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Chapter 5

ELEMENTS OF GROUP 5

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5.1 NITROGEN

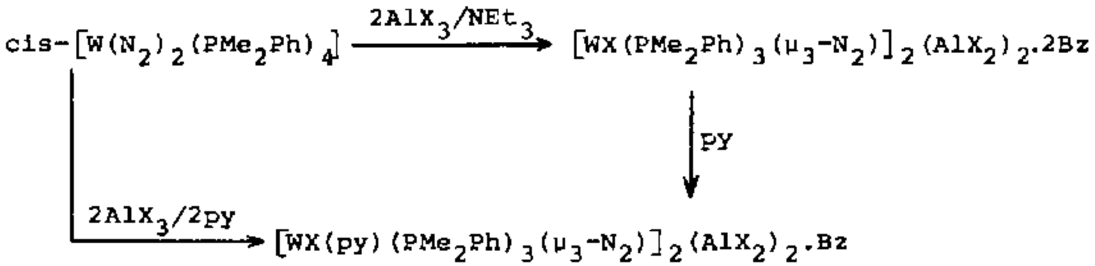
5.1.1 Elemental Nitrogen

More theoretical studies of cyclic D_{6h} hexaazabenzene, "carried out at a significantly higher level and degree of thoroughness than previous work", predict the D_{6h} structure of this molecule to be a relative minimum on the N_6 potential energy hypersurface.[1] The primary conclusion of this research is that the N_6 energy surface is very flat in the vicinity of $(D_{6h})N_6$. Changes in the N-N bond distance of up to 0.37Å may be accommodated with a rise in the total energy of only 10 kcal. mol^{-1}.

U.v. photolysis of $Cr(CO)_6$ in liquid Xe/N_2 mixtures at 183K has been shown by i.r. spectroscopy to generate the mixed metal carbonyl dinitrogen species, $Cr(CO)_{6-x}(N_2)_x$, x = 1-5.[2] The molecule $Cr(CO)_5N_2$ was shown to be thermally stable in liquid Xe at -35° whereas $Cr(CO)(N_2)_5$ is unstable at -90°C. Under similar conditions the photolysis of $Ni(CO)_4$ in Xe/N_2 mixtures produce unstable $Ni(CO)_3(N_2)$.[3] The subsequent thermal reaction of this compound with dissolved CO has been investigated by i.r. spectroscopy; it shows a first-order dependence on the nickel complex concentration and may be rationalised by two simultaneous pathways, one dissociative and the other, probably, associative. The $Ni-N_2$ dissociation energy, 10 kcal. mol^{-1}, was estimated from the study of the dissociative route. An unusually stable dinitrogen complex of Cr^0 has been prepared and characterised by X-ray methods:[4] the compound, $Cr(N_2)_2(dmpe)_2$, dmpe = 1,2-bis(dimethylphosphino)ethane, is claimed to be stable in solution to 90°C. The centrosymmetric molecule has a trans structure with an essentially linear Cr-N-N arrangement, N-N = 0.985(4)Å, significantly shorter than in all other known transition metal-N_2 complexes and also than in N_2 itself.

Novel reactions of dinitrogen complexes of tungsten with aluminium halides, Scheme 1, have been described.[5] The products contain the end-on triply-bridged dinitrogen ligand; the structure of one such product is shown in Figure 1. Ab initio calculations on model compounds, principally lithium derivatives representing supposed intermediates in the protonation of N_2 bonded to transition metals, have been carried out.[6] The results imply that there are stable configurations of the model compounds which have not yet been detected experimentally.

George et al.[7] have identified two isomeric hydrazido(-2)



$$\begin{tikzcd}
\text{cis-}[W(N_2)_2(PMe_2Ph)_4] \arrow[r, "2AlX_3/NEt_3"] \arrow[dr, "2AlX_3/2py"'] & {[WX(PMe_2Ph)_3(\mu_3\text{-}N_2)]_2(AlX_2)_2.2Bz} \arrow[d, "py"] \\
 & {[WX(py)(PMe_2Ph)_3(\mu_3\text{-}N_2)]_2(AlX_2)_2.Bz}
\end{tikzcd}$$

X = Cl or Br, Bz = C_6H_6.

Scheme 1

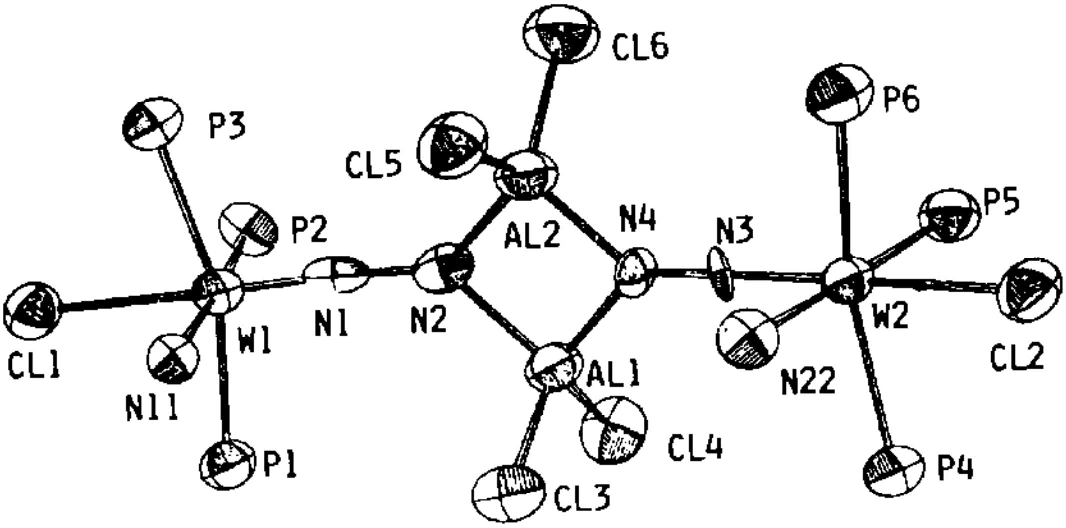
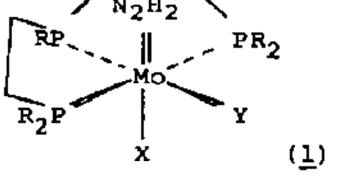


Figure 1. The structure of $[WCl(py)(PMe_2Ph)_3(\mu_3\text{-}N_2)]_2(AlCl_2)_2.2Bz$, omitting carbon and hydrogen atoms. Vibrational ellipsoids are drawn at the 50% probability level. (Reproduced by permission from J. Am. Chem. Soc., 105 (1983)1680).

complexes of Mo (1a and 1b) formed in the reaction of excess HBr with $[\text{trans-}Mo(N_2)_2(\text{triphos})(PPh_3)]$; these isomeric intermediates



(1)

1a, X = Br and Y = Ph_3P

1b, X = Ph_3P and Y = Br.

decompose to form a mixture of NH_3 and N_2H_4. However after 60h the overall reaction can be represented by equation (1).[8]

$$2[Mo(N_2)_2(triphos)(PPh_3)] \xrightarrow{HBr} 2NH_4Br + 3N_2 + 2MoBr_3(triphos) + 2PPh_3 \qquad ...(1)$$

5.1.2 Bonds to Hydrogen

An ab initio CI study of chemical reactions of singlet and triplet NH radicals with H_2 and C_2H_4 has been carried out.[9] The previously unreported NH_4^- ion has been detected by FT ion cyclotron resonance spectroscopy by the reaction of NH_2^- and formaldehyde in the gas phase.[10] Its formation is by reactions (2) and (3). The structure of NH_4^- is described as H^- solvated by an NH_3 molecule. The reaction of Cs and Y metals with NH_3 at

$$NH_2^- + CH_2O \rightarrow NH_3 + HCO^- \qquad ...(2)$$

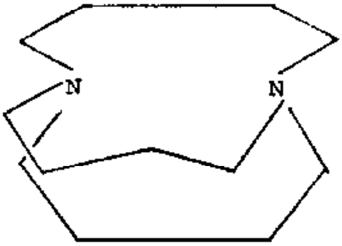
$$HCO^- + NH_3 \rightarrow CO + NH_4^- \qquad ...(3)$$

5-6 kbar and 190-220°C has been shown to yield $Cs_2(NH_2)N_3$ and YN, respectively.[11] This former compound was characterised by X-ray methods and the azide ion was found to have longer N-N bonds (1.255Å) than in simple alkali metal azides (1.17Å). The alkaline earth metal ammonia reductions of anthracene (AN) yields anthracene anion radical salts, e.g. $Ba(NH_3)_2(AN)_2$ which is a dark green solid stable at 100°C in vacuo.[12]

A multinuclear n.m.r. study of Li-$MeNH_2$ solutions covering the concentration range 2 mol.% Li to saturation at ca. 200K has been published.[13] The nuclei investigated included ^1H, ^{13}C, ^{14}N, ^6Li and ^7Li. The results have been used in conjunction with recent magnetic susceptibility data to provide a precise description of the unpaired electron spin-density distribution in both the solvated electron and in solvated lithium monomeric species, Li^+e^-. Ab initio m.o. calculations have been reported for lithiated ammonias, amide, and ammonium ions.[14] For NH_3, as well as PH_3, the differences between the ionisation potentials of pyramidal and planar forms have been calculated by an ab initio SCF method.[15] The lone pair IP difference (planar - pyramidal) is -1.0eV for NH_3 : the core binding energy shift (planar -

pyramidal) is -0.3eV. By combining these data with appropriate experimental valence and core IP's Jolly and Eyermann have quantified the bonding or antibonding character of m.o.'s of nitrogen (and phosphorus) compounds.

The effect of methyl and phenyl substituents on the gas phase basicities of amines and phosphines has been discussed;[16] the theoretical results were found to be in good agreement with the experimental data. A study of intrabridgehead H-bonded ions formed from medium ring bicyclic diamines[17] has been reinforced by an X-ray structural study[18] of 1,6-diazabicyclo[4.4.4]tetradecane (2) and its inside protonated ion (3). The N---N distances in (2) and (3) are 2.806 and 2.526(3)Å, respectively. N.m.r. and i.r. data on this and other inside protonated diamines have shown[19] that only the linear $\overset{+}{N}$-H--N bond within (3) is of the single minimum type. Knop et al.[20] have surveyed the structural features of hydrazinium(2+) salts; they have also determined the structure of the hexafluorosilicate and compared the H-bonding in this with other compounds.



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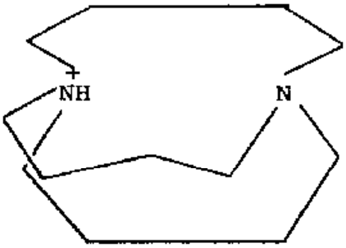


(3)

Numerous 'onium salts of the strong nitrogen acid dimesylamine, $HN(SO_2Me)_2$, have been characterised;[21] pyrolysis (200-250°C) of quaternary ammonium salts was shown to produce tertiary amines and N-alkyldimesylamines. Primary and secondary alkyl iodides also react with these quaternary ammonium salts in boiling $CHCl_3$ to form N-alkyldimesylamines.[22]

The protonation of HN_3 and alkylazides in HSO_3F/SbF_5, HF/SbF_5, or HF/BF_3 results in the formation of stable aminodiazonium, $HRN\text{-}\overset{+}{N}{\equiv}N$, rather than iminodiazenium, $HN{=}\overset{+}{N}{=}NR$, ions (R = H or alkyl) as shown by ^1H, ^{13}C and ^{15}N n.m.r. studies.[23] Aminodiazonium salts were found to effect electrophilic amination of aromatics in high yields. Fluorosulphuric acid at -120°C in

SO_2ClF protonates diazomethane on carbon, whereas the more acidic system HSO_3F/SbF_5 forms, in addition, the N-protonated methylenediazenium ion, $H_2C{=}\overset{+}{N}{=}NH$, the first example of this class of compound.[24]

The i.r. spectrum of the 1:1 complexes of HI with either NH_3 or NMe_3 have been obtained in four different matrices (Ar, O_2, N_2, C_2H_4) at 10K.[25] The symmetric I-H---N stretch was found to be markedly dependent on the nature of the matrix. A comparison with the spectra of the known $XH{-}NH_3$ and $XH{-}NMe_3$ adducts shows that the H-bond is stronger in the iodide analogues. The reaction of S_4N_4 with $HBF_4{-}Et_2O$ in CH_2Cl_2 leads to the precipitation of deep red crystals of $S_4N_3(NH)^+BF_4^-$ at 0^oC.[26] The structure of the salt shows that the boat-like S_4N_4 ring is protonated on N and that there are long contacts, 2.19 and 2.38Å, between the proton and 2 fluorines of the anion, with N-H---F angles near to 150^oC. The reaction between NO and NH_3 has been studied over platinum at low pressures and over a wide temperature range.[27] Below 850^oC the only products are N_2, N_2O and H_2O. The rate data could be fitted, within 15%, to a single rate expression.

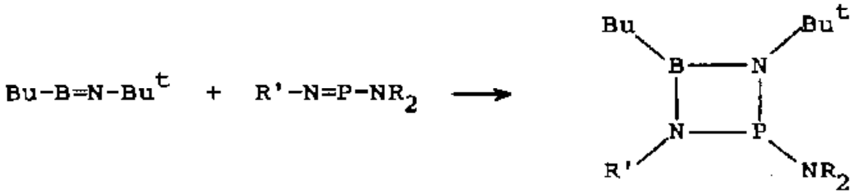
E.p.r. experiments have shown that dialkylaminyl radicals do not readily attack dialkylamines to form α-aminoalkylradicals, equation (4).[28] These results conflict with the earlier

$$(RCH_2)_2N + (RCH_2)_2NH \not\longrightarrow (RCH_2)_2NH + RCH_2NHCHR \qquad ...(4)$$

conclusions that processes, such as (4), provide the major pathway in these mixtures. By contrast $Bu^tO\cdot$ radicals were found to abstract H from dialkylamines to form aminyl and α-aminoalkyl radicals.

5.1.3 Bonds to Boron

The trimethylamine adducts of the mixed trihalides of boron have been studied by ^{15}N and ^{11}B n.m.r. spectroscopy.[29] The formation of two 1,3,2,4-diazaphosphaboretidines has been achieved in 70% yield by reaction (5) for R = R' = $SiMe_3$ and for R = Pr^i and R' = Bu^t.[30] On the basis of n.m.r. evidence the N_2PB ring is planar. The dimer of $Bu{-}B{=}N{-}Bu^t$ has been shown to function as a bidentate, 4-electron ligand towards M = Cr or W, as shown by reaction (6).[31] Komm et al.[32] have reported an improved synthesis, from $H_3N.BH_3$, and additional characterisation



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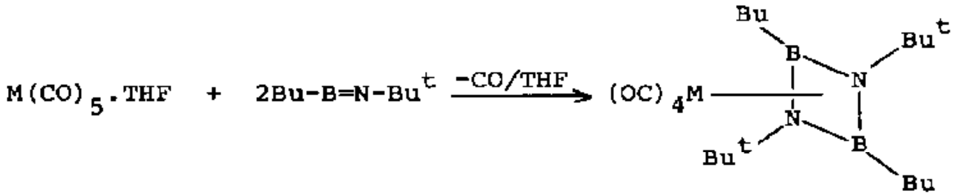


...(6)

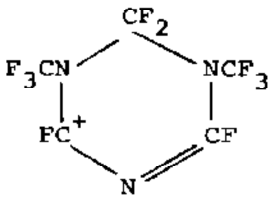
of a crystalline poly(aminoborane), $(H_2NBH_2)_x$, that may be identical with products obtained in earlier studies.

5.1.4 Bonds to Carbon, Silicon or Tin

Kaim[33] has reviewed organic, inorganic, and biochemical aspects of the chemistry of 1,4-diazines. The reaction of arc-generated C atoms with NH_3 have been reported in detail and the mechanism of the formation of amino acid precursors discussed.[34] The formation of HCN in such reactions appears to proceed via $\bar{C}$-$\overset{+}{N}H_3$ followed by the elimination of H_2 and then isomerisation of HNC.[35]

Evidence for the generation of the singlet phenylnitrenium ion from PhN_3, in the presence of trifluoroacetic acid, has been obtained : the nitrenium ion adds stereospecifically to some alkenes[36] giving aziridinium ions and substituted aromatic substrates,[37] in the presence of a catalytic amount of CF_3SO_3H, to form diarylamines. In the presence of O_2 a solution of $[(Ph_3P)_2N]_5[(NC)_5CoO_2Mo(O)(CN)_5]$ in CH_2Cl_2 shows e.s.r. signals characteristic of a number of species.[38] One of the products has been identified from its 9-line spectrum as the tetracyanoethene radical anion, $TCNE^{\bar{\cdot}}$, which is believed to be formed by the reaction of ·CN with CH_2Cl_2.

Perfluorotrimethylamine and SbF_5 react slowly (30d) at 60°C with the elimination of CF_4 and the formation of cation (4) in solution.[39] Hydrolysis of (4) yields (5) which was characterised by X-ray crystallography. Perfluorodimethylethylamine reacts faster with SbF_5 according to equation (7).



