-}CF_3C_6H_4)_3PSe$ is the shortest yet reported; P-C distances range between 1.801 and 1.834Å.[446] Neutron time of flight diffraction has been used to obtain greater precision over previous X-ray determinations in a new structural study of Tl_3PSe_4 and Tl_3AsS_4.[447]

5.3 ARSENIC

5.3.1 Polyarsines and Arsenides

Dehydrogenation occurs on heating the phenyl arsine complex $(OC)_5CrAsPhH_2$ in toluene giving the diarsine derivative (224); this in turn loses further hydrogen to produce (225) in the presence of Pd/C and a ligand L such as $P(OMe)_3$ or bipyridine.[448]

This π-bonded diarsene complex (As-As 2.366Å) is stabilised by



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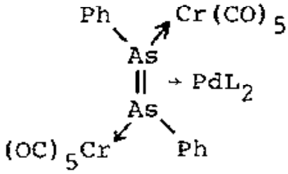

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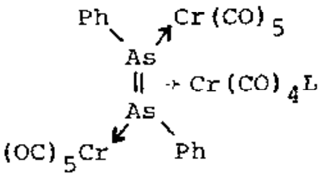
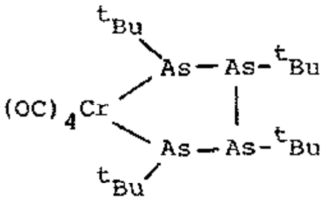


(226)

further coordination to palladium (Pd-As 2.46Å). A related compound (226), together with the cyclopentaarsine complex $(PhAs)_5[Cr(CO)_5)]_2$, is the product if Pt/C replaces Pd/C.

Two compounds, the arsinidine complex $(OC)_5Cr \leftarrow As^tBu \rightarrow Cr(CO)_5$ and the tetraarsine species (227), have been isolated from reactions between $^tBu_2AsCl$ and $Na_2Cr_2(CO)_{10}$.[449] An X-ray structure is available for (227).



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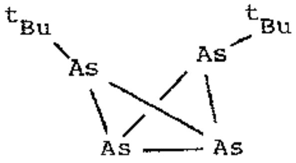


(228)

A bicyclotetraarsine (228), arising formally from the cleavage of one of the As-As bonds in As_4, has been isolated from the reaction in equation (70).[450] Other cyclic and linear species

$$2^tBuAsCl_2 + 2AsCl_3 + 10LiH \rightarrow As_4{}^tBu_2 + 10LiCl + 5H_2 \qquad \ldots(70)$$

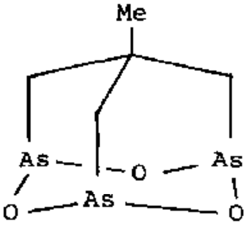
are also present in the reaction mixture.

A new Zintl phase, $Ba_3Sn_2As_4$, results when stoichiometric amounts of the elements are heated together.[451] Its structure contains the unusual Sn_2As_6 unit comprising pyramidal $SnAs_3$ units (As-Sn 2.586-2.691Å) joined by an Sn-Sn bond (2.795Å) in a staggered conformation; interconnection of these units by common edges then gives chains.

The range of homogeneity and the structure of the $[Ca_{2-x}\square_x][As_{1-x}Br_{1+x}]$ phase obtained from Ca_3As_2 and $CaBr_2$ has been investigated;[452] a number of new phases have been identified in the Zr-P and Zr-As systems.[453]

5.3.2 Bonds to Carbon

The cage arsenite (229) can be reduced by alkaline hypophosphite to the noradamantane-like product (230, X = O); the sulphur and selenium analogues (230, X = S or Se) result if the cyclo-triarsine (231) is treated with the appropriate element.[454] Compound (230, X = Se) can also be obtained when $MeC(CH_2AsI_2)_3$ reacts with NaSeH but attempts to produce the tellurium analogue were unsuccessful.[455] A third noradamantane derivative, (230, X = $C(COOEt)_2$) has been isolated when $MeC(CH_2AsI_2)_3$ is treated with diethylmalonate; crystal structure determinations for the latter and (230, X = Se) show As-As distances of 2.469 and 2.483Å respectively. The As-Se distances are 2.357 and 2.369Å while As-Se-As angles are 98.7 and 99.2°.



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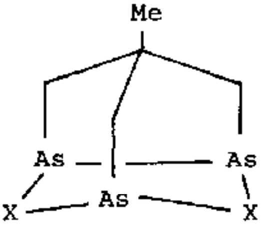

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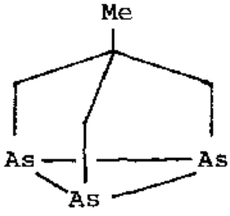


(231)

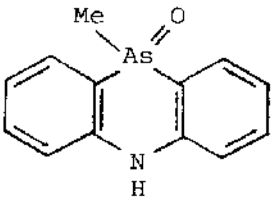
Zirconium complexes $Cp_2Zr(MPh_2)_2$ are the products when solutions of $LiMPh_2$ for M = As or Sb react with Cp_2ZrCl_2.[456]

Exchange and equilibria in the P_2Ph_4-As_2Ph_4 system have been investigated by ^{31}P n.m.r. methods in benzene, ether and chloroform solutions.[457] The reaction in benzene is fast and slightly endothermic ($\Delta H°$ = 1.3kcal.mol^{-1}) with a positive entropy ($\Delta S°$ = +3.5e.u.); the corresponding P_2Ph_4-Sb_2Ph_4 system shows a much lower extent of reaction. All the tetraphenyl derivatives can be reduced by sodium metal in THF solution and $NaAsPh_2$ has been isolated as a dioxane adduct. Its structure consists of infinite chains of alternate Ph_2As and solvated sodium atoms which are almost linear at arsenic (Na-As-Na 173.6°) but bent at sodium (As-Na-As 121.5°). The As-Na distances are 2.937 and 2.962Å and the geometry about arsenic is close to pseudo-trigonal bipyramidal.

Acrylonitrile and Me_2AsH or $MeAsH_2$ react to give respectively $Me_2As(CH_2)_2CN$ and $MeAs(CH_2CH_2CN)_2$, which on treatment with $LiAlH_4$ can be reduced to the corresponding amines.[458] The compounds are highly reactive at both the NH_2 and arsenic centres, the former with, for example, benzaldehyde, salicylaldehyde or acetylacetone, the latter with metal carbonyls to give complexes such as $(OC)_4Cr[AsMe_2(CH_2)_3NH_2]_2$.

Structural studies on one of the $TCNQF_4$-dihydrophenarsazine oxide (232) charge transfer complexes obtained from acetonitrile solution has shown the presence of the complex compound $[(\underline{232})_2H]^+[(TCNQF_4)_2]^-.(\underline{232}).MeCN$.[459] Single crystal structures have also been reported for both triclinic and hexagonal modifications of $(4\text{-}ClC_6H_4)_3AsO$ and for the corresponding sulphide.[460] Molecular parameters for the two oxide forms are similar but the packing modes are significantly different; the mean As-O and As-S distances are 1.639 and 2.074Å respectively.