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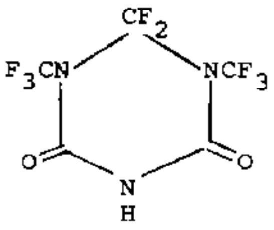

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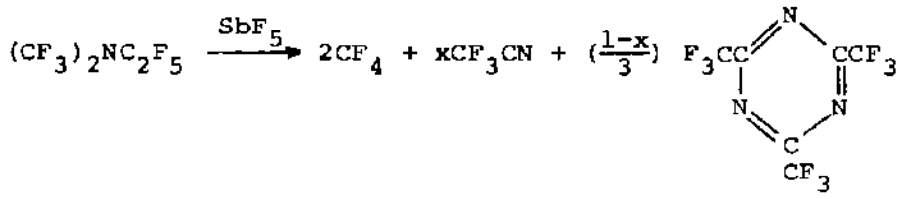


...(7)

The lowest IP for tertiary amines of the type $Me_{3-n}N(SiH_3)_n$, $Me_{3-n}N(SiMe_3)_n$ and $(Pr^n)_{3-n}N(SiMe_3)_n$ corresponds to ionisation from a nitrogen 2p lone pair orbital; the experimental data, obtained using PES, have been compared with the results of semi-empirical (MNDO) and ab initio calculations.[40] Livant et al. discussed the extent of the involvement of d orbitals on Si and their influence on the IP and on the approach to planarity of the $C_{3-n}NSi_n$ skeleton. Calculations for $(Bu^t)_3N$ suggest that the reason for its non-existence is entirely on steric grounds. X-ray structural data have been presented for bis(trimethylsilyl)amido- and (2,2,6,6-tetramethylpiperidinato)-lithium.[41] The former crystallises as a dietherate and has a Li_2N_2 skeleton, Figure 2, whereas the latter possesses a planar Li_4N_4 ring, Figure 3.

Klingebiel and Vater[42] have reported the stepwise synthesis of the cyclo-di- and cyclo-tri-silazanes, $(R_2SiNH)_n$, n = 2 or 3, via acyclic compounds starting from R_2SiF_2 and $LiNH_2$.[42] Chain compounds containing NHSiF skeletons have been similarly obtained from $RSiF_3$ and $LiNH_2$. Four- and five-membered silylhydrazine rings were also produced by the reaction of dilithiated hydrazines with N,N-bis(fluorosilyl)amines.[43] Both Me_3SiNSO and $Me_3SiN{=}S{=}NSiMe_3$ react with $SnCl_4$ to yield the same 1:1 adduct in which the sulphur diimide functions as a small bite (62.6%) bidentate nitrogen donor to tin(IV).[44]

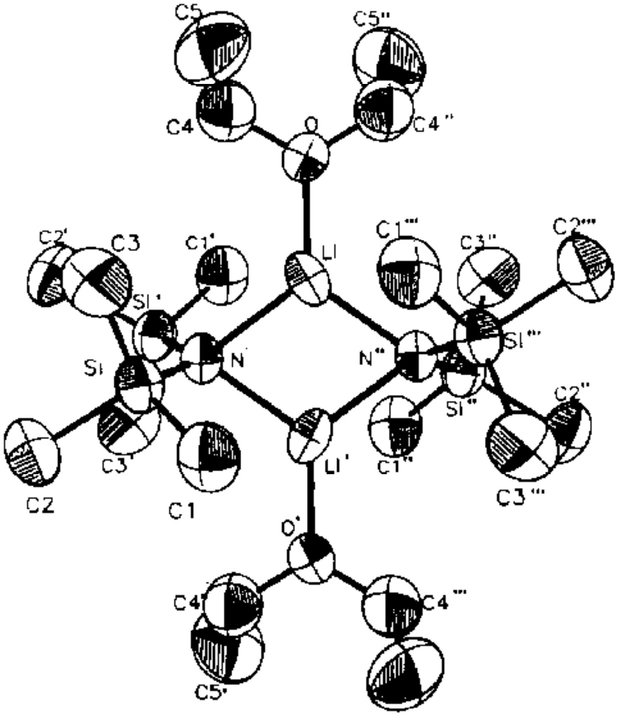


Figure 2. Molecular structure of $[Li\{N(SiMe_3)_2\}.OEt_2]_2$ with non-carbon atoms represented by 50% probability ellipsoids. (Reproduced by permission from J. Am. Chem. Soc., 105(1983)302).

5.1.5 Bonds to Oxygen

The first laser Raman spectra of both asymmetric and symmetric N_2O_3 have been measured from mixtures of the isomers stabilised in NO matrices at 12K.[45] Laser irradiation was used to interconvert them. Force constant calculations were carried out on both isomers. Bauschlicher et al.[46] have considered the electronic structure of N_2O_4; their calculations show that it is most appropriate to describe its formation in terms of the relatively weak interaction of two NO_2 groups. They presented an analysis of the factors causing the N-N bond to be longer than has been predicted by most theoretical studies. Swanson and coworkers[47] have investigated the behaviour of N_2O_4 at high pressures by Raman spectroscopy. They obtained evidence for two unreported crystalline modifications. Laser irradiation of α-N_2O_4 produced β-N_2O_4, the probable structure of which has N-N bonds aligned. At pressures in the 15-30 kbar region the β-form

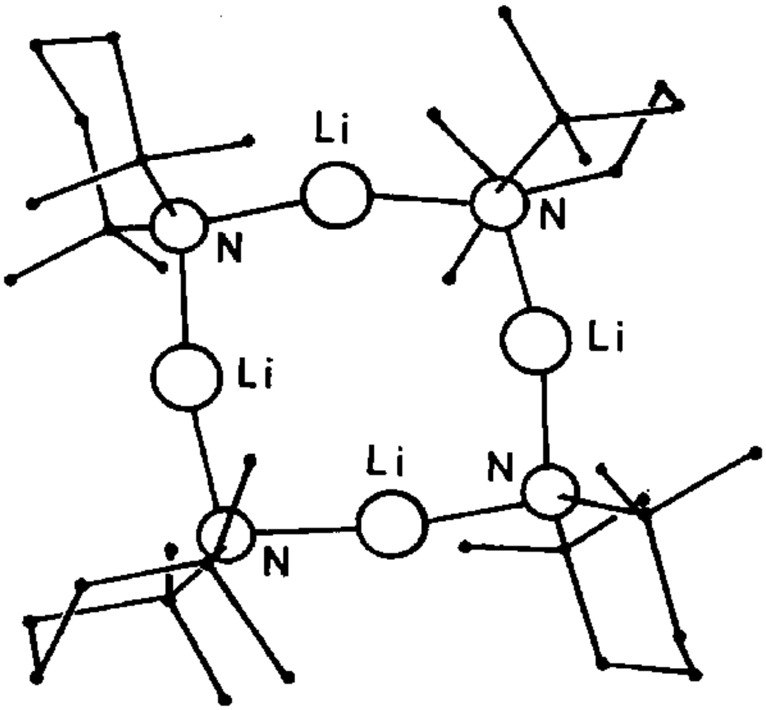


Figure 3. Structure of $[Li(\overline{NCMe_2CH_2CH_2CH_2CMe_2})]_4$

reversibly forms a third modification, ionic $NO^+NO_3^-$, whereas α-N_2O_4 is stable to at least 76 kbar.

The gas-phase structure of N_2O_5 has been investigated at -11°C by electron diffraction. The results were found to be consistent with C_2 molecular symmetry for the state of minimum energy, in which the dihedral angles between each NO_2 plane and the NON plane are approximately 30°.[48] Moreover the NO_2 groups were shown to undergo large amplitude torsional motions about the most stable configuration. Dimensions of the molecule not available from previous studies are N-O (1.492(4)Å) and NON angle (133.2(6)°). The nitric acid-NO_2^+ equilibrium has been studied by ^{14}N n.m.r. spectroscopy for solutions in H_2SO_4, 81-96%, and at 25°C. Seel and coworkers in 1972 observed only one ^{14}N resonance whereas Ross et al.[49] now report separate signals for NO_2^+ and HNO_3 : 50% conversion to NO_2^+ for a solution in 88% H_2SO_4 is consistent with the available Raman data. The pseudo-first order rate constants for the formation and hydration of NO_2^+ were obtained from line-shape analyses of the spectra. Examination of these data reveals certain inconsistencies between the currently accepted mechanism and the observed rates/orders of aromatic nitration.

Bursey et al.[50] have inferred that an anion formed from butyl nitrate by negative chemical ionisation mass spectrometry is the orthohyponitrite ion. From a consideration of the fragmentation products they have proposed that this species is $(HO)HNO^-$. The radical cation, $N_2O_4\cdot^+$, has been identified as the product of γ-radiolysis at 77K of N_2O_4 in $CFCl_3$.[51] This species can be considered as a $NO_2\cdot$ radical strongly perturbed by a linear NO_2^+ cation.

The effects of four species of denitrifying bacteria on the conversion of NO_2^- to trioxodinitrate ($HN_2O_3^-$) and N_2O or of $HN_2O_3^-$ to N_2O have been studied.[52] In all instances the N_2O produced in the presence of $^{15}NO_2^-$ and $HN_2O_3^-$ was isotopically randomised. Indeed it was concluded that both pathways to N_2O involve a common intermediate, which, from work with other systems, may be nitroxyl, HNO. Vitamin B_{12s}, the cobalt(I) derivative of vitamin B_{12}, reduces nitrate rapidly and cleanly to NH_4^+ at pH 1.5-2.5. The observed rate law (rate = $k[Co^I][NO_3^-][H^+]$) is consistent with initiation either by reaction of the non-protonated form of B_{12s} with molecular HNO_3 or by hydride transfer to NO_3^- from the protonated form of B_{12s}.[53]

The decomposition of HN_3 in nitric acid at 97°C has been shown to take place according to equation (8). The mechanism proposed[54] involves attack by NO_2^+ on HN_3, equation (9). Reaction sequence

$$0.486HNO_3 + HN_3 \rightarrow 1.15N_2 + 0.27NO + 0.46N_2O + 0.73H_2O \qquad ...(8)$$

$$NO_2^+ + HN_3 \xrightarrow{-H^+} N_3ONO \begin{array}{l} \longrightarrow N_2 + 2NO \\ \quad \text{or} \\ \longrightarrow N_3 + NO_2 \end{array} \qquad ...(9)$$

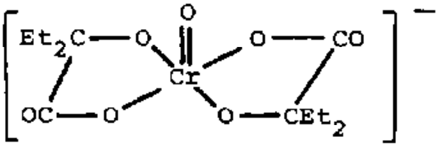
$$N_2O_4 + HN_3 \xrightarrow{-HNO_3} N_3NO \rightarrow N_2 + N_2O \qquad ...(10)$$

(10) was proposed to explain the formation of N_2O. In the reaction between hydroxylamine and H_3PO_5, when the former is in at least ten fold excess, equation (11) describes the overall process:[55] under other conditions the stoichiometry is variable

$$H_3PO_5 + NH_3OH^+ \rightarrow H_3PO_4 + \tfrac{1}{2}H_2N_2O_2 + H_3O^+ \qquad \ldots(11)$$

and HNO_2 and HNO_3 are other possible products of oxidation. Gowland and Stedman[56] have described the conditions under which a homogeneous solution of hydroxylamine in nitric acid can react to form a two-layer system, i.e. a nitrous-nitric acid mixture above a solution of hydroxylamine in nitric acid. New information on the hydroxylamine-nitrous acid reaction has been interpreted as providing definitive evidence that N_2O arises from a symmetrical precursor over the entire acidity range, 5M $HClO_4$ to pH9.[57]

The reaction between nitrite ion and hydroxylamine-N-sulphonate (HAMS) has been investigated in aqueous solution.[58] An empirical rate law and the rate constant were reported. The results were explained in terms of a mechanism involving the nitrosation of HAMS followed by a decomposition into the products, principally N_2O and sulphate ions. The chelated bis(carboxylato)chromium(V) complex anion, (6), reacts smoothly with NH_3OH^+ at pH 3.6-4.7 to form (7) and (8) as NO^+ derivatives of low-spin chromium(I).[59] The rate law is consistent with the loss of one carboxylato ligand followed by the formation of a Cr(V)-NH_2OH precursor and a net 4 electron internal transfer. A study of the rate of oxidation of HNO_2 by aqueous H_2O_2 has revealed that HNO_2 decomposes to NO,



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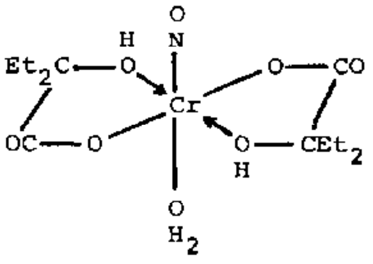

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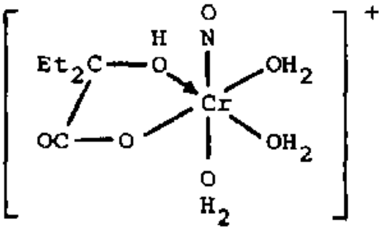


(8)

which is itself oxidised to NO_2 by H_2O_2.[60] The overall reaction is given by equation (12). The nitrosodisulphonate anion radical

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \qquad ...(12)$$

$ON(SO_3)_2{}^{2-}$ smoothly oxidises $Fe(CN)_6{}^{4-}$ to $Fe(CN)_6{}^{3-}$, probably by parallel outer-sphere paths, and H_2O_2 to O_2.[61] The treatment of secondary and tertiary amines with Fremy's salt in aqueous Na_2CO_3 or in pyridine gives moderate yields of the corresponding N-nitrosamines.[62]

Nisseren and Meeker[63] report that equation (13) is the only

$$NO_3{}^- \rightleftharpoons NO_2{}^- + \tfrac{1}{2}O_2; \qquad \Delta G^\circ/\text{cal. mol}^{-1} = 23000 + 20.6T \qquad ...(13)$$

significant process occurring in equimolar mixtures of $NaNO_3$ and KNO_3 over the temperature range 500-600°C. No evidence was obtained for the formation of any anionic oxo species, such as O^{2-}, $O_2{}^{2-}$ or $O_2{}^-$, at significant concentrations. The experimentally determined standard free energy change for the reaction is in good agreement with results for the simple salts. The reaction of $NaNO_2$ with silica in an Ar atmosphere occurs in two stages:[64] at 600°C the main gaseous products are initially NO and, in the later stages, nearly equimolar amounts of NO and O_2 are produced. Abe et al. inferred that some oxide species, probably including peroxide, can exist in the melt. Dark red, crystalline K_3NO_3 is cubic possessing a perovskite structure with the $NO_2{}^-$ anions disordered.[65] Below -42°C a new phase occurs in which the $NO_2{}^-$ group is ordered, according to X-ray powder data.[66]

Further studies of the photolysis of chlorine nitrate, $ClONO_2$, at 266 and 355nm, have provided clear evidence that the major (90%) photolysis route is to Cl· and NO_3· and that O and ClONO route accounts for the remainder.[67] In addition the rate of reaction (14) is ca. 50 times faster than had been previously

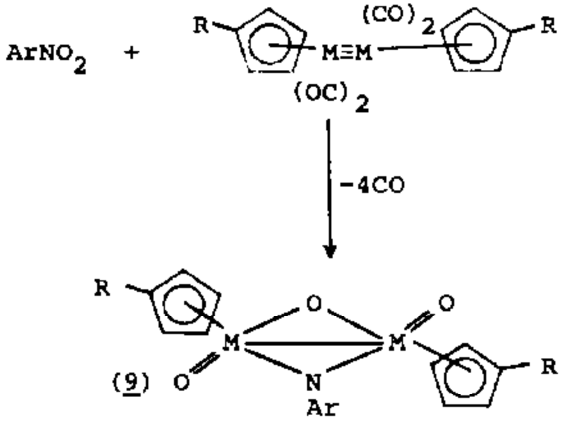
$$Cl\cdot + ClONO_2 \rightarrow Cl_2 + NO_3\cdot \qquad ...(14)$$

reported. The i.r. spectrum of matrix-isolated chlorine nitrate shows absorptions which may be associated with $ClONO_2$ and ClOONO isomers:[68] assignments for the latter were given.

The base hydrolysis of a series of complexes $[(NH_3)_5Co^{III}X]^{n+}$ in

1M $NaNO_2$ has now been shown to yield small amounts of both O- and N-bonded nitritopentamminecobalt(III) in the ratio ca. 2:1.[69] These results are consistent with a common five-coordinate conjugate base intermediate, $[(NH_3)_4Co(NH_2)]^{2+}$. The spontaneous nitrito-to-nitro linkage isomerisation for a variety of octahedral cobalt(III) ammine complexes has been studied in aqueous solution to examine the effect of inert ligands.[70]

Nitrocompounds react rapidly at room temperature with certain metal complexes containing M≡M bonds according to Scheme 2.[71]



(9)

Scheme 2

The same product (9), containing a μ-nitrene ligand, was also formed directly when $[cpMo(CO)_3]_2$ was refluxed with $PhNO_2$. Oxidation of coordinated nitrosyl in $[bpy(MeCN)_3Rh(NO)]^{2+}$ and $[(MeCN)_4Rh(NO)]^{2+}$ by O_2 yields the analogous nitro compounds, isolated as (10) and (11), respectively.[72] Both function as oxygen transfer reagents and effect olefin oxidation, although (10) is only active in the presence of $[(PhCN)_2PdCl_2]$.