Reactions of the arsenic ylid $Ph_3As{:}CH_2$ (L) with zinc and mercury chlorides give $[ML_2]Cl_2$ complexes but with beryllium and

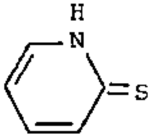


(232)

magnesium salts the products are $\mathrm{LM}\genfrac{<}{>}{0pt}{}{\mathrm{Cl}}{\mathrm{Cl}}\mathrm{ML}$.[461] Aluminium and indium chlorides react similarly giving species such as $[\mathrm{L_2M}\genfrac{<}{>}{0pt}{}{\mathrm{Cl}}{\mathrm{Cl}}\mathrm{ML_2}]\mathrm{Cl_4}$.

5.3.3 Bonds to Halogens

Evidence for the formation of all possible mixed halides has been obtained from an investigation of the $AsCl_3$-AsI_3 system in both CS_2 and CCl_4 solutions.[462] Equilibrium constants point to the preferential formation of $AsICl_2$ and a new band at 345nm is assigned to this species. Complex formation between the heavier Group 5 halides, MX_3 for M = As, Sb or Bi and X = Cl or Br and mercaptoazoles and mercaptoazines such as (233) and (234)(L) gives products with the stoichiometry $MX_3.2L$ and $MX_3.1\frac{1}{2}L$.[463]



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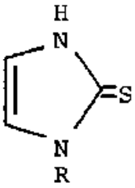

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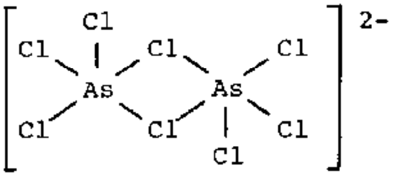
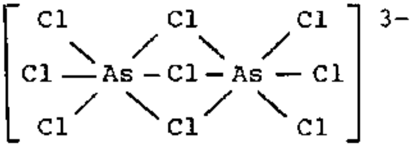


(235)

Four new anionic arsenic halides have been reported.[464,465] In the chloride series the compounds are $(PhMeNH_2)AsCl_4$ and $(pyH)_3As_2Cl_9$, the former obtained from N-methylaniline and arsenic trichloride in concentrated HCl solution and the latter from pyHCl and $AsCl_3$ in anhydrous acetonitrile.[464] Both species contain discrete anions; the tetrachloroarsenite is a centrosymmetric dimer (235)(As-Cl(terminal) 2.197-2.204, As-Cl(bridging) 3.035,3.063Å) while the $As_2Cl_9^{3-}$ anion is the triply bridged species (236). Terminal and bridging As-Cl distances here are 2.236-2.306 and 2.829-2.996Å respectively. The bromine analogues $(PhMeNH_2)AsBr_4$ and $(pyH)_3As_2Br_9$ have structures similar to those of (235) and (236) respectively, but the latter crystallises with 1.5 mols of acetonitrile.[465] Terminal and bridging distances are 2.347-2.387 and 3.152, 3.203Å respectively for the tetrabromoarsenite and 2.42-2.49 and 2.86-3.01Å respectively for the nonabromodiarsenate. Rather surprisingly, infinite chain anions with double cis-bromine bridges are present in pyridinium tetrabromoarsenite. Although the pyHCl-$AsCl_3$ reaction in anhydrous acetonitrile yields the $As_2Cl_9^{3-}$ salt mentioned above, in the presence of water an oxygen bridged compound (237), analogous to that already known in the corresponding antimony system, is the product.[464]



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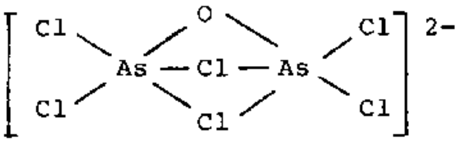


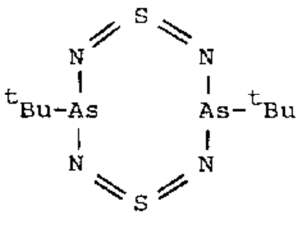
(237)

A pale yellow 1:1 adduct of AsF_5 with UO_2F_2 can be isolated from hydrogen fluoride solution and assigned a fluorine bridged structure from i.r. data.[466] Half a mol of AsF_5 is lost at 50-80°C and AsF_5 loss is complete at 200°C. A fluorine bridged structure is also proposed for the $1.5UF_5.AsF_5$ adduct which is stable only under a pressure of AsF_5; no similar adduct results when BiF_5 is used.[467]

Preparative quantities of the covalent mixed halide, $AsClF_4$ melting at ca. -90°C, have now been produced during pyrolysis of $AsCl_4[AsF_6]$.[468] I.r. and Raman spectra in an argon matrix have been analysed in terms of a trigonal bipyramidal molecule with an equatorial chlorine, ν(As-Cl) 460cm^{-1}. The series of anions $Et_4N[AsCl_nF_{6-n}]$ and $Et_4N[SbX_nF_{6-n}]$ where X = Cl or Br have been produced using reactions such as oxidation of AsF_3 with chlorine in the presence of Et_4NCl, treatment of $SbCl_6^-$ or $SbBr_6^-$ with liquid hydrogen fluoride, oxidation of SbF_3 with bromine in the presence of Et_4NBr and reaction of AsF_5 with Et_4NBr.[469] A detailed multinuclear n.m.r. study points to the formation of both cis and trans isomeric forms of the $MX_2Y_4^-$ species and both fac and mer forms of $MX_3Y_3^-$; the cis and mer forms are preferentially produced. The ions are stable in acetonitrile solution, showing the absence of fluorine redistribution reactions, but not in liquid hydrogen fluoride. Samples of $Et_4N[MClF_5]$ for M = As or Sb, $Et_4N[SbCl_2F_4]$ and $Et_4N[SbX_3F_3]$ for X = Cl or Br can be isolated and the ^{75}As n.m.r. spectrum of the $AsCl_6^-$ ion has been reported for the first time.

5.3.4 Bonds to Nitrogen

Reaction of $^tBuAsCl_2$ and Ph_2AsCl with the sulphur diimide salt, K_2SN_2, give the products (238) and (239) respectively.[470] X-ray structures show in each case attachment of the SN_2 group to two arsenic atoms with planarity in the As_2SN_2 systems; the open chain compound (239) has a cis-cis conformation with substantial As...As interaction (3.379Å). Oxidation with one mol of chlorine in dichloromethane at low temperatures, converts $(CF_3)_2AsN(SiMe_3)_2$



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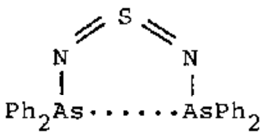
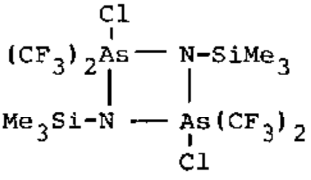


(239)

to the arsenic(V) species $(CF_3)_2AsCl_2N(SiMe_3)_2$ while an excess of chlorine gives the cyclic compound (240).[471]



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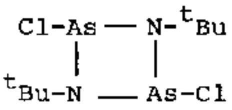
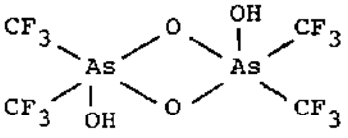


(241)

The dimeric arsine imide (241), obtained by treating $AsCl_3$ with the lithium salt $LiN^tBu(SiMe_3)$, contains an almost planar As_2N_2 ring with As-N distances in the range 1.799-1.827Å.[472] Ring angles at nitrogen are 98.6 and 99.9° and at arsenic 80.6 and 80.1°; the chlorine atoms are cis to each other. The possible molecular symmetry is reduced from approximately mm to m by the different conformations of the t-butyl groups.

5.3.5 Bonds to Oxygen

Three new compounds (242)-(244) each containing an As_2O_2 ring have been isolated and characterised by single crystal X-ray diffraction.[473] Compounds (242) and (244) were obtained by oxidising respectively $(CF_3)_3As$ or a CF_3AsI_2-$(CF_3)_2AsI$ mixture with aqueous hydrogen peroxide; compound (243) resulted by treating (244) with Me_3SiCl in dichloromethane. The arsenic



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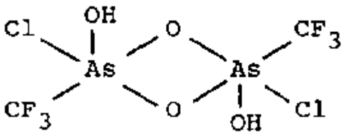

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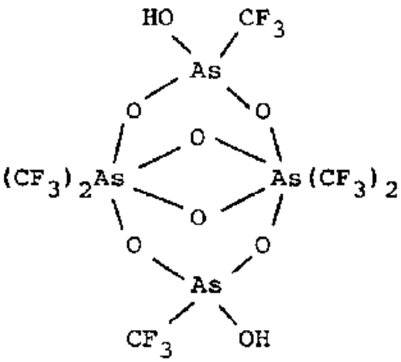


(244)

atoms in (242) and (243) are trigonal bipyramidal with oxygen atoms occupying an axial and an equatorial position. As expected the equatorial As-O distance 1.713Å for (242) is shorter than the axial distance (2.003Å). The novel cage in (244) contains arsenic atoms in both six and four fold coordination.

Kinetics and equilibria in the transesterification equation (71) have been investigated in acetonitrile solution for R = $PhCH_2$ and

$$As(OMe)_3 + ROH \rightleftharpoons As(OMe)_2OR + MeOH \qquad ...(71)$$

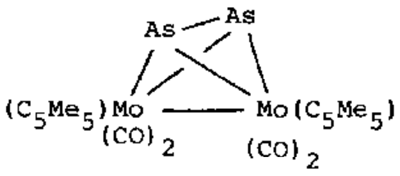
^tBu.[474] AsF_3 and the pentafluoroorthotellurate $As(OTeF_5)_3$ have been shown to have very similar σ- and π-acidities from their behaviour respectively to simple Lewis bases and low valent transition metal compounds.[475]

The metaarsenates, $KAsO_3$, $RbAsO_3$ and $CsAsO_3$, in nitrogen matrices show i.r. bands at (As=O) ca. 980 and 923, (As-O) ca. 880 and (AsO_3) ca. 377 and 335 cm^{-1}.[476] A high temperature modification of $Co_3(AsO_4)_2$, differing in cobalt coordination from the known monoclinic form, has been produced in single crystal form using a CO_2 laser at 180°C.[477] Single crystals of $NaNiAsO_4$ have been prepared by heating mixtures of $NiCO_3$ and NaH_2AsO_4 to 1000°C; its structure is based on octahedral layers of NiO_6 units and two tetrahedral AsO_4 layers.[478]

5.3.6 Bonds to Sulphur or Selenium

A nickel compound containing a coordinated As_3 unit, analogous to the well known P_3 species, has been isolated from a reaction between As_4S_3 and nickel tetrafluoroborate in the presence of triphos,[479] showing that a transition metal can cleave the As_4S_3 cage. The product at room temperature is $[(triphos)Ni(As_3)Ni(triphos)][BF_4]_2$ but the related singly charged cationic compound results when the reagents are refluxed. Realgar, As_4S_4, also serves as a source of arsenic units, in reactions with an equimolar quantity of the molybdenum complex $(C_5Me_5)(CO)_2Mo{\equiv}Mo(CO)_2(C_5Me_5)$; As_2 and As_3 units are coordinated in compounds (245) and (246), while in a third compound (247) an As_2S_3 unit is involved.[480]

Arsenic(III) sulphide on reaction with aqueous sodium sulphide gives AsS_3^{3-}, which can be isolated as the bis(triphenylphosphine)-iminium salt.[481] The product will react with $(MeCp)_2TiCl_2$ giving



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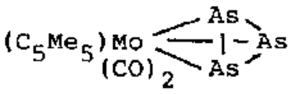

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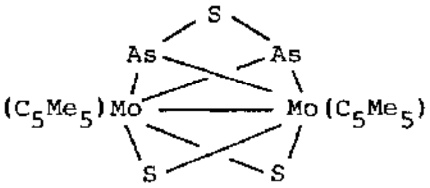
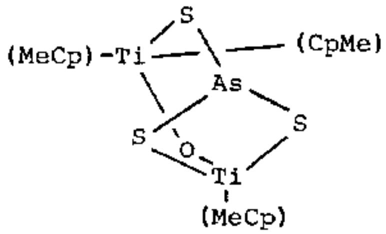


(247)

$(MeCp)_3Ti_2AsS_3O$ with structure (248); the compound, which can also be prepared from As_4S_4 and $(MeCp)_2Ti(CO)_2$, has As-S distances of



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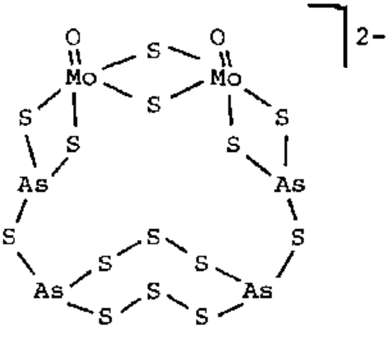
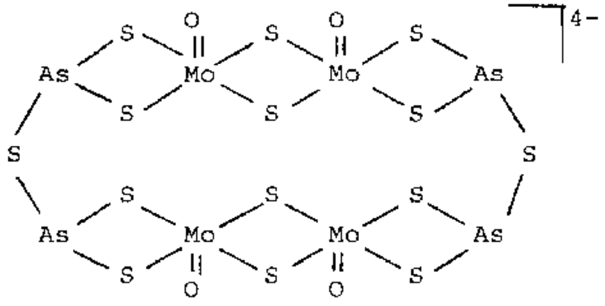


(249)

2.192 and 2.262, similar to those in As_2S_3, and S-As-S angles of 93.7, 96.5 and 106.8°. As_4S_4 also reacts with the anion MoS_4^{2-} to give the novel cyclic compound (249) as an orange tetraphenyl phosphonium salt, $(Ph_4P)_2[Mo_2O_2As_4S_{14}]$. The structure, which follows from an X-ray study, can be considered as comprising an $Mo_2O_2S_2^{2+}$ unit chelated by an $As_4S_{12}^{4-}$ anion. Treatment of (249) with $MoO_2S_2^{2-}$ in DMF gives a further macrocyclic anion $Mo_4O_4As_4S_{14}^{4-}$, formulated as (250) on the basis of spectral data.