$[bpy(MeCN)_2Rh(NO_2)](PF_6)_2$

(10)

$[(MeCN)_4Rh(NO_2)]X_2$

$X^- = BF_4^-$ or PF_6^-

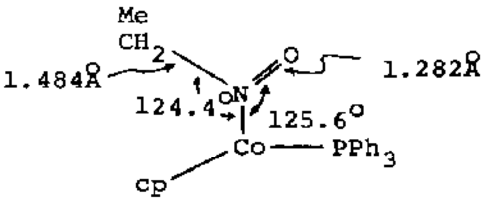
(11)

The products of reaction of F atoms with MeONO show characteristic i.r. bands, in an Ar matrix at 14K:[73] NO abstraction to form FNO and H atom abstraction are two reaction routes. Confirmatory evidence for the formation of FON was obtained, although the N-O stretching fundamental of this unstable isomer was not established. A modified pyrolysis procedure for decarboxylating CF_3CO_2NO has been proposed which increases the yield of CF_3NO to 77%.[74] Bis(triphenylphosphine)nitrogen nitrite, $(Ph_3P{=}N{=}PPh_3)^+NO_2^-$, has been found to be very effective for converting transition metal carbonyls into nitrosyl carbonyls.[75] A kinetic analysis of the reaction of $Fe(CO)_5$ with $((Ph_3P)_2N)NO_2$ in MeCN has verified that the reaction is first order in both iron and nitrite at 26°C.

Bell and coworkers[76] have observed deshieldings in the range 350-700 ppm in ^{15}N n.m.r. of strongly bent apical nitrosyl groups attached to Rh or Co, as compared with linear systems. In addition ^{15}N resonances of nitro and hyponitrite complexes were assigned.[77]

The previously uncharacterised $V(CO)_5(NO)$ has been prepared as a thermally unstable, deep red-violet and (at -25°C) remarkably reactive solid by the reaction of $Et_4N[V(CO)_6]$ with $NOBF_4$ in CH_2Cl_2 at -40°C.[78] Many new derivatives were obtained by the reactions of this new vanadium nitrosyl. Attempts to synthesise the Ta analogue were also described. Although the bis(dithiocarbamato) complexes of the type $(dtc)_2M(NO)$, M = Co, Fe, are isomorphous there are structural differences. Thus the diamagnetic Pr^i cobalt complex has a 129° CoNO bond whereas the iron complex has an angle of 179°.[79]

Solutions of Na[cpCo(NO)] react with MeI at -40°C to give cpCo(NO)Me which decomposes in the presence of at least one equivalent of Ph_3P to form $cpCo(MeNO)(PPh_3)$.[80] The molecular structure in the related ethyl compound (12) was established by X-ray analysis. The problem of attack by SO_3^{2-} on an electro-



(12)

philic nitrosyl ligand has been investigated for certain Fe and Ru complexes.[81] I.r. spectroscopy helped to identify the same $[N(O)SO_3]^-$ ligand in several products and X-ray data were used to obtain the structure of cis-$[RuCl(bpy)_2\{N(O)SO_3\}]$. The dimensions of the previously unreported ligand in this complex are shown in Figure 4; the length of the N-S bond clearly relates to the facile loss of SO_3^{2-} from this ligand. Legzdins et al.[82]

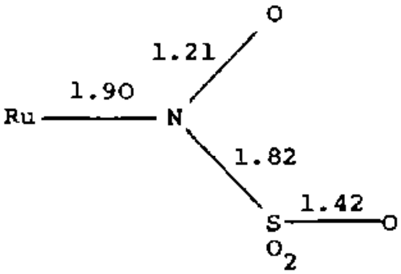


Figure 4. Dimensions of the $[N(O)SO_3]$ ligand (Å) in cis-$[RuCl(bpy)_2\{N(O)SO_3\}]$.

have investigated reactions of $(\mu_3\text{-NO})M_3$ complexes on the premise that the reduction in N-O bond order should be greater in terminal or μ_2-NO complexes. They have reported the unprecedented sequential transformations, where M = $(\eta^5\text{-}C_5H_4Me)Mn(\mu_2\text{-NO})$, involving the formal reduction of the μ_3-NO ligand, equation (15). Reaction was effected by the addition of $HBF_4.OMe_2$

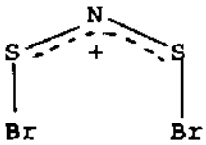
$$M_3(\mu_3\text{-NO}) \underset{Et_3N}{\overset{H^+}{\rightleftharpoons}} [M_3(\mu_3\text{-NOH})]^+ \xrightarrow[2e^-]{2H^+} [M_3(\mu_3\text{-NH})]^+ \qquad ...(15)$$

or HPF_6(aq) to the Mn complex in CH_2Cl_2. The identities of examples of the two types of reduced species were established by X-ray methods.

5.1.6 Bonds to Sulphur, Selenium or Tellurium

Roesky and Pandey[83] have reviewed recent advances in the chemistry of transition metal thionitrosyl and related complexes. The dibromodithionitronium cation, $(SBr)_2N^+$, has been prepared by the bromination of $NS_2^+AsF_6^-$ in liquid SO_2.[84] The cation appears to have the same cis planar structure (13) as the dichlorocation.

Neither iodination nor fluorination yielded analogous products, however the reaction with XeF_2 did produce $(SF_2)_2NAsF_6$ in



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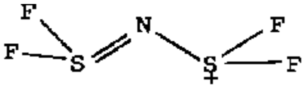
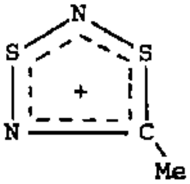
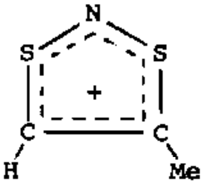


(14)

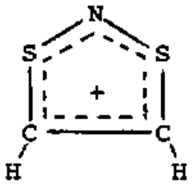
quantitative yield. The bonding in this new cation is described adequately by (14). The synthesis of cations (15)-(17), by the reaction of $NS_2^+AsF_6^-$ with MeCN, MeC≡CH, and HC≡CH, respectively, has been reported.[85] Reduction of these was achieved, either chemically or by electrolysis, to form long-lived free radicals, e.g. (18) from (15).



(15)



(16)



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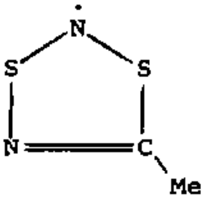


(18)

Fluoride abstraction from the thiazyl fluoride complex $[Re(CO)_5(NSF)]^+$ by AsF_5 has been shown to give a complex $[Re(CO)_5(NS)]^{2+}$, containing the thionitrosyl ligand (ν(NS) = 1371 cm^{-1}).[86] The reaction of Re-bonded NSF with $Me_3SiNMeR$, R = Me or Me_3Si, leads to the thiazylamido complex $[(OC)_5Re(NSNMeR)]^+AsF_6^-$.[87] Reaction of $Ph_2N.NH_2$ with S_2Cl_2 in the presence of Et_3N leads to the formation of 1,1-diphenylthionitrosamine, $Ph_2N.NS$.[88] This new, relatively unstable compound was isolated, but not purified, and used to generate an adduct with $Cr(CO)_5$. An X-ray structure determination showed that this ligand bonds to Cr through sulphur. Tetrakis(trifluoromethylthiazyl), $(CF_3SN)_4$, has been prepared from CF_3SCl and Me_3SiN_3, Scheme 3.[89] The new compound is stable at -30°C for a few days. The oxidation of ^{15}N-labelled $S_3N_3^-$ in MeCN by O_2 has been followed by ^{15}N n.m.r. spectroscopy.[90] Crystal and molecular structures of PPN^+ salts of $S_3N_3O^-$ and $S_3N_3O_2^-$ were obtained by X-ray methods.

$$\begin{tikzcd}
CF_3SCl + Me_3SiN_3 \arrow[r, "-40^{\circ}C", "-Me_3SiCl"'] & CF_3SN_3 \arrow[r, "-N_2"'] & \frac{1}{x}(CF_3SN)_x \arrow[d, "20^{\circ}C"] \\
 & & (CF_3SN)_4
\end{tikzcd}$$

Scheme 3

Numerous Te-N compounds have been synthesised starting from H_2NTeF_5 and $Me_3SiNHTeF_5$.[91] Almost all of them contain the $NTeF_5$ group, which stabilises many double bonded systems, such as in $O{=}C{=}NTeF_5$ and $Cl_4W{=}NTeF_5$:$Cl_2Se{=}NTeF_5$ is a rare example of a compound containing a discrete Se=N double bond. TeF_5Cl, but not SeF_5Cl, reacts photolytically with the nitriles XCN, X = Cl or CF_3, according to equation (16), to form compounds containing Te-N bonds.[92] A number of reactions of these compounds were also

$$TeF_5Cl + XCN \xrightarrow{h\nu} TeF_5N{=}CClX \qquad ...(16)$$

reported, equations (17)-(19).

$$TeF_5N{=}CCl_2 \xrightarrow[70^{\circ}C]{CsF\ xs} Cs^+[TeF_5NCF_3]^- \qquad ...(17)$$

$$TeF_5N{=}CCl_2 \xrightarrow[45^{\circ}C]{HF\ xs} TeF_5NHCF_3 \xrightarrow[75^{\circ}C]{HgF_2\ xs} Hg[N(CF_3)TeF_5]_2 \qquad ...(18)$$

$$Hg[N(CF_3)TeF_5]_2 \xrightarrow{ClF} HgF_2 + 2ClN(CF_3)TeF_5 \xrightarrow{h\nu} CF_3N(TeF_5)_2 \qquad ..(19)$$

5.1.7 Bonds to Nitrogen

A reversible homolytic cleavage reaction of $[(CF_3S)_2N]_2$ occurs in perhaloalkane solvents over the temperature range 250-315K:[93] the radical species $(CF_3S)_2N\cdot$ was identified by e.s.r. spectroscopy, Figure 5, and the N-N bond energy in the parent compound estimated to be 32±2 $kJ.mol^{-1}$. The first stage of the electrochemical reduction of fluorenone triphenylphosphazine, $Fl{=}NN{=}PPh_3$, in DMF - $0.1M(Bu_4N)ClO_4$, is a one electron process

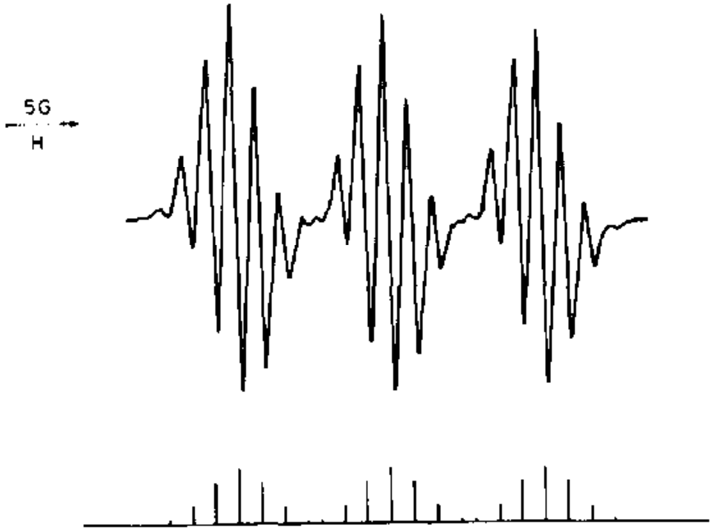
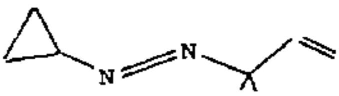
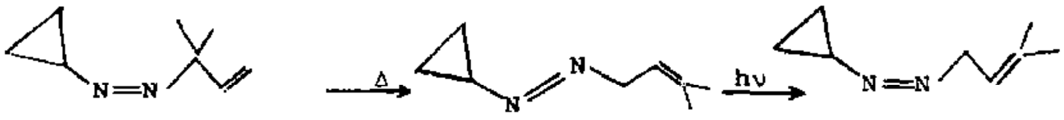


Figure 5. E.s.r spectrum of a solution of $[(CF_3S)_2N]_2$ in $CFCl_3$ at 298K: $a(^{14}N) = 13.20G$, $a(^{19}F) = 1.95G$ (Reproduced by permission from J.Am. Chem. Soc., 105(1983)1504).

which generates the corresponding radical anion.[94] The latter is unstable and decomposes with loss of Ph_3P to give the 9-diazofluorene anion radical, $FlN_2\cdot^-$, which itself reacts further either with the starting material or with itself. The decomposition of nitroamine, $H_2N\cdot NO_2$, has been studied in concentrated aqueous $HClO_4$, H_2SO_4 and HCl over a range of temperatures.[95] For each there is strong evidence of an acid-catalysed reaction. Hughes et al. interpret these results in terms of a rate determining nucleophilic attack of H_2O upon the protonated $H_2N\cdot NO_2$ to give NH_2OH and HNO_2, which then interact to give N_2O.



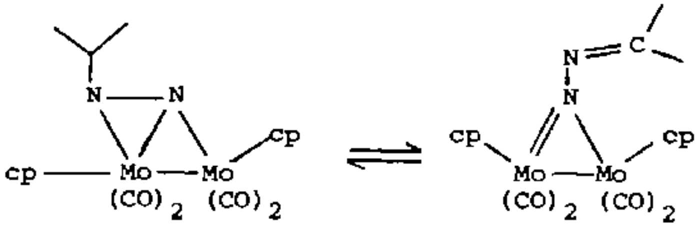
(**19**t)



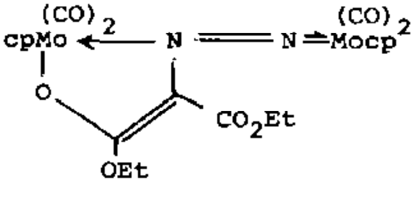
(**19**c) (**20**t) (**20**c)

Irradiation with a 337nm laser of trans-α,α-dimethylallylazoalkanes, such as (19t), produces two new azoalkanes (20t) and (20c), along with a mixture of hydrocarbon degradation products.[96] The intermediacy of (19c) was established by u.v. spectroscopy. Such a turn around of the allyl group is consistent with the recombination of alkyldiazenyl radicals, RN=N·, at the primary end of the dimethylallyl radical.

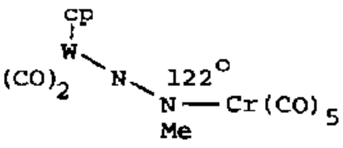
Floriani and co-workers have shown that the -N=N- grouping in azo and diazo compounds may be reduced by $cpTiCl_2$.[97] Thus from the reduction of PhN=NPh they were able to characterise the binuclear complex $(cpTiCl)_2(\mu\text{-}Ph_2C{=}NN)_2$. In $[cp_2Ti(PhN{=}NPh)]$ the conformation and dimension of the cis-azobenzene ligand differ considerably from those of the free molecule.[98] Two more distinct modes of coordination for the diazoalkane ligand have been reported by Curtis et al.[99] in their studies of the reactions of the Mo≡Mo complex, $cp_2Mo(CO)_4$: (i) diazopropane, Me_2CN_2, forms a 1:1 adduct which exists as an equilibrium mixture of (21a) and (21b); (ii) diethyl diazomalonate inserts in the Mo≡Mo bond to



(21a) (21b)

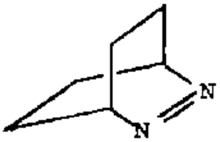


(22)



(23)

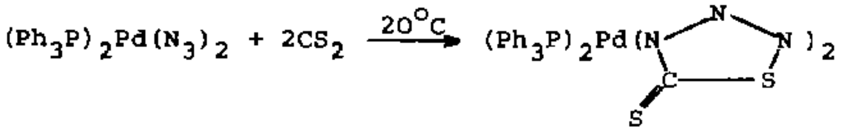
form (22), the structure of which was established by X-ray methods. The interaction of $cpW(CO)_2(N_2Me)$ with $Cr(CO)_5$.THF gives a binuclear complex (23) containing the bridging organodiazo ligand.[100] Attachment of the $Cr(CO)_5$ causes the W-N distance to decrease and the N-N distance to increase, both by 0.03Å. Engel et al.[101] have studied the photolysis of a range of compounds containing the 2,3-diazabicyclo[2.2.2]oct-2-ene skeleton, (24).



(24)

Compounds of this type often prove to be remarably stable towards the loss of N_2; the compound studied was chosen to assess the effect of bridgehead substituents and fused rings on the photochemistry.

Coordinated azido ligands, in $(Ph_3P)_2Pd(N_3)_2$ and $Co(N_3)_4^{2-}$, react with CS_2 by a 1,3-dipolar cycloaddition to give thiatriazoline-5-thionato complexes, e.g. equation (20).[102] Although (25) is stable the anionic cobalt(II) species is not and rapidly loses N_2 and S_8 with the formation of $Co(NCS)_4^{2-}$. The first X-ray crystallographic analysis of a compound containing a planar five-membered N_5 ring has been reported:[103] the N-N bond distances in 4-dimethylaminophenylpentazole, $Me_2N{\cdot}C_6H_4{\cdot}N_5$, at 128K lie in the range 1.30 to 1.35Å, i.e. intermediate between single bonds (1.45Å in N_2H_4) and double bonds (1.25Å in trans-diimine). Interestingly the NC_3 framework of the dimethylaminophenyl group is also planar.



...(20)

(25)

The reaction of CF_3NO and NH_2OH at -78° followed by treatment with a base in the presence of arene- or alkane-sulphonyl halides, RX, has been shown to generate N-trifluoromethyl-N-nitrososulphonamide, equation (21).[104] The gas-phase reaction of ppm

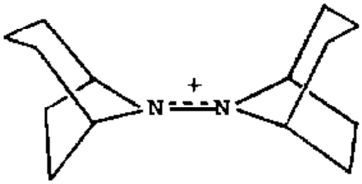
$$CF_3NO \xrightarrow{NH_2OH} \begin{bmatrix} CF_3N{=}N(OH) \\ \uparrow\downarrow \\ CF_3NH(NO) \end{bmatrix} \xrightarrow[\text{base}]{RX} CF_3\text{-}N(NO)R \qquad ...(21)$$

concentrations of NO_2 and $Me_2N\cdot NH_2$ in air and in N_2 at 298K has been studied by FTIR spectroscopy.[105] The overall stoichiometry, equation (22), is independent of the initial reaction ratios and

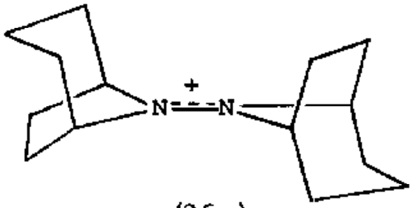
$$Me_2N\cdot NH_2 + 2NO_2 \rightarrow 2HONO + \tfrac{1}{2}Me_2N\cdot N{=}N\cdot NMe_2 \qquad \ldots(22)$$

and of the presence of air. Nitrogen(II) oxide reacts with $Me_2N.NH_2$ only in the presence of NO_2 to form N_2O, N-nitrosodimethylamine and another product.

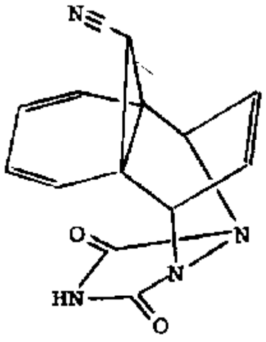
Two isomeric radical +1 cations of 8,8'-bi(8-azabicyclo[3.2.1]-octane) (26s) and (26a) have been recognised in cyclic voltammetric experiments.[106] One, (26s), provisionally assigned as the syn isomer, is 1.5±0.1 kcal. mol^{-1} more stable than the other to oxidation to the +2 cation. The +2 syn cation was shown to be less stable than the +2 anti cation. Studies of the kinetics of isomerisation of the +1 species indicated that the rotational barrier is 23.3 kcal. mol^{-1}. The first example of a simultaneous double N-inversion in the solid state has been reported.[107] The thermodynamically less stable exo isomer (27a) is transformed into the endo isomer (27b) at ca. 175°C. The structures of both were obtained by X-ray diffraction methods. The change of configuration probably occurs via a doubly planar transition state.



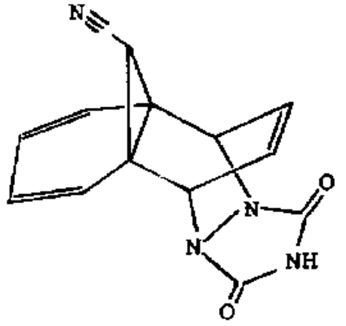
(26s)



(26a)

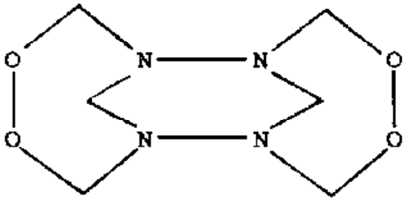


(27a)



(27b)

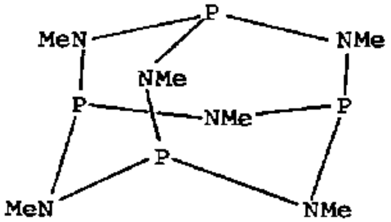
Electron diffraction maps obtained by Dunitz and Seiler,[108] from an accurate low-temperature X-ray analysis of 1,2,7,8-tetraaza-4,5,10,11-tetraoxatricyclo[6.4.1.1]tetradecane, (28), reveal deformation densities, associated with "bent" bonds, decreasing along the series C-N > C-O > N-N > O-O. Although electron density maxima correspond to tetrahedrally oriented lone pairs are recognisable at N and O atoms the densities along the N-N and, to a greater extent, the O-O bonds are negative.



(28)

5.1.8 Bonds to Phosphorus or Arsenic

^{13}C N.m.r. and valence shell photoionisation spectra have been measured for compounds of the type $X_nP_4(NMe)_6$, with X = O or S and n = 0 to 4, based on the closo-tetraphosphorushexakis(methylimide) framework, (29).[109] Cotton and coworkers proceed to



(29)

discuss electron distribution in these molecules with particular regard to the extent of P-N π-bonding. The adduct $H_3N.PF_5$ has been obtained in 8% yield from the reaction of NH_3 and PF_5 but in 41% yield from HF and $(NPF_2)_3$.[110] The structure of the adduct was examined and shows a P-N bond length of 1.842Å. Triphenylphosphine reacts with $ReCl_3(NO)_2$ to form a phosphaniminato complex $ReCl_3(NO)(NPPh_3)(OPPh_3)$, which was characterised by i.r., ^{31}P n.m.r. spectroscopy and by an X-ray structure determination. The geometry of the Ph_3PN ligand, Figure 6, is unlike that of previously characterised complexes in which it is linear.

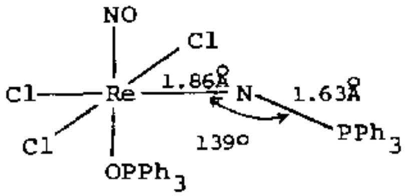
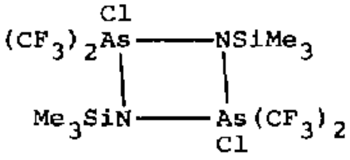


Figure 6. Dimensions of the Ph_3PN ligand in $ReCl_3(NO)(NPPh_3)(OPPh_3)$.

The reaction of $(CF_3)_2AsN(SiMe_3)_2$ with Cl_2 proceeds with the loss of Me_3SiCl and formation of $(CF_3)_2AsCl(NSiMe_3)$, containing an As=N double bond.[112] This As(V) compound dimerises, on standing or when the solvent is removed, to form (30), which Roesky and coworkers characterised by X-ray crystallography.



(30)

Subsequent decomposition of (30) occurs with the loss of Me_3SiCl and the formation of trimeric and tetrameric bis(trifluoromethyl)-arsazenes; the structure of the tetramer, approximately S_4 symmetry, has As-N distances of 1.716(7) and 1.732(9)Å.[113] The reactions of $R_3SiNSOF_2$ with transition metal hexafluoroarsenates in SO_2 yield $M(NSOF_2)_2$, M = Co,Ni or Cu, in which the AsF_6^- has been displaced.[114] Indeed the authors were able to show that anion attack occurred with the formation of fluoro(imidodifluoro-sulphato)arsenate salts, as in $Ni(SO_2)_2[AsF_4(NSOF_2)_2]_2$ in which the imidodifluorosulphonato ligand serves to bridge arsenic and nickel.

5.1.9 Bonds to Xenon

The synthesis of ^{15}N-enriched $Xe[N(SO_2F)_2]_2$ has enabled Schumacher and Schrobilgen[115] to confirm the presence of two equivalent Xe-N bonds. The dissociation of $F[XeN(SO_2F)_2]_2^+AsF_6^-$

was also investigated and the formation of $Xe[N(SO_2F)_2]_2$ in SO_2ClF was established.

5.1.10 Bonds to Halogens

The low temperature e.s.r. spectrum of (rigid) NF_3^+ has now been simulated by means of an appropriately modified computer program.[116] In addition the results of ab initio SCF molecular orbital calculations have been reported for this radical cation and also for the isoelectronic series, $\cdot CF_3$ and $\cdot BF_3^-$.[117] High resolution ^{14}N and ^{15}N n.m.r. spectra have been obtained for fluoronitrogen cations in either HF or CF_3SO_3H.[118] This study reports σ fluoro (downfield) shift effects in non-planar (tetrahedral) species as well as π fluoro (upfield) effects for linear or planar species.

The reaction of HOCl and $NHCl_2$ is general base (B)-catalysed, see reaction (23).[119] Nitrogen trichloride reacts with $NHCl_2$ to generate more HOCl and hence speeds the decomposition. The presence of NH_4^+ inhibits the decomposition of $NHCl_2$; in ammoniacal solutions NH_2Cl is formed from $NHCl_2$ by two pathways.

$$NHCl_2 + HOCl + B \rightarrow NCl_3 + OH^- + HB^+ \quad \ldots(23)$$

The reactions of cyanogen, HgF_2 and X_2, X = Cl or Br, proceed according to equation (24);[120] however, the tetrabromo compound is very unstable and the main products of bromination are $BrN{=}CFCF_2NBr_2$ and $BrN{=}CFCF{=}NBr$. The tetrachloro compound could be obtained in quantitative yield.

$$(CN)_2 + 2HgF_2 + 4X_2 \rightarrow X_2NCF_2CF_2NX_2 + 2HgX_2 \quad \ldots(24)$$

15-Difluoroaminopentadecanoic and 12-difluoroaminododecanoic acids have been prepared by the reactions of the corresponding lactams with F_2 in aqueous MeCN.[121] The NF_2 group stability in aqueous solutions was investigated as a function of pH and the advantages of using $-CH_2NF_2$ groups rather than $-CH_2F$ groups as labels in organic compounds were stressed. The thermal decomposition of NF_4XeF_7 has been studied by DSC. From the observed enthalpy of decomposition a value of -491 kJ.mol^{-1} was calculated for $\Delta H_f^o(NF_4XeF_7)$.[122] The reaction of NF_4SbF_6 with excess BrF_3 cannot be used to determine thermochemical data owing to uncontrolled side reactions. The O,N, and F core binding energies of ONF_3 have been redetermined:[123] the data are consistent with strong hyperconjugation of N-O π bonds with N-F σ bonds.

N,N-Difluoro-O-perhaloalkylhydroxylamines, R_fONF_2, have been successfully prepared by the Lewis acid (BF_3) catalysed addition of ONF_3 to olefins:[124] thus the new compounds $XC_2F_4ONF_2$, X = F,Cl or Br, resulting from the anti-Markownikoff addition, was obtained and characterised. Perfluoroalkylhypofluorites react with NHF_2 in the presence of alkali metal fluorides, MF, equation (25), to produce the corresponding ONF_2 substituted perfluoroalkanes.[125] This method has been used to prepare the known CF_3ONF_2, $(CF_3)_2CFONF_2$ and the previously unknown $FOCF_2ONF_2$ and $CF_2(ONF_2)_2$. Azidotrifluoromethane reacts readily with $XOSO_2F$, X = F, Cl, Br or OSO_2F, to form new compounds $CF_3NX(OSO_2F)$ in high yield:[126] ClF and BrF at room temperature convert the azide to CF_3NFCl and $CF_3N{=}NCF_3$ respectively. Photochemical activation of the azide leads rapidly to a mixture of $CF_3N{=}CF_2$ and $(CF_3)_2N{-}N(CF_3)_2$. Reactions of $CF_2{=}NF$ with $XOSO_2F$, X = F, Cl, Br or SO_3F, yield FSO_2OCF_2NFX at room temperature.[127] Many other oxidising agents were found to be inactive under these conditions. In the presence of CsF, i.e. the formation of $Cs^+CF_3NF^-$ in situ, reactions with Cl_2 or Br_2 produced CF_3NClF or CF_3NBrF. Similar CsF-catalysed chlorination and bromination reactions were reported to occur with $R_fCF{=}NF$ and certain nitriles.

$$R_fOF + MF.HNF_2 \xrightarrow{-142\ \text{to}\ -78^{\circ}C} R_fONF_2 + MF.HF \qquad ...(25)$$

The reactions of $PhCH_2NH_2$ and $(PhCH_2)_2NH$ with Cl_2O_7 yield the corresponding N-perchloryl compounds;[128] the acidic nature of the proton on nitrogen in $PhCH_2NHClO_3$ was exploited to generate anionic derivatives. A number of reactions of SF_5NCl_2, equations (26), (27) and (28), have been reported by Thrasher and

$$SF_5NCl_2 + 2PCl_3 \rightarrow SF_5N{=}PCl_3 + PCl_5 \qquad ...(26)$$

$$3SF_5NCl_2 + 2Se_2Cl_2 \rightarrow 3SF_5N{=}SeCl_2 + SeCl_4 \qquad ...(27)$$

$$SF_5NCl_2 + Se \rightarrow SF_5N{=}SeCl_2 \qquad ...(28)$$

Seppelt.[129] The product expected from the reaction with SCl_2 or S_2Cl_2, namely $SF_5N{=}SCl_2$, reacts further, apparently according to equation (29). The amine hydrochloride $SF_5NH_2.HCl$, formed

$$SF_5NCl_2 + Cl_2S{=}NSF_5 \rightarrow 2Cl_2 + SF_5N{=}S{=}NSF_5 \qquad \text{...(29)}$$

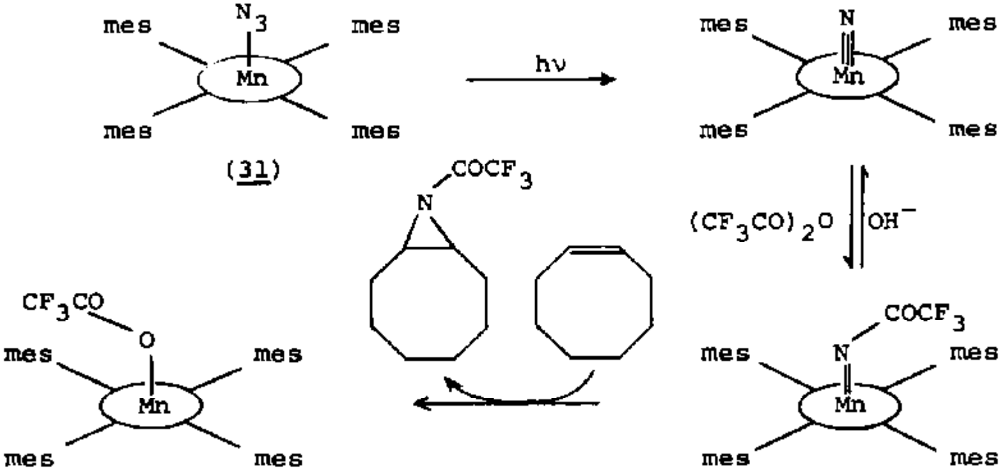
initially in the reaction of SF_5NCl_2 with HCl, decomposes gradually to $N{\equiv}SF_3$.

The reaction of 2,2'-dipyridyl with IN_3 in CH_2Cl_2 forms the 1:2 adduct, m.p. 73°C, the crystal structure of which shows linear N-I-N intramolecular interactions and a dihedral angle of the pyridyl rings of 63.4°.[130]

5.1.11 Bonds to Metallic Elements

The reaction between $Ru_3(CO)_{12}$ and N_3^- has been found to generate a series of isocyanato complexes;[131] initially $[Ru_3(NCO)(CO)_{11}]^-$, with a terminal RuNCO group, is formed and then $[Ru_3(NCO)(CO)_{10}]^-$ and, more slowly, $[Ru_4(NCO)(CO)_{13}]^-$ both with a μ-NCO ligand. Eventually a new nitrido cluster $[Ru_6N(CO)_{16}]^-$ is produced. These reactions are, to some extent, reversible, e.g. the nitrido cluster reacts with 3000 psig CO at 70°C to reform some $[Ru_4(NCO)(CO)_{13}]^-$. The cluster anion $[Rh_6N(CO)_{15}]^-$ contains a trigonal biprism of Rh atoms with an interstitial N atom, mean Rh-N distance 2.13Å.[132] The reaction of $[Ru_4H_3(CO)_{12}]^-$ with $NOBF_4$ in CH_2Cl_2 gives the nitride cluster $[Ru_4(\mu\text{-}H)_3(CO)_{11}(\mu_4\text{-}N)]$ as one of the products.[133] The corresponding product of the reaction of the Os analogue is $Os_4(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}N)$, from which $[Os_4(CO)_{12}(\mu_4\text{-}N)]^-$ is formed by treatment with $(Ph_3P)_2N^+NO_2^-$. The structure of the neutral Ru nitride and the anionic Os nitride clusters were determined and shown to have a butterfly arrangement of metal atoms capped by nitrogen.

The crystal and molecular structures of $(Bu^tO)_3W{\equiv}N$ reveal a linear polymer involving alternating short (1.74(1)Å) and long (2.66(1)Å) W-N distances, i.e. localised triple and single (weak) bonds.[134] Red nitrido-manganese(V) and -chromium(V) porphyrins have been prepared by the oxidising nitridation, using OCl^- in the presence of NH_3, of the metal(III) porphyrins.[135] Groves et al.[136] have produced a related nitridochromium(V) compound by the irradiation of an azidochromium(III) porphyrin. They[137] have also reported the first example of metal nitride activation to give aziridines in the presence of double bonds, the aza analogue of epoxidation. Scheme 4 summarises the processes thought to be responsible for the conversion of cyclo-oct-1-ene and azido(5,10-15,20-tetramesitylporphyrinato)manganese(III), (<u>31</u>), through to the Mn(V) nitride and the 9-(trifluoroacetyl)-9-azabicyclo[6.1.0]-nonane.