Vibrational data for the mixed sulphide As_3PS_3 in the solid and melt have been assigned; partial decomposition to $As_2P_2S_3$ and α-As_4S_3 occurs in the melt.[482]



(250)

The tris-xanthate, $As(S_2COEt)_3$, structure shows the arsenic atom lying on a three fold axis of symmetry with asymmetrically coordinated xanthate groups (As-S 2.307 and 2.956Å).[483] The geometry about arsenic is intermediate between octahedral and trigonal prismatic. Full spectroscopic data have also been collected for a range of substituted xanthates, $PhAs(S_2COR)_2$ where R = Me, Et, Pr, ^{i}Pr, Bu and allyl, indicating the formation of square pyramidal monomers with chelating ligands.[484]

Few data are available on the interaction of arsenic, antimony and bismuth compounds with biological molecules but recently complex formation with cysteine (cys) in aqueous solution has been investigated, showing the formation of $As(cysH)_3$, $Sb(cysH)_3.H_2O$, and $Bi(cysH)_3.H_2O$.[485] Mass spectrometry implies bonding via sulphur, confirmed by the absence of S-H stretching modes in the i.r. spectra.

Dithioarsinate complexes, $R_2Sn(S_2AsPh_2)_2$ for R = Me, Bu or Ph and $R_3Sn(S_2AsPh_2)$ for R = Me, ^{c}Hex or Ph, have recently been isolated from reactions of the appropriate chlorostannane and the sodium salt of the dithio acid.[486] From X-ray crystallography, $Me_2Sn(S_2AsMe_2)_2$ contains monodentate ligands with the tin atom in distorted tetrahedral coordination; As-S distances are 2.089 and 2.171Å.

The ternary species $Co_2As_2Se_5$ and $CoAs_6Se_{10}$ have been identified in the As_2Se_3-CoSe system whereas the corresponding Sb_2Se_3 system gives $CoSb_2Se_4$.[487]

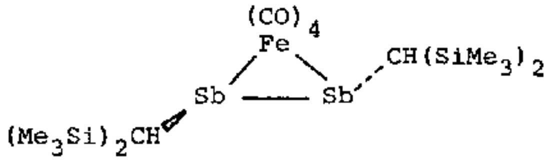
5.4 ANTIMONY

5.4.1 Polystibines and Antimonides

Two X-ray studies[488,489] on the thermochromic Me_4Sb_2 show the presence of short intermolecular Sb...Sb contacts (3.67Å, Sb-Sb...Sb 179.2°) linking the molecules into chains as a major feature. The intramolecular Sb-Sb distance is 2.86Å with mean Sb-C distances of 2.15Å; Sb-Sb-C and C-Sb-C angles are ca. 93.5°. The molecules have the antiperiplanar conformation and packing is similar to the in the tetramethyldistibolyl structure determined previously.

Cleavage of the Sb-Sb bond in R_2SbSbR_2, where R = Me or Et, with either selenium or tellurium in typically benzene solution gives $R_2SbXSbR_2$, where X = Se or Te, as yellow to red solids rather than isomeric $R_2Sb(:X)SbR_2$ species.[490] Reorganisation of a mixture of Et_4Sb_2 and $(4\text{-}MeC_6H_4Te)_2$ leads to a quantitative yield of the novel tellurostibine, $4\text{-}MeC_6H_4TeSbEt_2$.[490] The distibine $(Me_3Sn)_4Sb_2$ can be obtained in 45% yield by air oxidation of $(Me_3Sn)_3Sb$,[491] with $(Me_3Sn)_2O$ and a little Me_3SnOH as byproducts.

Red cyclo-tri- and -tetra-stibines, $[(Me_3Si)_2CHSb]_{3,4}$, have been isolated when chlorine is abstracted from $(Me_3Si)_2CHSbCl_2$ by magnesium in THF,[492] while treatment of the dichlorostibine with $Na_2[Fe(CO)_4]$ in THF at room temperature gives the novel stibinidene complex (251).[493] The Sb-Sb separation, 2.774Å, points to a bond order of ca. 1.5. Reaction of (251) with $Fe_2(CO)_9$ breaks the Sb-Sb bond to give an Fe_2Sb heterocycle (252) in which the antimony is in pyramidal coordination.



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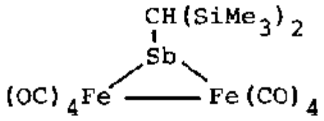
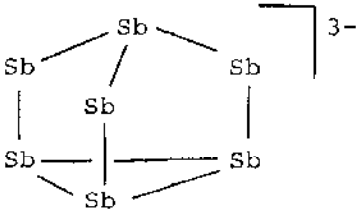


(252)

Related, but structurally very different, highly coloured, stibinidene complexes such as $[(OC)_5Cr]_2SbR$ for R = Cl, I, ^tBu or SEt, $[Cp(OC)_2Mn]_2SbBr$ and $[MeCp(OC)_2Mn]_2SbBr$ have also been isolated,[494] which contain the antimony in trigonal planar coordination. In $[MeCp(OC)_2Mn]_2SbBr$ the Sb-Br and Sb-Mn distances are 2.61 and 2.40Å, the Mn-Sb-Mn angle is 138.6 while the Mn-Sb-Br angles are ca. 110.5°.

The dark red solution, obtained by treating KGeSb with 2,2,2-crypt in ethylenediamine solution, yields crystals of $[K(crypt)]_2Sb_4$ and $[K(crypt)]_3Sb_7.2en$, which have been examined crystallographically.[495] The tetraantimonide anion is square planar with bond lengths 2.749 and 2.751Å and angles of 90° within the quoted standard deviations, and is isostructural with Bi_4^{2-}. The Sb_7^{3-} anion (253) has ca. C_{3v} symmetry but one Sb-Sb distance in the basal plane (2.876Å) is substantially shorter than the other two (2.904 and 2.906Å); it is surprising that the compound is not isostructural with the previously isolated sodium cryptate derivative.

Three new ternaries, MMnSb for M = Ti, V or Cr, with the Ni_2In structure have been synthesised from the elements at 900°C and 5.0GPa,[496] and new Zintl phases $Na_7Al_2Sb_5$,[497] Ca_3AlSb_3[498] and Ca_5AlBi_6 result when the elements are heated in argon to ca. 1100K. The former (254) contains $AlSb_4$ tetrahedra (Al-Sb 2.713-2.759Å) interconnected by corners, edges, and Sb_2 units (Sb-Sb 2.900Å) into sheets. Sodium ions are located between the sheets and angles at aluminium and antimony within the four membered rings are 104 and 76° respectively. The Ca_3AlSb_3 structure also contains $AlSb_4$ tetrahedra connected by corner sharing into infinite chains (Sb-Al 2.709, 2.723 and 2.732Å, Sb-Al-Sb 103.2-110.5, Al-Sb-Al 110.5°), and although $AlBi_4$ tetrahedra are also present in the third compound corner sharing here leads to double chains (Bi-Al 2.800-2.869Å).



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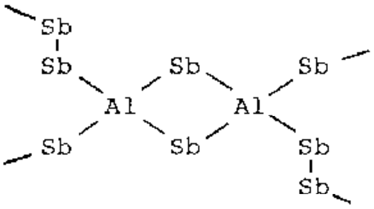
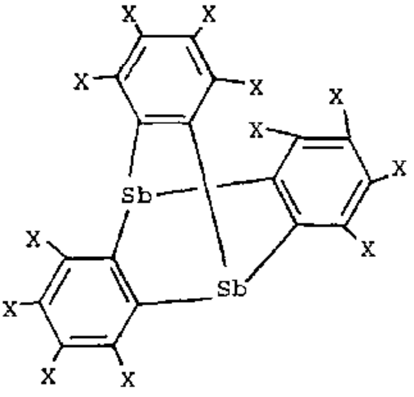


(254)

5.4.2 Bonds to Carbon

The 1982 literature on organo-antimony chemistry has been reviewed.[499] Antimony powder and 1,2-diiodoperhalogenobenzenes, $C_6X_4I_2$ for X = F or Cl, when heated together in a sealed system at 250°C lead to benzostibanthrenes (255, X = F or Cl), which can be isolated as solvates with half a molecule of, for example, hexane, cyclohexane or benzene.[500] Compound (255, X = F) can be oxidised with either chlorine or nitric acid to give respectively $Sb_2(C_6F_4)_3Cl_4$ and probably the basic nitrate $Sb(C_6F_4)_3(OH)_2(NO_3)_2$.



(255)

The former is hydrolysed to $Sb_2(C_6F_4)_3O_2$ in boiling water and the latter is converted by water to the tetrahydroxide.

The $(Me_2SbBr_2)_2CH_2$ structure contains two independent molecules with basically trigonal bipyramidal geometry about the antimony atoms.[501] The bromine atoms occupy axial positions (Sb-Br 2.609-2.645Å); the Sb-C-Sb angle is 120.5° in both molecules and the greatest difference between the two is in the twist angles about the central Sb-C-Sb bonds.

5.4.3 Bonds to Halogens

The compounds $[Ni(H_2O)_6][SbF_4]_2$ and $[Cu(H_2O)_6][SbF_4]_2$ have recently been identified in the appropriate $MF_2-SbF_3-H_2O$ system.[502] A number of mixed chloro-amino-stibines, including $Cl_2Sb(NR_2)$ where R = Me or Et, $Cl_2Sb(NMeEt)$ and the equivalent monochlorides $ClSb(NR_2)_2$, have been isolated from exchange reactions between $SbCl_3$ and the appropriate tris(amino)stibine.[503] Full vibrational spectroscopic data are also reported showing dimerisation in the solid state via Sb...N bridges for the dichlorides and $ClSb(NMe_2)_2$; ethyl containing monochlorides are sterically hindered and do not dimerise. Further reactions of the compounds have been investigated, for example, with methanol, $Cl_2Sb(NMe_2)$ is converted into $ClSb(NMe_2)(OMe)$.

Antimony(III) and bismuth(III) halides have given a series of complexes with substituted dithiooxamides RNHC(S)·C(S)NHR for R = Me, Et, ^{i}Pr, Bu, ^{c}Hex or CH_2Ph.[504] Such species are of interest as the ligands contain both hard (N) and soft (S) donor sites. The stoichiometry for the antimony chloride and bromide complexes is $SbX_3L_{1.5}$ and a crystal structure of the chlorine compound with R = ^{i}Pr shows three dimensional polymeric structure in which the antimony is coordinated to three sulphur atoms of different ligands (Sb-S 3.197Å) in addition to the three chlorine atoms (Sb-Cl 2.413Å). There is no evidence for a sterically active antimony lone pair. In addition to $BiCl_3.2L$, a series of tin and titanium halide complexes were also prepared.

An infinite chain structure with cis bridging chlorines is present in the structure of the triethanolammonium salt, $[(HOCH_2CH_2)_3NH]SbCl_4$, obtained from $SbCl_3$ and triethanolamine in hydrochloric acid.[505] The central antimony is in distorted octahedral coordination to five chlorine atoms, three at distances of 2.392-2.453Å with two longer contacts at 2.902 and 3.321Å, and an Sb-O contact to the cation at 2.743Å. In addition, the nitrogen of the cation forms an intramolecular hydrogen bond (2.833Å) to one of the oxygen atoms. A new hexachloroantimon(III) ate in which coordination is distorted octahedral has been prepared with a triply protonated diethylenetriamine cation.[506] The anion geometry, with three short (2.415-2.521) and three longer (2.836-3.114Å) Sb-Cl distances, is in strong contrast to the accurate octahedral geometry of the anion in the related $[Co(NH_3)_6]SbCl_6$. Five of the chlorine atoms in the new structure form hydrogen bonds to the cation providing a mechanism for the distortion from octahedral coordination.

From X-ray powder diffraction both tetragonal and cubic modifications are possible for the mixed oxidation state species, $Cs_4Sb_2Cl_{12}$; conversion from cubic to tetragonal occurs irreversibly on heating to above 150°C.[507]

Molten mixtures of $AlCl_3$ and n-butylpyridinium chloride provide useful media for electrochemical investigations, as the acid-base nature of the medium can be varied by changing the ratio of the two components.[508] Recent cyclic voltametry of, inter alia, antimony(III) chloride in this system has pointed to the importance of $SbCl_2^+$ in acid media; the reduction is irreversible and no oxidation process was observed. Both $SbCl_4^-$ and $SbCl_6^-$ are important in basic melts with the oxidation of Sb(III) to Sb(V) showing quasi-reversibility.

^{121}Sb Mössbauer spectroscopy of a series of substituted pyridinium bromoantimonates, including $SbBr_4^-$, $Sb_2Br_9^{3-}$, $SbBr_5^{2-}$ shows that both the isomer shift and the quadrupole coupling constant decrease with increase in the number of bromines about antimony.[509] These parameters are also affected for a given anion by changes in substitution of the pyridine ring and may result from anion disorder. The Raman spectral region between 1000 and 300cm^{-1} is not particularly sensitive to changes in anion stoichiometry but large variations occur below 300cm^{-1} even with compounds of the same stoichiometry.

Six-fold coordination about antimony in $SbOF_3$, SbO_2F, $SbOFCl_2$, $Sb_5O_7Cl_{11}$ and $[SbCl_4(O_2PMe_2)]_2$ is suggested by recent ^{121}Sb Mössbauer data,[510] and this in conjunction with previous data shows an almost linear dependence of isomer shift on the difference in electronegativity between antimony and the sum of the ligand electronegativities.

Ternary adducts, including $UF_4O.SbF_5.2MeCN$, $UF_4O.2SbF_5.6MeCN$, $UF_4O.2SbF_5.6Ph_3PO$, $UF_5.SbF_5.2MeCN$, $UF_5.SbF_5.2Ph_3PO$ and $UF_5.2SbF_5.5MeCN$, can be isolated and assigned ionic structures such as $[UOF_3(MeCN)_2]SbF_6$, $[UF_4(MeCN)_2]SbF_6$, $[UF_3(MeCN)_5][SbF_6]_2$, etc. on the basis of their i.r. spectra.[511]

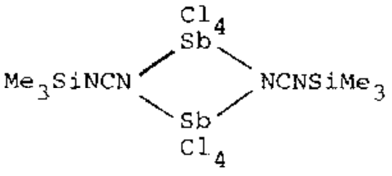
Complex formation between $SbCl_5$ and a range of Schiff bases in benzene gives coloured amorphous solids considered to be 1:1 electrolytes containing six coordinate antimony atoms;[512] the preparation, i.r. spectra and enthalpy of solution of the $SbCl_5$ adducts with 2-aminopyridine, 3-aminopyridine, 2,2'-bipyridyl, nicotinamide and piperidine have also been reported.[513]