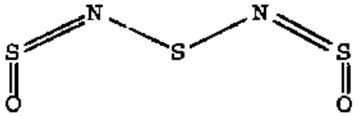
<u>Scheme 4</u>

New rhenium nitrene complexes $Re(NR)(S_2CNR'_2)_3$ and $Re(OR'')(NR)(S_2CNR'_2)_2$, R = Me,Ph or p-$MeC_6H_4$, R' = Me or Et, R" = Me or Et, have been produced.[138] In one of these a CNRe angle of 155.5(5)° is associated with a long Re-N bond 1.745(5)Å. A series of tertiary alkylimido complexes have been prepared for d^0 transition metals in groups 5 to 7;[139] the Ta=N bond in $(Me_2N)_3Ta(N\text{-}Bu^t)$ is unreactive towards CS_2 whereas the Me_2N-Ta bond undergoes an insertion reaction to form a tris-(dithiocarbamato) complex. Analogous complexes of Nb and Ta having the formula $(R'_2NCS_2)_3M{=}NR$, R' = Me or Et, have been produced from MCl_5 and $Me_2SiS_2CNR'_2$ in the presence of excess RNH_2 or R_4N_2.[140]

Niobium(V) chloride reacts with $(NSCl)_3$ to form $Cl_5NbNSCl$;[141] X-ray data have shown that the thiazyl chloride molecule is attached to Nb through N in a relatively loose manner, Nb-N distance 2.26Å. On the other hand $ReCl_5$ and $(NSCl)_3$ in $POCl_3$ form two thionitrene complexes $[(Cl_3PO)ReCl_4(NSCl)]$ and $[(Cl_3PO)ReCl_3(NSCl)_2]$.[142] The former is converted by Ph_4AsCl to

$Ph_4As[ReNCl_4]$ whereas the latter yields $Ph_4As[cis\text{-}ReCl_4(NSCl)_2]$.-$CH_2Cl_2$. Dehnicke[143] has also reported on the analogous $MoCl_5/(NSCl)_3/POCl_3$ system, in which $MoCl_4(NSCl)$ and $(Cl_3PO)MoCl_4(NSCl)$ were produced and $Ph_4As[Cl_5Mo(NSCl)]$ formed in the reaction with Ph_4AsCl.

Tetrasulphur tetranitride interacts with VCl_4 in CH_2Cl_2 to form $S_2N_2.VCl_4$ and $VCl_2(S_2N_3)$; the structure of the latter contains essentially planar VNSNSN rings with VN distances of 1.714(3) and 1.841(3)Å.[144] Bis(sulphinylnitrilo)sulphur, $S(NSO)_2$, (32), has



(32)

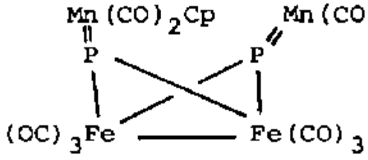
been shown to function as an O-donor and an N-donor ligand towards Ag(I) in $[Ag_4\{S(NSO)_2\}_9](AsF_6)_4.SO_2$.[145] A complex of Ag(I) with four $N_4S_3(SO_2)$ ligands has been prepared and characterised as its AsF_6 salt by Roesky et al.[146] The N-donor $S_4N_4O_2$ ligands are approximately planar except for the SO_2 units. Stable, but light-sensitive, gold(III) amido complexes have been prepared in high yield by the reactions of Me_2AuI with KNH_2 or $LiNMe_2$.[147] The crystal structure of $[Me_2AuNMe_2]_2$ shows a planar Au_2N_2 ring. The reaction of SF_5NSF_4 and HgF_2 at 20-60°C yields $Hg[N(SF_5)_2]_2$ (50% yield).[148] Snaith and coworkers[149] have described what may be the first examples of electron-deficient bridging of Li_3 triangles by the nitrogen of $N{=}CBu^t_2$ and $N{=}C(NMe_2)_2$.

5.2 PHOSPHORUS

5.2.1 Phosphorus, Polyphosphines and Phosphides

Interest in this area continues to centre on the behaviour of phosphorus atoms or groups of atoms as ligands and in the preparation of new molecules with, in particular, multiple bonds between phosphorus atoms.

Single phosphorus atoms behave as η^3 ligands in compound (33) obtained by reductive dehalogenation of $CpMn(CO)PBr_3$ with $Fe_2(CO)_9$.[150] The unconventional structure shows the largest downfield ^{31}P n.m.r. shift (977ppm) observed thus far. The



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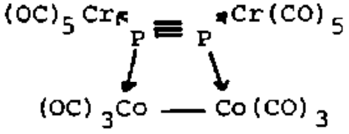
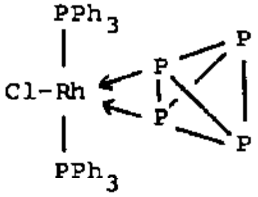
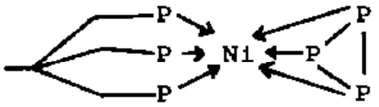


(34)

phosphorus atoms are in trigonal planar coordination and back coordination from manganese reduces the Mn-P distance to 2.10Å. A P_2 group (P-P 2.06Å) is coordinated to both cobalt and chromium atoms in the complex (34), where the unit behaves as an eight electron donor.[151] This compound and the corresponding tungsten complex result when $Co(CO)_4^-$ is treated with $[(OC)_5M]PBr$. As suggested earlier by n.m.r. spectroscopy, the P_4 unit is η^2 coordinated in (35) with Rh-P distances of 2.285 and 2.302Å.[152]





(36)

(35)

The most significant distortion of the P_4 unit is a lengthening of ca. 0.25Å of the edge involved in bonding.

The nickel atom in compound (36) is in six fold coordination by phosphorus and from an X-ray structure contains an η^3-P_3 group.[153] The P-P distances fall between 2.120 and 2.126Å with Ni-P distances of ca. 2.309 and 2.241Å to the P_3 unit and triphos ligand respectively.

The orthorhombic to rhombohedral to cubic phase transitions in polycrystalline phosphorus with increase in pressure have been confirmed and there is no further change with pressures up to 32GPa.[154]

Reactions between monosubstituted phosphines and dichlorophosphines usually yield cyclopolyphosphines but when the substituents are bulky and the reactions are carried out in the presence of the base DBU (1,5-diazabicycloundec-5-ene) double bonded dimers are obtained.[155,156] In this way, synthesis of the unsymmetrical diphosphenes, $Bu^t{}_3C_6H_2P{=}PR$, where R = $CH(SiMe_3)_2$,[155]

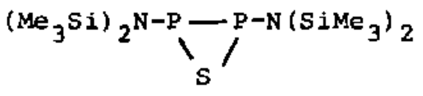
$Me_3C_6H_2$[156] and Ph,[156] has been achieved. The compounds show two ^{31}P shifts in the 450-540 ppm region with J(PP) of ca. 570Hz.

The unsymmetrical diphosphene, $Bu^t_3C_6H_2P{=}PC(SiMe_3)_3$, has been isolated and characterised together with the two symmetrical derivatives from a reaction between $(Me_3Si)_3CPCl_2$ and $Bu^t{}_3C_6H_2PCl_2$ with sodium naphthalenide in THF.[157] Dehalogenation of $(Me_3Si)_3CPCl_2$ with lithium under argon in THF at room temperature gives the symmetrical $(Me_3Si)_3CP{=}PC(SiMe_3)_3$,[158] while two nitrogen substituted diphosphenes, RR'NP=PNRR' where R = R' = $SiMe_3$ and R = $SiMe_3$ and R' = Bu^t, have been obtained from the lithium amide, LiNRR', on successive treatment with PCl_3, $LiAlH_4$ and Et_3N.[159] It was not possible to prepare the related compound, $(Me_2Bu^tSi)_2NP{=}PN(SiBu^tMe_2)_2$, in a similar way. The product was in fact $H_2PN(SiBu^tMe_2)_2$, but treatment of $(Me_2Bu^tSi)_2NPCl_2$ with either lithium or Bu^tLi gave the desired compound. A further nitrogen substituted diphosphene can be obtained when hydrogen chloride is lost from $(Me_3Si)_2NPH\text{-}PClN(SiMe_3)_2$ in the presence of $(Me_3Si)Bu^tNLi$.[160] The ruby red $(Me_3Si)_2NP{=}PN(SiMe_3)_2$ is stable for several days in solution but dimerises in a few hours in the ligand phase to the cyclo-tetraphosphine $[(Me_3Si)_2NP]_4$.

Ab initio MO calculations on the model compound HP=PH have shown that the trans form is ca. 2.7 kcal. mol^{-1} more stable than the cis form.[161] The electronic characteristics of the two diphosphenes RP=PR, where R = $Bu^t{}_3C_6H_2$ and $(Me_3Si)_3C$, have been probed by p.e. spectroscopy.[162] The lowest ionisation energies 7.27 and 8.10eV for the former and 7.55 and 9.0eV for the latter are characteristic of the P=P system.

There are two reports on the X-ray structure of $(Me_3Si)_3CP{=}PC(SiMe_3)_3$.[163,164] The P-P distance is ca. 2.0Å with P-P-C angles of ca. 108.5°. Diphosphenes readily undergo electrophilic attack but recent experiments[163] with HCl in ether or with $HBF_4.Et_2O$ have shown differences in the behaviour of alkyl and aryl substituted diphosphenes.

Although the nitrogen substituted diphosphene $(Me_3Si)_2NP{=}PN(SiMe_3)_2$ gives the cyclo-addition compounds (<u>37</u>) and (<u>38</u>) on reaction with sulphur and cyclopentadiene respectively,[160] the 2,4,6-tri-butyl^t analogue reacts with sulphur in the presence of trimethylamine in the dark to give the diphosphene sulphide (<u>39</u>, X = S).[165] This has been confirmed by X-ray crystallography which shows a slight increase in the P-P bond distance (2.054Å



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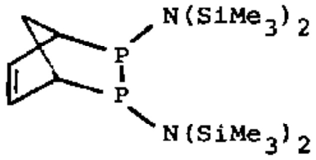

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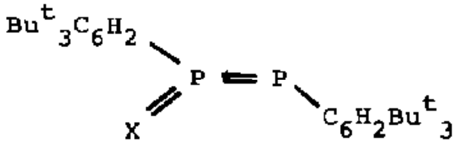
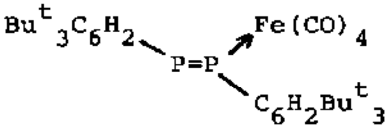


(39)

compared with 2.034Å in the substituted diphosphene). The P-S distance is 1.93Å with P-P-S, and P-P-C and C-P-S angles of 129.0, 106.1 and 124.9° respectively. The related oxide (39, X = O) is an intermediate in the oxidation of the diphosphene with m-chloroperbenzoic acid but the final products are the primary phosphine $Bu^t{}_3C_6H_2PH_2$ and $Bu^t{}_3C_6H_2P(O)(OH)(O_2CC_6H_4Cl)$.[166] The compound does however result as a yellow crystalline product melting at 174-6°C when the phosphonic dichloride $Bu^t{}_3C_6H_2POCl_2$ is dechlorinated with magnesium under ultrasonic irradiation.

Only one $Fe(CO)_4$ group is attached to phosphorus when $Fe_2(CO)_9$ and $(Bu^t{}_3C_6H_2)_2P_2$ react to give (40) in which the P-P distance



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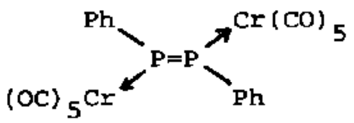

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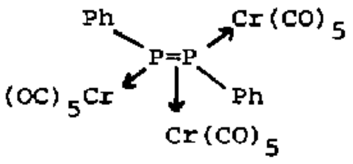
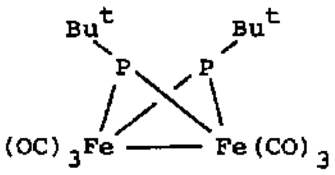


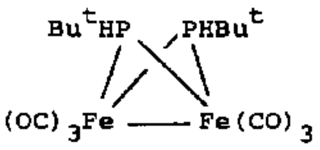
(42)

(2.050Å) is little different from that in other diphosphene compounds.[167] Attachment of only one $Fe(CO)_4$ group is probably a function of steric effects as only one $Ni(CO)_3$ group is similarly complexed even in the presence of a large excess of the carbonyl. Further there is no complexation with the very bulky diphosphene $(Me_3Si)_3CP{=}PC(SiMe_3)_3$. With the unsymmetrical $Bu^t{}_3C_6H_2P{=}PCH(SiMe_3)_2$, reaction with $Fe_2(CO)_9$ yields a complex where the $Fe(CO)_4$ group is attached to the alkyl substituted phosphorus.

A complex (<u>41</u>) in which both lone pairs of a diphosphene are coordinated to transition metals has been obtained by heating the trisubstituted compound (<u>42</u>).[166] The unstable t-butyl substituted diphosphene, $Bu^tP{=}PBu^t$, has been stabilised in the iron carbonyl complex (<u>43</u>) obtained by deprotonation of the doubly bridged t-butyl phosphine complex (<u>44</u>).[169]



(<u>43</u>)

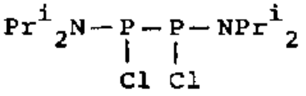


(<u>44</u>)

The P-P bond length (2.059Å) implies a doubly bonded system with the ligand behaving as a six electron donor, i.e. from the phosphorus lone pairs and the π-bond.

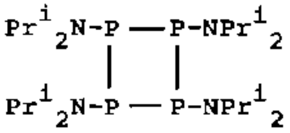
The first examples of compounds containing P=As and P=Sb bonds have been prepared from reactions between $Bu^t{}_3C_6H_2PCl_2$ and $(Me_3Si)_2CHMCl_2$, where M = As or Sb, in the presence of DBU.[170] Both compounds are orange solids but the antimony derivative is unstable in solution, decomposing to the diphosphene $(Bu^t{}_3C_6H_2)_2P_2$. A structure determination for the arsenic compound however shows isolated molecules with a P-As distance (2.124Å) substantially shorter than the sum of the covalent radii (2.35Å). Two isomeric products result on treatment with $Fe_2(CO)_9$ where an $Fe(CO)_4$ group is probably attached to either the phosphorus or arsenic centre.[167]

Dehalogenation of $RPBr_2$, where R = Ph or a 4-substituted phenyl, with magnesium gives RPBr.PRBr; the bromine atoms in the phenyl derivative have been substituted with butyl lithium.[171] Both a diphosphine (<u>45</u>) and a cyclotetraphosphine (<u>46</u>) can be obtained by a similar dehalogenation of $(Pr^i{}_2N)_2PCl$, constituting the first examples of P-P bonded species which do not contain P-C bonds.[172] The cyclotetraphosphine reacts with sulphur to give a tetrasulphide, and it appears that stability with these compound types requires a large dialkylamino group.