$SbCl_5$ reacts with the carbodiimide, $Me_3SiNCNSiMe_3$, in a 1:1 ratio to give a dimeric substitution product (<u>256</u>)[514] and in a 2:1 ratio with μ-oxo tin species, $R_3SnOSnR_3$, where R = Pr, Bu or Ph, $SbCl_5$ gives $[(R_3Sn)_2OSbCl_4][SbCl_6]$.[515] Sb-N distances in (<u>256</u>) are 2.111 and 2.136Å with ring angles at antimony and nitrogen of 72.7 and 107.3°; the NCNSi group is almost linear (N-C-N 178.9, C-N-Si 169.8°). Transfer of organo groups from substituted tin chlorides, e.g. R_nSnCl_{4-n} where R = Me or Ph and $0 \leq n \leq 4$, to antimony occurs with $SbCl_5$ in dichloromethane solution;[420] phenyl group migration occurs more readily than methyl and compounds such as Me_2SbCl_3, Ph_2SbCl_3 and $PhSbCl_4$ have been produced.[516]

5.4.4 Bonds to Oxygen

Powdered antimony is converted by hot concentrated nitric acid into a mixture of orthorhombic Sb_2O_3 and the basic nitrate $Sb_4O_4(OH)_2(NO_3)_2$;[517] with an excess of nitric acid the product is almost exclusively the basic nitrate, which on heating in air is decomposed to Sb_2O_3.

Concentration regions for separation of Sb_2O_3, $Sb_4O_5Cl_2$, SbOCl and $SbCl_3$ in the $SbCl_3$-Sb_2O_3-H_2O system have been refined[518] and the synthesis and structures of two oxide halides $Sb_8O_{11}Cl_2$ and $Sb_8O_{11}Cl_2.6H_2O$ reported.[519] The anhydrous material is identical with onoratoite and the two compounds contain the same basic ladder-like unit (257), with Sb-O distances ranging between 1.957 and 2.241Å. Each antimony is in pseudo-trigonal bipyramidal coordination with the lone pair in an equatorial position, forming long contacts (3.217-3.837Å) to chlorine. The compounds are disordered with 88% occupancy at the oxygen positions implying that three out of eight antimony atoms would be in three fold coordination.



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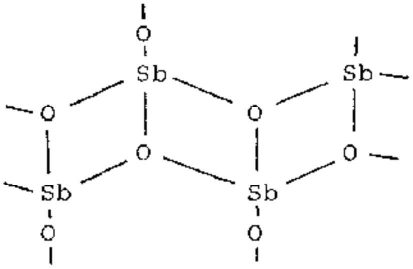
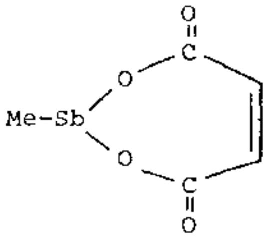


(257)

Maleic and phthalic acids react with $MeSb(OEt)_2$ at low temperatures in ethanol solution to give respectively (258) and (259) but, at room temperature, the reactions give isomeric species with linear chain structures.[520] The carboxylate groups in (259)



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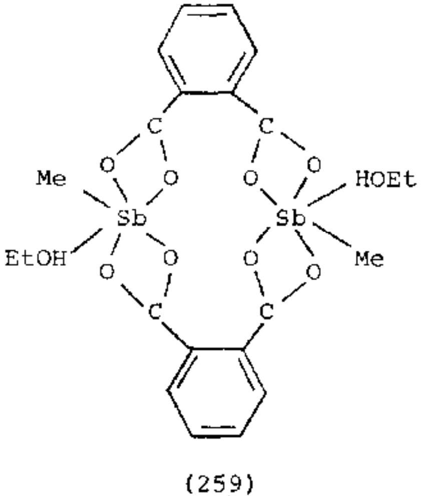
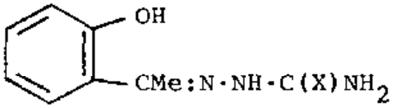


(259)

behave as asymmetric short-bite chelates with Sb-O distances of 2.113, 2.653 and 2.088, 2.985Å, and octahedral coordination is completed by the methyl group at 2.107Å and an oxygen atom from a molecule of solvate ethanol at 2.647Å. Similar maleic and phthalic acid derivatives have been isolated using $PhSb(OEt)_2$ and a range of dicarboxylates, $PhSb(O_2CR)_2$ where R = CF_3, Ph or ^tBu.[521] Semicarbazones and thiosemicarbazones with the stoichiometry $Sb(O^iPr)L$ and Sb_2L_3 are formed on treatment of $Sb(O^iPr)_3$ with (260, X = O or S) ($\equiv LH_2$) and have Mössbauer spectra



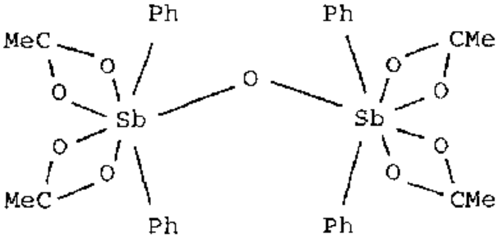
(260)

typical of species in which the lone pair is stereochemically active.[522]

A cadmium antimonite, $Cd(OH)_{0.5}(SbO_2)_{1.5}$, with a distorted calcium ferrite structure, has been synthesised by treating Sb_2O_3 in concentrated KOH with aqueous $CdCl_2$.[523] Biphasic products containing the non-stoichiometric vanadium antimonate, $VSb_{1-y}O_{4-2y}$ for $0 < y < 0.1$, and antimony tetroxide are obtained on heating Sb_2O_4 with either vanadium(III) or (V) oxide in nitrogen.[524] The related reaction between Sb_2O_3 and V_2O_4 on the other hand gave oxidised products formulated as $V_{1-y}Sb_{1-y}O_4$ for $0 < y < 0.1$. X-ray p.e. spectroscopy indicates surface enrichment of the Sb_2O_3-V_2O_5 product with antimony.[525]

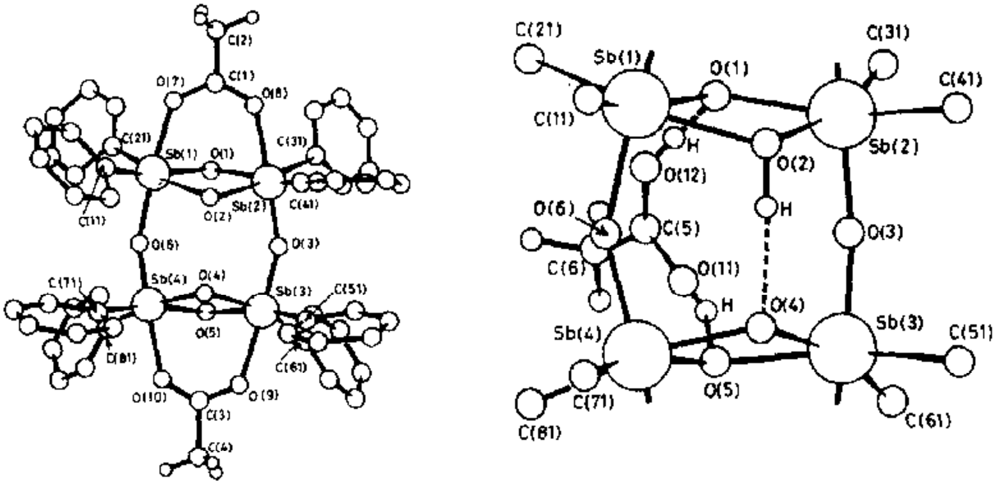
Hydrated antimony(V) oxide, formulated as $H_{2-n}[H(H_2O)]_nSb_2O_6.H_2O$ for $0 \leq n \leq 2$, contains mobile hydrogens which can be substituted by alkali metal cations on contacting with MOH solutions.[526] For M = Na, a phase with the approximate composition $Na_{0.4}[H(H_2O)]_{1.6}Sb_2O_6.H_2O$ was isolated.

Two new substituted antimony(V) basic acetates, $[Ph_2Sb(OAc)_2]_2O$ and $[(Ph_8Sb_4O_6)(HOAc)_3].CH_2Cl_2$ have been isolated and characterised by single crystal X-ray diffraction as hydrolysis products of $Ph_2Sb(OAc)_3$.[527] The first compound with structure (261) is interesting as the effective coordination number of each antimony atom is raised to seven (distorted pentagonal bipyramidal geometry) by the presence of two asymmetrically bidentate acetate groups. The Sb-O(acetate) distances fall in



(261)

two sets of four with mean distances of 2.16 and 2.47Å. The second compound contains a $Ph_8Sb_4O_6$ cage with acetate groups bridging between pairs of antimony atoms as shown in Figure 3a; two of the oxygen atoms are, in fact, hydroxyl groups and the structure is completed by hydrogen bond formation across the cage and incorporation of a molecule of hydrogen bonded acetic acid (see Figure 3b).



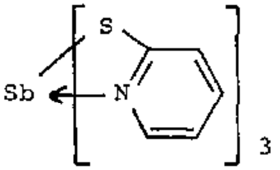
(a) (b)

Figure 3. (a) the cage structure in $[(Ph_8Sb_4O_6).(HOAc)_3]$
(b) Hydrogen bonding across the cage (reproduced by permission from J. Chem. Soc., Chem. Commun., (1984) 896).

Cation exchange equilibria in the $H^+/Li^+,Na^+,K^+$ and Rb^+ systems on iron(III) antimonate have been investigated[528] and both iron and antimony Mössbauer data have been obtained for $Ni_{10}Fe_6Sb_2O_{24}$ and the spinels $M(II)_{12}Fe(III)_3Sb(V)_3O_{24}$ where M = Zn, Mg, Co or Ni.[529] The lanthanoid derivatives, Ba_2LnSbO_6 for Ln = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er or Yb, are perovskite like and can be obtained in polycrystalline form by heating BaO_2, Ln_2O_3 and Sb_2O_3 mixtures to temperatures in excess of 1000K.[530]

5.4.5 Bonds to Sulphur

The heavy atom in antimony thiobenzoate, $Sb(SOCPh)_3$, lies on a three fold axis and is bonded to the sulphur atoms of the ligand at distances of 2.493Å;[531] the S-Sb-S angles are 91.1° giving a pyramidal structure. There are however weaker Sb-O interactions (2.802Å) with O-Sb-O angles of 120.0°. Distances to sulphur and oxygen are similar to those in $Sb(SOCMe)_3$. The pyridine thiolate complex (262) also has three fold symmetry with distances from antimony to sulphur and nitrogen of 2.472 and 2.830Å respectively; a weak intermolecular Sb...Sb interaction (3.657Å) is also present.[532]



(262)

Thiophosphinic acids, $R_2P(S)OH$ where R = Me, Ph or ^{c}Hex, react with antimony(III) acetate to give the tris(thiophosphinates) $Sb(SOPR_2)_3$ for which structures have been obtained for the products with R = Ph and ^{c}Hex.[533] In each case, antimony is coordinated to three oxygen atoms (mean Sb-O 2.03Å) but there are contacts to the three sulphur atoms at 3.18-3.29Å. The O-Sb-O angles fall in the range 81-88°. The cyclo-hexyl compound is monomeric, but an intermolecular Sb...S contact at 3.554Å leads to dimerisation in the phenyl analogue. Phenylantimony dichloride and a range of monothio-β-diketone salts, $[RCSCHCOR^1]Na$, for R = Ph, R^1 = Ph, $C_6H_4(X-4)$ where X = F, Cl, Br or Me and R = Me, R^1 = $C_6H_4(Me-4)$, give non-volatile, coloured products which are monomeric in refluxing benzene.[534] Their i.r. data are interpreted in terms of five coordinate species with chelating ligands.

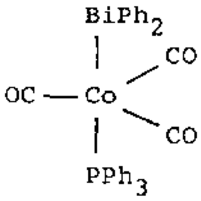
The new sulphide, $SrSb_4S_7.6H_2O$, can be obtained by treating $Sr(OH)_2$ and Sb_2S_3 with a saturated solution of H_2S at 120°C for 10 days.[535] Its structure consists of $(Sb_4S_7^{2-})_\infty$ strings containing chair form Sb_3S_3 rings (Sb–S 2.473-2.539Å) interlinked by longer (2.818Å) Sb-S bonds. The structure of Tl_3SbS_3, obtained by heating a 3:1 mixture of the components is polymeric with three short (2.430Å) and three longer (3.601Å) Sb-S bonds.[536] Sb-S-Tl bridges strongly bond the SbS_3 units to thallium atoms giving Tl_3SbS_{12} groups. $SnSb_2S_4$ previously identified in the SnS-Sb_2S_3 system has now been shown to be $Sn_6Sb_{10}S_{21}$, i.e. $(SnS)_6(Sb_2S_3)_5$ rather than $(SnS)(Sb_2S_3)$, from experiments on mixtures of Sn-Sb-S heated for 120h at 763K.[537] The structure shows tin-antimony disordering over the 16 metal sites. Among the other antimony sulphides obtained this year are Nd_3SbS_6, $Ce_6Sb_8S_{21}$ (isomorphous with $La_6Sb_8S_{21}$) and $Ce_3Sb_3S_{10}$ (isomorphous with $La_3Sb_3S_{10}$).[538]

5.5 BISMUTH

High yields of Me_4Bi_2 can be obtained by treating Me_2BiBr with an equivalent quantity of sodium in liquid ammonia.[539] The compound, a red oil, reacts rapidly with oxygen and sulphur at -30°C to give $(Me_2Bi)_2X$ where X = O or S and with phenyl lithium to give $PhBiMe_2$ but this is more directly obtained from phenyl lithium and Me_2BiBr. Tetraphenyldibismuth, Ph_4Bi_2, obtained similarly from Ph_2BiI and sodium in ammonia, has a staggered trans structure with a Bi-Bi separation of 2.990Å.[540] Reaction with iodine regenerates Ph_2BiI and related oxidative addition reactions occur with sulphur, p-benzoquinone, diazomethane[540] and $Co_2(CO)_8$[541] to give, respectively $(Ph_2Bi)_2S$, $Ph_2BiOC_6H_4OBiPh_2$, $(Ph_2Bi)_2CH_2$ and $Co(BiPh_2)(CO)_4$. The latter, isolated as the triphenylphosphine adduct, $Co(BiPh_2)(CO)_3(PPh_3)$ (263), has a trigonal bipyramidal structure with a Co-Bi separation of 2.692Å.