$Pr^i_2N-P(Cl)-P(Cl)-NPr^i_2$

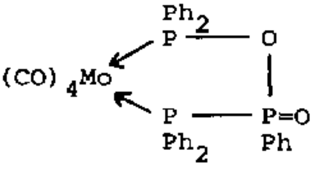
(45)



(46)

Scrambling reactions between $(MeEtP)_2$ and $(R^1R^2P)_2$, for $R^1 = R^2 = Pr^i$, $R^1R^2 = Bu^tPr^i$, Bu^tEt, Bu^tMe and Pr^iEt, yield the unsymmetrical diphosphines $R^1R^2PPMeEt$ which have been identified in situ by ^{31}P n.m.r. spectroscopy.[173] The compounds exist in diastereomeric forms and provide examples of the variation in n.m.r. parameters with chirality. The variation in $^1J(P-P)$ in a series of substituted P-P bonded diphosphate species with the electronegativity of the substituents has been discussed.[174]

Sulphur dioxide behaves as an oxidising agent when Ph_4P_2 and the zinc salt, $Zn(SO_2)_3(AsF_6)_2$, react in $C_2F_3Cl_3$ solution giving the diphosphine dioxide complex, $Zn(O_2P_2Ph_4)(AsF_6)_2$.[175] When the P(III)-P(V) ligand, $P[P(O)(OEt)_2]_3$, was used instead of Ph_4P_2 the product was $Zn\{P[P(O)(OEt)_2]_3\}_2(AsF_6)_2$ in which an X-ray structure shows coordination of zinc by the three phosphoryl oxygens from the two ligands. A crystal structure has also been obtained for (47) in which a tautomer of the unknown bis(phosphoryl)phosphine $PhP[P(O)Ph_2]_2$ is coordinated to molybdenum.[176]

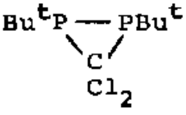


(47)

The compound is obtained by reaction of phenyl dichlorophosphine and the hydrogen bridged chelate $Et_3NH^+[cis-Mo(CO)_4(PPh_2O)_2]H^-$. Complex cationic species with formulae such as $CpNi(Ph_2PAsPh_2)Cl$ and $[CpNi(Ph_2PAsPh_2)_2]BF_4$ result when $[CpNi(C_5H_6)]BF_4$ reacts with unsymmetrical ligands such as Ph_2PMPh_2, where M = As or Sb.[177]

Two molecules of pyrrolidine react with $P[P(O)(OPr^i)_2]_3$ to give a salt of the anion $P[P(O)(OPr^i)_2]_2^-$; the P-P distances are short (2.120 and 2.124Å) implying some degree of (p-d) π bonding.[178]

Dehalogenation of $RPCl_2$ where R = Pr^i or Bu^s with magnesium gives the cyclotriphosphines, $(RP)_3$ together with the corresponding cyclotetraphosphines and $(Pr^iP)_5$ as by-products.[179] The pure triphosphines were investigated by ^{31}P n.m.r. spectroscopy which allowed identification of the expected four diastereoisomers for $(Bu^sP)_3$. Treatment of $K_2(Bu^tPPBu^t)$ with carbon tetrachloride in pentane at low temperatures gives the two carbon containing cyclic compounds (48) and (49) in addition to $(Bu^tP)_3$ and 4.[180] Compound (49) is a mixture of two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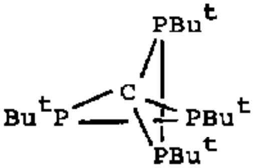
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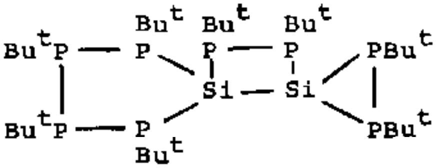
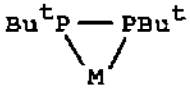

(50)

isomers differing in the arrangement of the t-butyl groups. The silicon analogue of (49) is already known and has recently been shown to dimerise on heating to the unusual dispiro derivative (50); an X-ray structure is available.[181]

A three membered heterocycle (51, M = $GeEt_2$ or $GePh_2$) results from the cyclocondensation of $K_2(Bu^tP)_2$ and R_2GeCl_2, while the reaction with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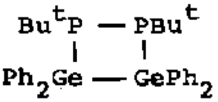
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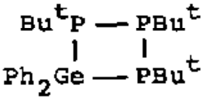
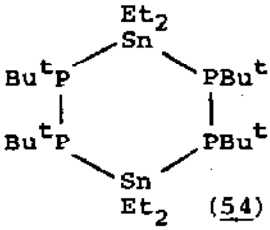

(53)

Ph_2GeCl_2 also yields two four membered compounds identified as compounds (52) and (53).[182,183] A structure determination for (53) shows a non-planar P_2Ge_2 ring with P-P, P-Ge and Ge-Ge distances of 2.216, 2.340 and 2.421Å respectively.[184] A tin analogue of (51) with M = $SnBu^t_2$ has been obtained by treating $K_2(PBu^t)_2$ with $Bu^t_2SnCl_2$ but this reaction also gives $(Bu^tP)_2(SnBu^t_2)_2$ and the six membered ring compound $(Bu^tP)_4(SnBu^t_2)_2$ as by-products.[185] The corresponding reaction with Et_2SnCl_2 gives as major product the six membered Sn_2P_4 compound (54) together with smaller amounts of $(Bu^tP)_3SnEt_2$ and $(Bu^tP)_3(SnEt_2)_2$. The antimony heterocycle (51, M = $SbBu^t$) can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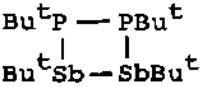
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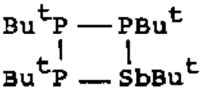
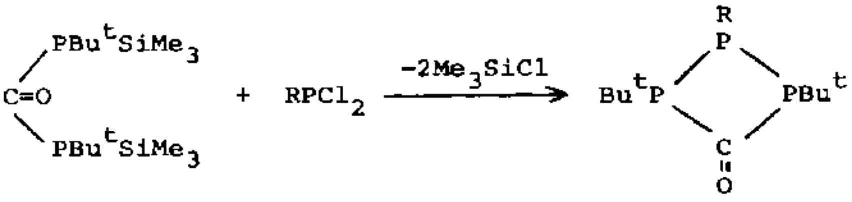

(56)

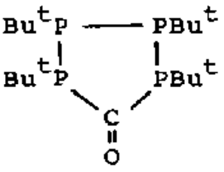
also be obtained but because of its high reactivity it could not be obtained pure.[186] Two diastereomeric forms are present, the more stable being that with trans t-butyl groups at the phosphorus atoms. The preparation also gives smaller amounts of the four membered ring compounds (<u>55</u>) and (<u>56</u>).

The phospha-urea derivative (<u>57</u>) on treatment with a dichlorophosphine as shown in equation (31) gives the triphosphetanone (<u>58</u>), which for R = Bu^t loses CO in sunlight to give $(Bu^tP)_3$.[187]

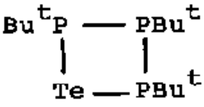


...(31)

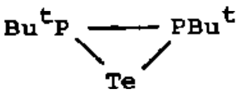
(<u>57</u>) (R = Me,Bu^t or Ph) (<u>58</u>)



(<u>59</u>)



(<u>60</u>)



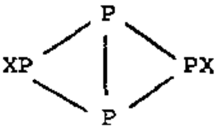
(<u>61</u>)

A related five-membered analogue (<u>59</u>) is the final product of the reaction of phosgene with $Bu^t(Me_3Si)_2P$ in which the Me_3SiCl is eliminated.[188] Again on photolysis, carbon monoxide is lost to give the cyclotetraphosphine $(Bu^tP)_4$. An unusual red liquid telluratriphosphine (<u>60</u>) together with $(Me_3Si)_2Te$ is obtained when the disilylphosphine, $Bu^t(Me_3Si)_2P$, reacts with elemental tellurium.[189] At higher temperatures the three membered heterocycle (<u>61</u>) is the reaction product together with cyclotri- and tetraphosphines.

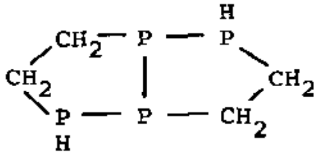
MNDO calculations on the bicyclobutane derivative (<u>62</u>), which is often postulated as an intermediate in the reactions of white phosphorus, show, inter alia, that the central bond possesses olefinic character.[190]

Trimethylchlorosilane on reaction with $K_2(Bu^tP)_4$ yields the disilyltetraphosphine, $Me_3Si(Bu^tP)_4SiMe_3$,[191] which in turn can be converted into the parent tetraphosphine, $H(Bu^tP)_4H$, on treatment with alcohols.[192] This compound, which exists in three diastereomeric forms in solution, can also be obtained by reacting t-butyl chloride with $K_2(Bu^tP)_4$. An isotetraphosphine, $P(PHBu^t)_3$, has been isolated from the $LiAlH_4$ reduction of $P(PBrBu^t)_3$.[193]

Reactions of either the bicyclic phosphine (63) or its lithium salt with dihalides (ECl_2) such as $MePCl_2$, $EtPCl_2$ or Me_2SiCl_2 yield the tricyclic derivatives (64).[194] Small amounts only of the expected silyl derivative, $[(Me_3Si)_2P]_2PPPh_2$, are obtained when $[(Me_3Si)_2P]_2PLi$ and Ph_2PCl react in pentane at -40°C.[195] The major products are, in fact, $(Me_3Si)_2PPPh_2$ and Ph_4P_2, which arise via metallation of the Ph_2PCl by the lithium derivative, together with $(Me_3Si)_3P$ and Ph_2PSiMe_3. When either PCl_3 or Bu^tPCl_2 is substituted for Ph_2PCl, the reaction gives the tetraphosphine (65, R = H or Bu^t) with smaller amounts of $[(Me_3Si)_2P]_2PSiMe_3$.



(62)



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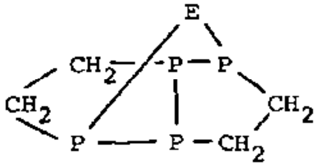

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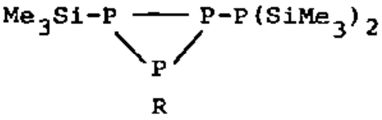


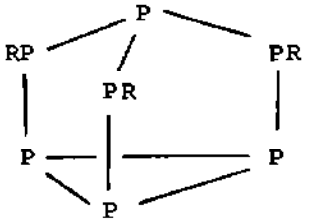
(65)

White phosphorus and t-butyl lithium react in the presence of Me_3SiCl to give the tetraphosphine, $P_4Bu^t{}_3(SiMe_3)$, which with BuLi is converted to the lithium salt $LiP_4Bu^t{}_3$.[196] Similarly, trans-$P_4Bu^t{}_2(SiMe_2)_2$ with BuLi gives $LiP_4Bu^t{}_2(SiMe_3)$ which is unstable and decomposes in a few hours to a mixture of silylphosphines, their lithium salts, and the cyclophosphine lithium salts. A range of derivatives based on the P_7X_3 cage system have been obtained directly from white phosphorus - lithium alkyl reactions.[197] With MeLi in either THF or DME, the products are Li_3P_7, Li_2P_7Me and LiP_7Me_2, from which can be obtained $P_7(SiMe_3)_3$, $P_7Me(SiMe_2)_2$ and P_7Me_3 by treatment with either Me_3SiCl or methyl bromide. The reaction with Bu^tLi gives in addition to the analogues of the methyl derivatives mentioned above, the two cyclophosphine salts $Li(Bu^t{}_3P_4)$ and $Li(Bu^t{}_2P_3)$. Evidence has also been obtained for compounds in the two series, $P_8Bu^t{}_n(SiMe_3)_{8-n}$ and $P_5Bu^t{}_n(SiMe_3)_{5-n}$. Two lithium silyl phosphines can be obtained by the reactions in equations (32) and (33),[198] and on treatment with a range of monohalides (RCl), such

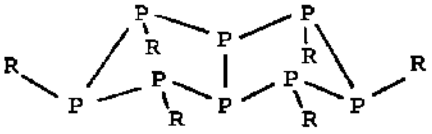
$$Li_3P_7 + 2P_7(SiMe_3)_3 \rightarrow 3LiP_7(SiMe_3)_2 \qquad ...(32)$$

$$2Li_3P_7 + P_7(SiMe_3)_3 \rightarrow 3Li_2P_7(SiMe_3) \qquad ...(33)$$

as Ph_3SiCl, H_3SiI, Me_3GeCl, Me_3SnBr, Pr^iBr and $CpFe(CO)_2Br$, Li_3P_7 and Na_3P_7 can be converted to the P_7R_3 derivatives (66).[199] Structures have been determined for the isotypic compounds (66,



(66)

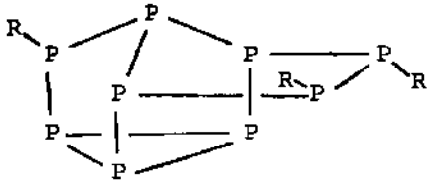


(67)

R = EMe_3) where E = Si,Ge,Sn and Pb, showing that the bond lengths in the cage (2.180-2.222Å) are little affected by changes in substituent. The ^{31}P n.m.r. spectrum of (66, R = Me) has been analysed completely and the observed spectrum can be simulated by the superposition of spectra for two forms where the methyl substituents are symmetrically and unsymmetrically orientated.[200]

Pure cyclooctaphosphines (67, R = Et or Pr^i) have been prepared by the magnesium dehalogenation of a 3:1 mixture of the appropriately substituted dichlorophosphine and PCl_3.[201] The pentalene structure, which is based on ^{31}P n.m.r. data, contains mutually trans oriented substituents and is the same as that found for P_8H_6; these however differ from the $P_8Bu^t{}_6$ structure already known. A methyl analogue can also be prepared but a pure sample has not yet been obtained.

A substituted nonaphosphine, $P_9Bu^t{}_3$, has been obtained by the reaction of magnesium on a Bu^tPCl_2/PCl_3 mixture and a related i-propyl derivative by treating $(Pr^iP)_4$ with PCl_3; the deltacyclane structure (68) follows from n.m.r. spectroscopy.[202]



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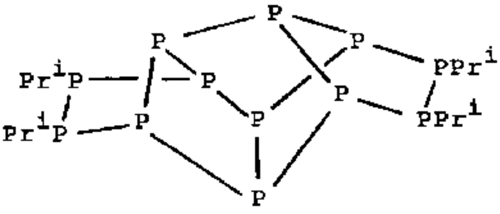

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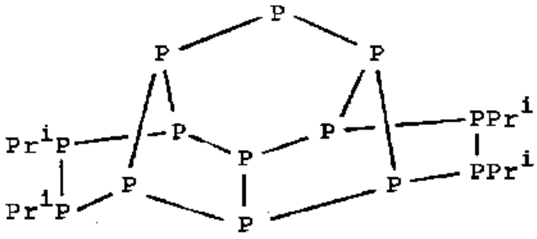


(70)

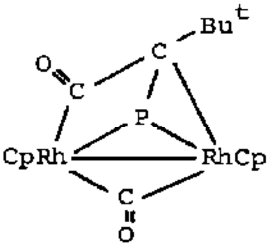
Two further new polycyclic derivatives $P_{12}Pr^{i}_{4}$ and $P_{13}Pr^{i}_{5}$ have been isolated as thermolysis products of a polyphosphine mixture.[203] It is worth noting that the frameworks in the suggested structures, (69) and (70), are structural units of Hittorf's phosphorus. Finally it has been shown that good yields of solvated Li_2P_{16} can be obtained when white phosphorus reacts with $LiPH_2$ in a ratio of 1.9:1 in THF solution.[204]

The chemical transport of FeP_2 and FeP_4 with iodine has been investigated[205] and crystalline samples of MoP_2 and α- and β-WP_2 prepared and their structure determined.[206] The new compound, $Ba_6Sn_2P_6$, has been prepared from the elements by a high temperature reaction and shown to contain the $Sn_2P_6^{12-}$ anion (Sn-P 2.487-2.544Å).[207] The ternary phosphides $MoFe_2P_{12}$ and WFe_2P_{12} are isotypes and a full structure for the molybdenum compound shows that all phosphorus atoms are in four fold coordination either to one metal and three phosphorus atoms or two metal and two phosphorus atoms.[208] All near neighbour contacts can be rationalised on the basis of two electron bonds in agreement with the observed diamagnetism. The compound $TiCu_2P$, prepared from $CuP_{0.15}$ and titanium in a sealed tube at 800°C, belongs to the Cu_2Sb family with a structure that can be derived from the Mn_3As structure by a glide.[209]

5.2.2 Bonds to Carbon or Silicon

As in previous reviews this section is subdivided by oxidation state and within each of the sections multiple bonds between phosphorus and carbon are considered first.

The +3 Oxidation State. The HeI photoelectron spectra for $Bu^{t}C\equiv P$ and $PhC\equiv P$ have been assigned using ab initio SCF-MO calculations. The first ionisation energy at 9.61 and 8.68 eV respectively corresponding to electron loss from an orbital with basically C-P π-bonding character.[210] There are close similarities between alkyne chemistry and that of the phospha-alkyne $Bu^{t}C\equiv P$; the latter adds to the metal-metal bonds in $[CpRh(CO)]_2$ and $[CpMo(CO)_2]_2$ to give compounds (71) and (72) respectively.[211] The structure of (72) has been determined by X-ray methods.



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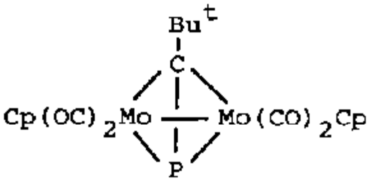
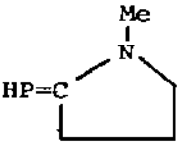


(72)

Acyl-, alkylidene- and alkylidyne-phosphine chemistry has been reviewed[212] and ab initio calculations using a double zeta set carried out on the model compound $HP{=}CH_2$.[213] A high yield of the ylid $CF_3P{=}CF_2$, which is stable at -78°C and in the gas phase at 100°C, can be obtained by treating $(CF_3)_2PH$ with $ZnMe_2$ in the presence of trimethylamine as a catalyst.[214] On polymerisation both the cyclic dimer and trimer, $(CF_3PCF_2)_2$ and $_3$, are obtained. P-hydrogen (73)[215] and -nitrogen (74)[216] species have been stabilised, the latter for R = $N(SiMe_3)_2$ or $N(SiMe_3)Bu^t$ from a



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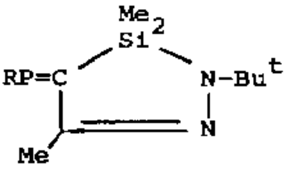

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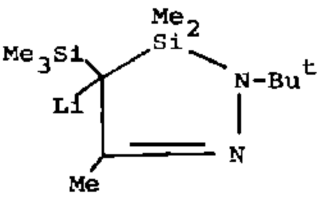
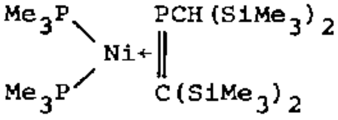


(75)

reaction between the lithium derivative (75) and RPF_2.

A major feature of interest in these compounds is their behaviour as ligands and a timely review (251 references) emphasises current interest in this general area.[217] A stabilised phospha-alkene (76) showing η^2 coordination to nickel has been produced in the reaction between the sodium derivative, $Na[(Me_3Si)_2CH]_2P$, and $(Me_3P)_2NiCl_2$.[218] The P-C bond length (1.773Å) is midway between that for single and double bonded systems while the angle at carbon implies hybridisation between sp^2 and sp^3, thus suggesting there is back coordination from nickel 3d orbitals into the π^* orbital of the P-C system. Similar η^2 bonding has been confirmed by X-ray diffraction on the complex (77) obtained from the phospha-alkene and (bipy)Ni(cod),[219] but η^1 structures with Ni-P bonds were assigned to the unstable products, $LNi(CO)_3$ and $L_2Ni(CO)_2$ obtained from (mesityl)P=CPh_2 (L) and $Ni(CO)_4$. This mesityl derivative coordinates differently in Pt(0) compounds depending on the other groups present, with for example, η^2 character in the complex $MeC(CH_2PPh_2)_3PtL$ and donation via the phosphorus atoms in PtL_3 and $PtL_2(P{\equiv}CBu^t)$.[220]



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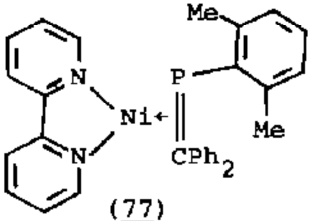
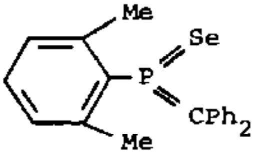
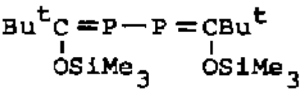


(77)

Although the oxygen and sulphur oxidation products of the phospha-alkene, $2,6\text{-}Me_2C_6H_3P{=}CPh_2$, are too reactive to be isolated, a three coordinate phosphorus(V) selenide (78) can be isolated.[321] This compound adds ethanol across the P=C double bond.



(78)

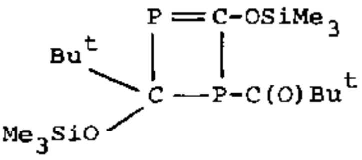


$$Bu^tC(OSiMe_3){=}P{-}P{=}CBu^t(OSiMe_3)$$

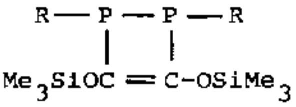
(79)

A diphosphorus analogue of butadiene (79) can be prepared either by treating the silyl phospha-alkene $Me_3SiP{=}CBu^t(OSiMe_3)$

with hexachloroethane or by reacting the diphosphine $(Me_3Si)_4P_2$ with Bu^tCOCl.[222] From X-ray crystallography, the P-P distance is 2.171 and the P-C distances are 1.684 and 1.692Å; the P-P-C bond angles are 100.3 and 100.7°. Cyclic species (80) and (81) based on P_2C_2 rings have also been isolated. The former from a reaction between phosgene and $(Me_3Si)_2PC(O)Bu^t$ and the latter by treating



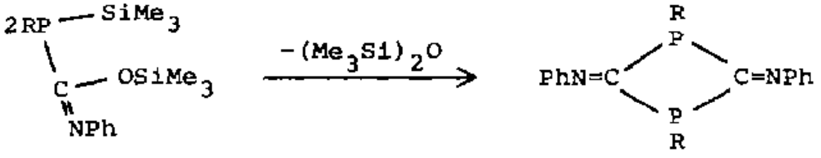
(80)



(81)

silylphosphines $RP(SiMe_3)_2$ where R = Ph or Bu^t with oxalyl chloride. Phosgene has again been used with $(mesityl)P(SiMe_3)_2$ to synthesise the first room temperature stable phosphaketene, RP=C=O.[223] The monomeric formulation is supported by a high field n.m.r. shift (-207.4 ppm) and by an i.r. band assigned to $\nu_{as}PCO$ at 1953 cm^{-1}. The intermediate $(mesityl)P(SiMe_3)C(O)Cl$ can be detected at low temperatures by ^{31}P n.m.r. spectroscopy.

A general method for preparing phosphorus analogues of carbodiimides, i.e. species containing the P=C=N grouping, involves initial formation of the cyclic dimer (82) by loss of $(Me_3Si)_2O$ in the presence of a catalytic amount of sodium hydroxide [see equation (34)].[224] Flash vacuum photolysis then



...(34)

R = Et, Bu^t, Ph or $PhCH_2$

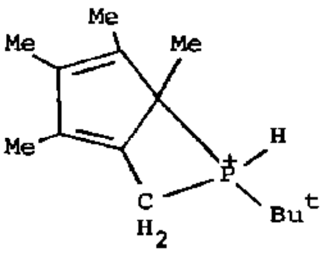
(82)

gives the monomer PhN=C=PR, which is stable at low temperatures and shows an i.r. band at ca. 1840 cm^{-1}.

A series of potentially tridentate ligands, $PhP(XC_5H_4N)_2$, where X = CH_2, O or NH, has been synthesised at low temperatures by reacting $PhPCl_2$ with, respectively, 2-picolyl lithium, 2-hydroxypyridine and 2-aminopyridine and complexes with Cr, Mo and W carbonyls have been described.[225] An X-ray structure on $(OC)_3W[PhP(NHC_5H_4N)_2]$ shows coordination via phosphorus and two pyridine nitrogen atoms.

Acyl phosphines, RC(O)PPh$_2$ for R = ClC$_6$H$_4$, Cl$_2$C$_6$H$_3$, C$_9$H$_{19}$[226] and a series of olefinic groups[227] including CH$_2$:CH, MeCH:CH, CH$_2$:CMe, Me$_2$C:CH, have been prepared by treating Ph$_2$PSiMe$_3$ with an acyl chloride. The products are air sensitive and readily hydrolysed and with an olefinic substituent only the propenoyl derivative can be isolated. Stable manganese complexes can be obtained with some of these derivatives and with Ph$_2$POMe they can be converted via an Arbusov reaction to the substituted phosphine oxide, RC(O)P(O)Ph$_2$.

Phosphenium cations have been stabilised in the species, FePX$^+$ AlCl$_4$$^-$ where X = Fc, Cl or NMe$_2$, resulting from the treatment of the ferrocenyl (Fc) substituted phosphorus(III) chlorides Fc$_2$PCl, FcPCl$_2$ and Fc(Me$_2$N)PCl with the stoichiometric amount of AlCl$_3$ in dichloromethane.[228] Addition of further AlCl$_3$ to FcPCl$_2$ does not give the FcP^{2+} cation nor is the Fc$_2$P$^{\cdot}$ radical produced when Fc$_2$PCl is treated with an active metal. In the latter reaction, the product is the new diphosphine Fc$_2$PPFc$_2$. A further new, two coordinate, cation has been obtained by reacting the pentamethylcyclopentadiene substituted phosphorus chloride, (Me$_5$C$_5$)Bu^{t}PCl, with AlCl$_3$, and confirmed by both ^{31}P and ^{27}Al n.m.r. spectroscopy.[229] The ^{31}P signal however changes on standing indicating formation of the new cation (83) resulting from insertion of P$^+$ into the C-H bond of an ortho methyl group.



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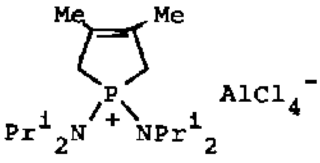
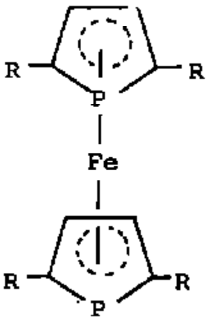


(84)

1,3-Dienes, such as 2,3-dimethylbutadiene, react with the phosphenium compound, (Pr$^i_2$N)$_2$P$^+$AlCl$_4$$^-$, to give five membered ring systems such as (84).[230] An X-ray structure shows that there is little change in the geometry of the two coordinate cation on reaction.

The bis(phosphino)ethane, Bu^{t}HPCH$_2$CH$_2$PHBu^t, can be synthesised from Cl$_2$PCH$_2$CH$_2$PCl$_2$ and Bu^{t}MgCl followed by reduction of the intermediate dichloride with $LiAlH_4$.[231] Hydrolysis of this intermediate gives the bis(phosphine oxide), $Bu^tH(O)PCH_2CH_2P(O)HBu^t$, and the phosphine itself can be oxidised to give $Bu^tHP(X)CH_2CH_2P(X)HBu^t$ for X = O, S or Se. The diphosphine, $Ph_2PCH_2CH_2PHBu^t$, can be oxidised similarly.

Molecular orbital calculations have been reported for the phospha- and diphospha-ferrocenes[232] and three diphospha-derivatives (85, R = H or Ph) and (86) have been synthesised.[233]



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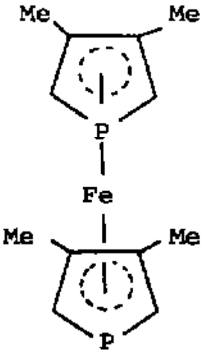
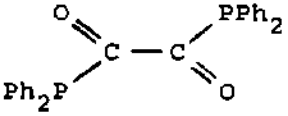
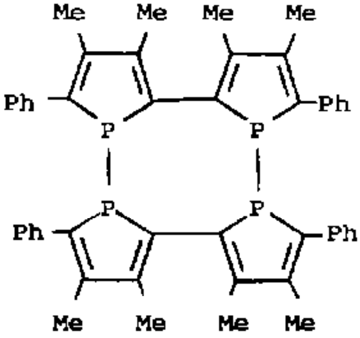


(86)

Compounds of the type, $4\text{-}X\text{-}C_6H_4SiMe(EMe_2)(CH_2CH_2E'Me_2)$ where E, E' = N, P or As and X = F or Cl[234] and $2\text{-}EMe_2C_6H_4SiMe_2E'Me_2$, the latter behaving as chelating ligand,[235] have been synthesised. The diphosphino-methanes, $R_2PCH_2PR_2$ for R = PhO or Bu^t, have been isolated and investigated[236] and new mono- and poly-dentate phosphines can be synthesised by reactions between Me_2PCH_2Li and $Me_{4-n}ECl_n$ where X = Si or Sn.[237] Oxalyl bis(diphenylphosphine) (87) reacts with molecular oxygen eliminating both CO and CO_2 to give $[Ph_2P(O)]_2O$, $Ph_4P_2O_2$ and Ph_4P_2.[238]

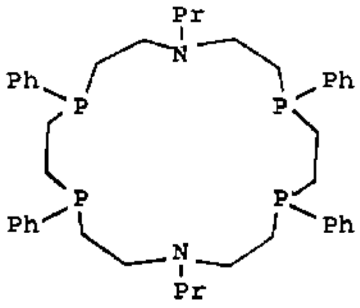


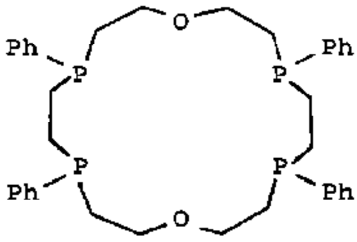
(87)



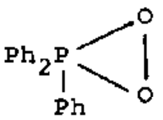
(88)

A new P_4C_4 ring compound (88) has been obtained in a one step reaction by the tetramerisation of 3,4-dimethyl-1-phenyl phosphole.[239] An X-ray structure points to short P-P (2.191) and C-C (1.47Å) bonds implying some conjugation between adjacent phosphole rings. A new macrocyclic ligand (89) containing four phosphorus and two nitrogen donor groups has been synthesised as a mixture of isomers from 2,2'-dichlorodiethyl propylamine and the dipotassium salt of $(PhPCH_2CH_2PPh)^{2-}$.[240] Pure samples of four of the five possible stereoisomers have been isolated together with a nickel compound, which has been investigated by single crystal methods. The structure has also been determined for a nickel borohydride complex of the related oxygen macrocycle (90) in which all four phenyl groups are in cis positions.[241]


(89)


(90)

Diethylazodicarboxylate and hydrogen peroxide react successively with triphenylphosphine to give, unexpectedly, phenyl diphenylphosphinate $Ph_2P(O)OPh$.[242] The most likely mechanism is via a phenyl migration from phosphorus to oxygen in the unknown dioxide intermediate for which either a monomeric (91) or dimeric (92) structure is possible.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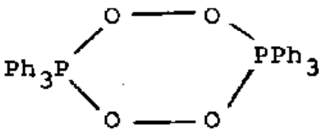

(92)

^{13}C n.m.r. shifts have been reported for compounds in the series R_3M, where M = P, As or Sb and R = Me, Et, Bu or Ph; R_3Bi, where R = Me or Ph; and Ph_2MX and $PhMX_2$, where M = P or As and X = Cl, Me, Et or Bu.[243] Data for the nickel complexes $LNi(CO)_3$ are also available.

Mixed methyl and trifluoromethyl substituted main group compounds, including P, As, Sn, Pb and Hg, have been synthesised by the interaction of the permethylated main group compound with CF_3 radicals generated by a radio frequency discharge on C_2F_6.[244] HeI p.e.s. for such mixed compounds in the phosphorus, arsenic and antimony series, $Me_nM(CF_3)_{3-n}$ for n = 0-3,[245] and for the mixed methyl phenyl phosphines, PMe_nPh_{3-n},[246] have been measured.

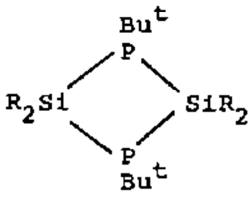
The trifluoromethyl derivatives, $M(CF_3)_3$ where M = P, As or Sb, react with O-nitrosobis(trifluoromethyl)hydroxylamine to give $(CF_3)_2NOM(O)(CF_3)_2$ for M = P or As while with the antimony compound the product is $[(CF_3)_2NO]_2SbCF_3$.[247]

Silicon Derivatives. The lithium derivative of t-butylphosphine reacts with fluorosilanes as shown in equation (35) to give the silyl phosphines (93) and (94).[248,249] Treatment with butyl

$$R_2SiF_2 + LiPHBu^t \rightarrow \underset{(93)}{R_2SiFPHBu^t} + \underset{(94)}{R_2Si(PHBu^t)_2} \qquad ...(35)$$

R = Bu^t or $NMeSiMe_3$

lithium converts compound (93) to the cyclic species (95) which contains a planar four membered ring and Si-P distances in the range 2.241-2.280Å. Compound (94) similarly gives the four-membered derivative (96) on reaction with BuLi and phenyl dichlorophosphine. The bicyclo[2.2.2]octane derivative (97) is produced when a mixture of sodium/potassium phosphide reacts with 1,2-dichlorotetramethyl disilane; the compound has been completely characterised spectroscopically.[250]



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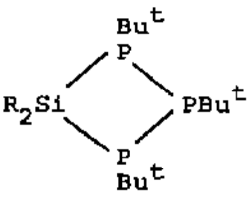

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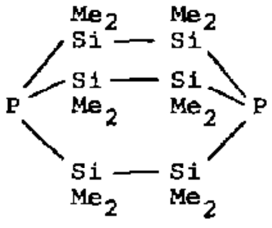
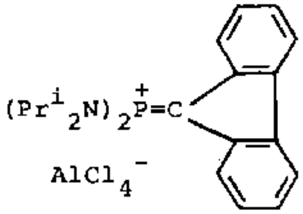


(97)

The +5 Oxidation State. P-chloromethylenephosphoranes such as $(R_2N)_2PCl{=}CR^1R^2$ lose chlorine on treatment with $AlCl_3$ in dichloromethane to give phosphonium species identified by ^{31}P n.m.r. spectroscopy.[251] One such compound (98) has been isolated from a solution in liquid sulphur dioxide. Depending on the inductive and mesomeric effects of the substituents, P-chloroalkylidene phosphoranes can be converted to α-chloroalkylphosphines by a 1,2-chlorine shift (see equation 36).[252]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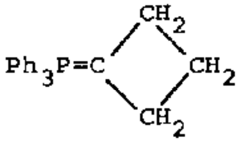
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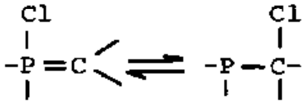
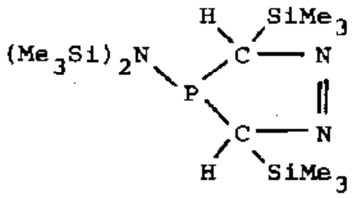


$$-\overset{\overset{\textstyle Cl}{|}}{\underset{|}{P}}=C\!< \;\rightleftharpoons\; -\underset{|}{P}-\overset{\overset{\textstyle Cl}{|}}{\underset{|}{C}}- \qquad \ldots(36)$$

M.O. calculations on the cyclopropylide model compound $H_3P{=}C(CH_2)_2$ point to a pyramidal carbanion centre in the ground state,[253] and the structure of the related compound (99), obtained by reacting the phosphonium bromide, $[Ph_3P(CH_2)_4Br]Br$, with sodium amide in liquid ammonia, has been determined.[254]

The sterically crowded $Ph_2P[C(SiMe_3)_3]$ has been synthesised from $Li[C(SiMe_3)_3]$ and Ph_2PCl, and can be quaternised by both HI and MeI.[255] The latter compound on heating loses Me_3SiI to give the ylid $Ph_2PMe{=}C(SiMe_3)_2$.