The bibismole (264) can be obtained by treating the stannole (265, M = $SnBu_2$) successively with I_2, BuLi and $PhBiI_2$;[542] the final step involves reaction of the intermediate (265, M = BiPh) with sodium in ammonia and 1,2-dichloroethane.

Doak and Freedman[543] have reviewed the organometallic chemistry of bismuth for 1982. Substituted bismuth carboxylates, $R_2BiO_2CR^1$ and $RBi(O_2CR^1)_2$ where R = Ph, 4-MeC_6H_4, 4-$(MeO)C_6H_4$, etc. and R^1 = Me or CF_3, result when the appropriate triaryl-



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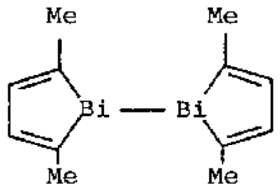

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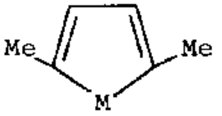

(265)

bismuth is treated, under anhydrous, oxygen-free conditions with either acetic acid or trifluoroacetic acid.[544] Identification was mainly by ^1H n.m.r. spectroscopy as the products are readily hydrolysed.

Stable trialkylbismuth complexes, $Fe(CO)_4.BiR_3$ where R = Et, Pr or Bu, can be prepared from $Fe_2(CO)_9$ in pentane while $M(CO)_5.BiBu_3$ complexes result on irradiation of mixtures of Bu_3Bi and $M(CO)_6$ where M = Cr, Mo or W.[545]

Three bismuth fluoride complexes, KBi_2F_7, $KBiF_4$ and KBi_3F_{10} have been identified as products from $KF-BiF_3$ mixtures heated to 280°C and then quenched.[546] Complex polymorphism is shown by $KBiF_4$ and the β-form is decomposed to K_2BiF_5 on heating to 320°C.

Bismuth in seven-fold, pentagonal bipyramidal, coordination occurs in $BiCl_3[EtNHC(S)C(S)NHEt]_2Me_2CO$,[547] whose preparation was described in ref. 504. Axial positions are occupied by chlorines at distances of 2.635 and 2.717Å while equatorial sites are filled by the third chlorine (2.651Å) and sulphur atoms from two chelating ligands (Bi-S 2.818, 3.042 and 2.910, 2.977Å).

Complexes between $BiCl_3$ and both 6-amino-8-mercaptopurine (L)[548] and 1-H^+-S-methylisothiocarbonahydrazidium iodide[549] have been isolated. The former gives $(HL)_2[BiCl_5(HL)]Cl$, isolated as both a di- and penta-hydrate, in which the anion is octahedrally coordinated to five chlorines at 2.536-2.825Å and the sulphur of a ligand molecule. The second ligand gives salts of the $Bi_2Cl_{10}{}^{4-}$ and $BiCl_{5.67}I_{0.33}{}^{3-}$ anions. The former is centrosymmetric with two almost symmetrical bridging chlorine atoms (Bi-Cl 2.844, 2.866Å) and four terminal chlorines (2.597-2.715Å) giving distorted octahedral coordination about bismuth. The mixed chloride iodide is also distorted octahedral (bond angles 85.5-94.5°) but the iodine component is located in one specific bond.

The bromobismuthate, $Hg_9As_4Bi_2Br_{12}$, from X-ray diffraction consists of a polymeric $[Hg_7(HgBr)_2As_4]^{4+}$ cation and a singly bridged $Bi_2Br_{10}^{4-}$ counterion.[550] This designation is preferred over considering the anion to be a Bi_2Br_{11} species as one of the "terminal" distance (3.258Å) is very much longer than the remainder (2.705-2.952Å) and is better considered as forming one of the HgBr units. The Bi-Br bridging distances are 2.952 and 2.987Å.

Contrary to previous results, a reinvestigation of the $CsI-BiI_3$ system has shown formation of Cs_3BiI_6 with hexagonal symmetry rather than $3CsI.2BiI_3$.[551]

The bismuth oxide halides, Bi_5O_7I and Bi_5O_7Br, can be produced either by sintering $Bi_2O_3-BiX_3$ mixtures at ca. 600°C or in solution by treating Bi_2O_3-HX mixtures with KOH.[552] A new oxide sulphide, Bi_2O_2S, has been synthesised hydrothermally from a 2:1 mixture of Bi_2O_3 and Bi_2S_3 in 10% NaOH solution at 673K for 3d at 93MPa.[553] The compound, which is blackish silver but red by transmitted light, contains bismuth atoms in square antiprismatic coordination (mean Bi-O 2.311, Bi-S 2 x 3.040, 2 x 3.415Å). The sheet structure of $Bi(B_3O_6)$ consists of triangular BO_3 and tetrahedral BO_4 units in a 2:1 ratio with bismuth atoms in six fold coordination to oxygen at distances in the range 2.087-2.629Å.[554]

Distorted dodecahedral BiO_8 polyhedra (mean Bi-O 2.44Å) are linked by dichromate groups into layers in the ab plane as the basis of the structure of $RbBi(Cr_2O_7)_2$.[555] From time of flight neutron powder diffraction, $\gamma-Bi_2MoO_6$ consists of corner sharing MoO_6 octahedra separated by Bi_2O_3 layers, similar to that in the mineral, koechlinite.[556]

Slow evaporation of different ratios of aqueous solutions of bismuth nitrate and thiourea has yielded crystals of two complexes, $[Bi(NO_3)tu_5](NO_3)_2.H_2O$ and $[Bi(NO_3)_3tu_3]$.[557] In the former, bismuth is coordinated to five sulphur atoms (Bi-S 2.637-2.937) and two oxygens of a bidentate nitrate (Bi-O 2.818, 2.916Å); if the nitrate is counted as a single unit the bismuth geometry is close to octahedral. In the second, yellow, compound there is eight fold coordination about bismuth by three sulphur atoms (Bi-S 2.668, 2.672 and 2.681), oxygens from two bidentate nitrate groups (Bi-O 2.66, 2.94 and 2.80, 2.81) and an oxygen from a unidentate nitrate (Bi-O 2.579Å). Again if the bidentate groups are counted as a single unit, the geometry can be reduced to a fac substituted octahedral arrangement.

Bismuth xanthate, $Bi(S_2CO^iPr)_3$, has a polymeric structure as, in addition to coordination by three bidentate xanthate groups (Bi-S 2.682(x2), 2.936(x2) and 2.825, 3.175Å), the units are linked into infinite chains by a Bi...S intermolecular interaction at 2.842Å.[558] As sometimes found, one of the ligands behaves as a simultaneous chelating and bridging group.

Investigation of complex formation between Bi(III) and 2-mercaptoethanol in aqueous 1M $HClO_4$ led to isolation of the yellow complex, $[Bi(SCH_2CH_2OH)_2]ClO_4$.[559] Bismuth is coordinated to both the sulphur and oxygen atoms of the ligands and distorted octahedral coordination is completed by interaction with mercapto groups of two neighbouring molecules. A redetermination of the structure of $Cu_4Bi_4S_9$ has shown that the actual formula is $Cu_{4.2}Bi_{3.76}S_9$.[560]

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