On photolysis, the diazaphosphole (100) loses nitrogen to give the pure bismethylenephosphorane (101), which on warming partially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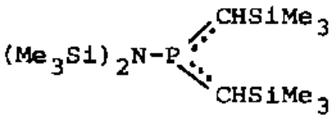
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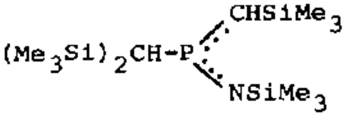
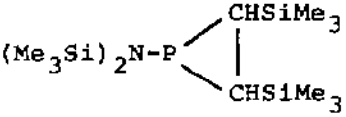


(<u>102</u>)



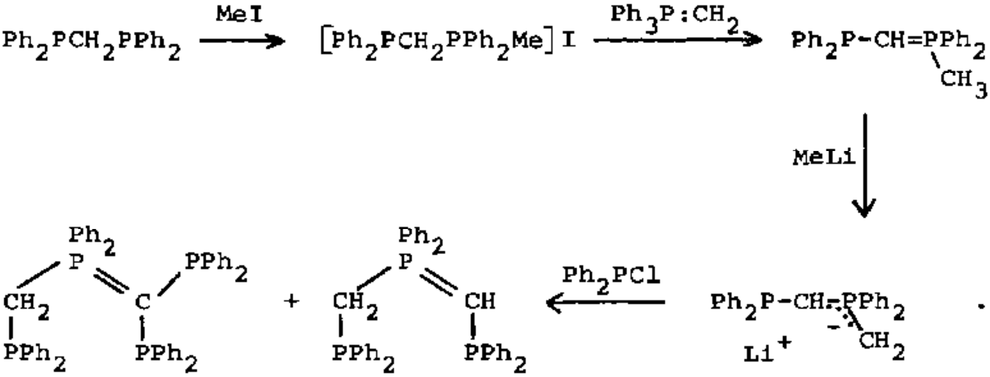
(<u>103</u>)

isomerises to the iminomethylene phosphorane (<u>102</u>).[256] If compound (<u>101</u>) is heated to 190°C, on the other hand, there is gradual formation of the phosphorinane (<u>103</u>). The conversion of (<u>101</u>) to (<u>103</u>) corresponds to a conrotatory ring closure and the reaction sequence is strictly controlled by orbital symmetry.

The structure of $\mathrm{Ph_3P{=}C(SPh)SePh}$ obtained by the reaction sequence in equation (37) shows a planar arrangement about the

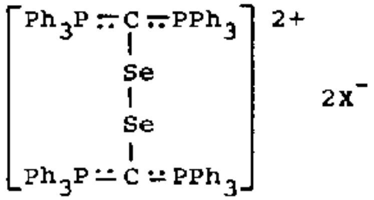
$$\mathrm{Ph_3P} \xrightarrow[\mathrm{-HCl}]{\mathrm{PhSCH_2Cl}} \mathrm{Ph_3P{=}CHSPh} \xrightarrow[\mathrm{-HCl}]{\mathrm{PhSeCl}} \mathrm{Ph_3P{=}C(SPh)(SePh)} \qquad ...(37)$$

ylidic carbon with bonds to phosphorus, sulphur and selenium of 1.707, 1.732 and 1.919Å respectively.[257] New ylides containing the PCPCP atom sequence can be prepared by the reactions outlined in equation (38).[258]



...(38)

Hexaphenylcarbodiphosphorane, $\mathrm{Ph_3P{=}C{=}PPh_3}$, is the starting material for a number of novel reactions. It is converted, for example, by a range of halides RX into salts of the diphospha-allyl cation $\mathrm{[Ph_3P{\overset{...}{-}}CR{\overset{...}{-}}PPh_3]X}$, where X = Cl, Br or I and R = Me, Et, $\mathrm{PhCH_2}$, PhS, $\mathrm{MeOCH_2}$, $\mathrm{MeSCH_2}$, $\mathrm{Me_3Si}$ etc., while with bromo-acetic ester, on the other hand, it yields the carbanion, $\mathrm{(Ph_3P{\overset{...}{-}}CH{\overset{...}{-}}PPh_3)^+}$.[259] The selenoate, $\mathrm{Ph_3P{-}C(Se){-}PPh_3}$, prepared from the carbodiphosphorane and selenium, can be oxidised either by halogens or electrochemically to give the salts (104);[260] iron(III) chloride gives the corresponding $FeCl_4^-$ salt and in the presence of water, $FeCl_3$ yields a salt containing the $Fe_2OCl_6^{2-}$ anion.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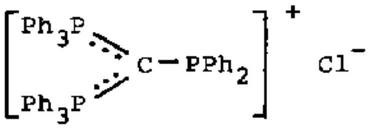

(105)

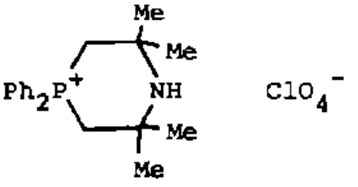
The Ph_3P groups in the addition compound (105), prepared by treating $Ph_3P=C=PPh_3$ with Ph_2PCl, are non-equivalent at low temperatures according to ^{31}P n.m.r. data, probably as a consequence of restricted rotation of the Ph_2P group.[261] On the other hand, all phosphorus atoms in the dication $[(Ph_2MeP)_3C]^{2+}2I^-$, obtained from $Ph_2MeP=CH_2$ with Ph_2PCl and MeI, are equivalent. 1:1 complexes of $Ph_3P=C=PPh_3$ with the chlorides of copper, silver and gold in the +1 oxidation are stable in air to 200°C; an X-ray structure of the CuCl complex indicates the presence of discrete molecules with a linear C-Cu-Cl system and a planar arrangement about the ylidic carbon.[262]

A series of amine substituted carbodiphosporanes, including $R_3P=C=PCl(NMe_2)_2$ and $R_3P=C=P(NMe_2)_3$ where R = Ph or Me_2N, has been obtained by reacting $R_3P=CCl_2$ with $R_2'PCl$ in the presence of $P(NMe_2)_3$ as a chlorine abstracting agent.[263] The fully dimethylamine substituted derivative has a structure with a linear P-C-P system, and P-C bonds of 1.584Å.

The structure has been reported for the mesomerically stabilised anion $[Ph_2P(S)]_3C^-$, obtained by proton abstraction from $[Ph_2P(S)]_3CH$.[264] The central carbon is in planar coordination to the three phosphorus atoms (mean P-C-P 119.9°, P-C 1.746-1.774Å) with two of the sulphur atoms lying on the same side of the plane. A mercury complex of the related uninegative anion $\{[Ph_2P(S)][Me_2P(S)]_2\}C^-$ has been prepared and X-ray crystallography shows that it is tridentate to mercury through the sulphur atoms, with tetrahedral coordination about mercury being completed by a chlorine atom.[265] The mean P-C-P angle about the central carbon is 116.4° and some double bond character remains in the P-C bonds which vary in length between 1.753 and 1.790Å.

Treatment of $Me(CF_3)_3PCl$ with silane gives the fluxional phosphorane $Me(CF_3)_3PH$, which from n.m.r. data has been assigned a trigonal bipyramidal ground state with two axial CF_3 groups.[266] The compound decomposes above room temperature with elimination of CF_3H to give $Me(CF_3)_2P$.

Structures have been determined for the azaphosphorinanium perchlorate (106) and the stable nitroxyl radical (107) showing a ring with a chair conformation in each compound.[267] A multinuclear n.m.r. investigation has been carried out using Ph_4PBPh_4 and the corresponding arsenic compound.[268]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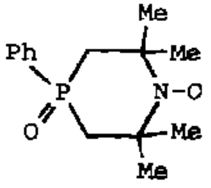

(107)

5.2.3 Bonds to Halogens

The +3 Oxidation State. A range of alkyl difluorophosphites, $ROPF_2$ where R = neo-pentyl, adamantyl or p-substituted benzyl, has been obtained by treating PF_2Cl with a trimethylsilyl ether, $ROSiMe_3$.[269] The compounds react with $(R_3P)_2PtCl_2$ to give complexes of the type $[(R_3P)_2PtCl(POF_2)]$ while $[p\text{-}XC_6H_4CH_2PPh_3{}^+]_2[Pt(POF_2)_4]^{2-}$ can be obtained via an Arbuzov-Michaelis reaction involving C-O bond cleavage.

Conditions have been reported for the preparation of two further iron carbonyl complexes with the short bite ligand $MeN(PF_2)_2$.[270] In $(OC)_4Fe\leftarrow PF_2NMePF_2$, the ligand is monodentate and in common with other such species it can be converted by solvolysis into $(OC)_4Fe\leftarrow PF_2NMe$. The binuclear complex, $[MeN(PF_2)_2]_3Fe_2(CO)_3$, is the previously unknown member of the $[MeN(PF_2)_2]_nFe_2(CO)_{9-2n}$ series and is thought to have a structure based on three bridging ligands and one bridging carbonyl group.

Electron diffraction measurements on $S(PF_2)_2$ and $Se(PF_2)_2$ indicate C_{2v} structures with large amplitude torsional vibrations.[271] Important molecular parameters for the sulphur compound are as follows (corresponding data for the selenide are in parentheses): P-S 2.132 (2.272)Å, P-S-P 91.3 (94.6) F-P-S 100.2 (98.7°). The sulphur derivative is a useful reagent for synthesising new compounds containing OPF_2 groups. With hydroxyphosphorus(V) starting materials, the reactions can be summarised by equation (39).[272] The product with phosphorous acid is $PHO(OPF_2)_2$ but on prolonged reaction $P(OPF_2)_3$ can be isolated;[273]

$$PO(OH)_nR_{3-n} \;+\; nS(PF_2)_2 \rightarrow PO(OPF_2)_nR_{3-n} \;+\; nPF_2(S)H \qquad \ldots(39)$$

R = Ph, n = 1-3
R = F, n = 2,3.

the dimethyl and diphenyl phosphites, $PHO(OR)_2$, yield $P(OR)_2(OPF_2)$ while with Ph_2PHO the product is probably Ph_2POPF_2 but a pure sample could not be obtained. The reaction can not be extended to hypophosphorous acid which gives only orange-yellow decomposition products.

The compound previously described as $2PI_3.AlI_3$ has been shown by X-ray crystallography to be the salt $P_2I_5{}^+AlI_4{}^-$.[274] The cation, which forms weak I---I contacts with the $AlI_4{}^-$ anion, is the P-P bonded species $I_3P\text{-}PI_2{}^+$ with P-I distances at the three coordinate phosphorus slightly longer (2.42Å) than those at the four coordinate atom (2.40Å). A second derivative, $PI_4{}^+AlI_4{}^-$, has been obtained as a deep red, hydrolytically unstable compound by treating PI_3 and AlI_3 in carbon disulphide solution with iodine.[275] The structure contains tetrahedral cations (mean P-I 2.396Å) and anions interconnected again by weak I---I contacts (3.39-3.45Å) to give a three dimensional structure.

The +5 Oxidation State. A 1:1 adduct $H_3N.PF_5$ has been prepared either by reaction of a 1:1 ratio of the constituents or by treating the cyclotriphosphazene $(NPF_2)_3$ with hydrogen fluoride; the latter reaction also yields NH_4PF_6.[276] Detailed i.r. and n.m.r. data are reported and an X-ray structure shows the phosphorus atom in slightly distorted octahedral coordination with a P-N bond distance of 1.842Å. PF_5 also gives 2:1 adducts with aminophosphines of the type $R_2P(B_{10}H_{10}C_2)P(NMe_2)_2$, in which it is suggested there are bonds between phosphorus atoms in the +3 and +5 oxidation states.[277] In acetonitrile solution, ionisation of the adduct $(Me_2N)FP(B_{10}H_{10}C_2)PF(NMe_2).2PF_5$ to yield two $PF_6{}^-$ anions and a cation containing phosphorus(III) atoms in two-fold coordination is confirmed by conductance measurements and the observation of a ^{31}P n.m.r. shift at +358ppm. The interaction of PF_5 and a number of other phosphorus(V) compounds, which are potential stabilisers for the HNO_3-N_2O_4 mixtures designated as HDA, has been investigated by ^{31}P and ^{19}F n.m.r. spectroscopy.[278] The evidence points to conversion of PF_5 to PF_6^-, HPO_2F_2 and HF, HPO_2F_2 to H_2PO_3F and HF while P_4O_{10}, the reaction gives $P(OH)_4^+$, $H_4P_2O_7$, $(HPO_3)_4$ and a mixture of cyclic and branched phosphoric acids.

The reaction of the $PF_5.MeCN$ adduct with SH^- has been followed by n.mr. spectroscopy showing formation of a range of compounds that can be rationalised by cleavage of P–F bonds or reaction of the coordinated nitrile.[279] Among the former are PF_6^-, $[F_4P{<}^{S}_{S}{>}PF_4]^{2-}$ and $PS_2F_2^-$ while the latter include $[F_5P\text{-}N{:}C(SH)Me]^-$ and $[F_5P\text{-}NHC(S)Me]^-$.

Phosphorus anions containing both chlorine and fluorine atoms have been isolated following the reactions in equations (40)-(42).[280] In

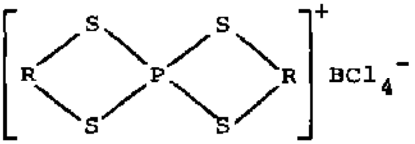
$$PF_3 + Et_4NCl + Cl_2 \rightarrow Et_4NPF_3Cl_3 \qquad \ldots(40)$$

$$PF_2Cl + Et_4NCl + Cl_2 \rightarrow cis\text{-}Et_4NPF_2Cl_4 \qquad \ldots(41)$$

$$PFCl_2 + Et_4NCl + Cl_2 \rightarrow Et_4NPFCl_5 \qquad \ldots(42)$$

subsequent reactions with either LiN_3 or AgNCS, only the chlorine atoms are replaced and evidence is available for the formation of the two series, $PF_3Cl_{3-n}(N_3)_n^-$ and $PF_3Cl_{3-n}(NCS)_n^-$. ^{31}P n.m.r. spectroscopy has been used to identify members of two further series of mixed phosphorus(V) anions, i.e. $PF_{6-n}(CN)_n^-$ for n = 1-4 and $PF_3Cl_{3-n}(CN)_n^-$ for n = 1-3,[281] and mixed cationic species, $[PX_{4-n}(CN)_n]^+$ and $[PX_{4-n}(NCS)_n]^+$ where X = Cl or Br, have been identified as products of reactions between PX_5 and respectively $Zn(CN)_2$ or AgNCS.[282]

The 1:1 adduct $PCl_5.UCl_5$ is isomorphous with the $NbCl_5$ and $TaCl_5$ adducts and from a recent structure determination should be formulated as $PCl_4^+UCl_6^-$.[283] The related tetrachloroborate, $PCl_4^+BCl_4^-$, reacts in 1,2-dichloroethane with dithiols to give the spiro compounds (108), where R = $(CH_2)_2$, $(CH_2)_3$ or $MeCH\text{-}CH_2$.[284] The P-S distances in the ethanedithiol product are 2.045 and 2.052Å.



(108)

An unusual transition metal complex, $[Ir(CO)Cl_2(PEt_3)_2PCl_4]$, has been isolated from the chlorine oxidation of $[Ir(CO)Cl_2(PEt_3)_2PCl_2]$, but it has not yet been possible to confirm the five coordinate phosphorus structure by X-ray crystallography.[285]

The gaseous phosphorus(III) species, POCl and PSCl, have been produced by high temperature (ca. 1100K) reactions of either $POCl_3$[286] or $PSCl_3$[287] with silver. They have been detected mass spectrometrically in the vapour phase, the data leading to ΔH^{o}_{298} values of -250.7 and -11.9 kJ mol^{-1} respectively, and in argon matrices by i.r. spectroscopy. Bands at 1257.7 and 489.4 cm^{-1} for POCl have been assigned to P-O and P-Cl stretching respectively with a calculated O-P-Cl angle of ca. 105°.[286] The corresponding sulphide shows bands at 716.1 (ν_{P-S}), 462.4(ν_{P-Cl}) and 229 cm^{-1} (δ_{SPCl}).[288] The corresponding arsenic and antimony(III) oxide chloride have been prepared similarly[510] and PO_2Cl, the phosphorus analogue of NO_2Cl, has been generated at ca. 1200K by reacting POCl with oxygen.[289] ΔH^{o}_{298} for the compound is -264.9 kJ mol^{-1}.

^{35}Cl n.q.r. spectra for $P_2O_3Cl_4$, $P_2OS_2Cl_4$[290] and for the $SnCl_4$ and $SbCl_5$ complexes with the former[291] have been measured. The antimony compound has a 2:1 stoichiometry and the data point to discrete molecules in which the two phosphoryl groups each coordinate to antimony. For tin with a 1:1 stoichiometry, the $P_2O_3Cl_4$ group bridges between tin atoms giving infinite chains.

Two new perfluoro-t-butoxy derivatives, $OP(OC_4F_9)Cl_2$ and $OP(OC_4F_9)_2Cl$ have been isolated from reactions between phosphoryl chloride and $NaOC_4F_9$ but even with an excess of the reagent and long reaction times it was not possible to prepare the trisubstituted compound.[292]

Tetraphenylphosphonium fluoride has been shown to exist in a number of different forms depending on the method of production.[293] For example, anion exchange of Ph_4PBr led to the ionic species $Ph_4P^+HF_2^-$ which, when treated with aqueous hydrogen carbonate, gave Ph_4PF showing significant P---F interaction in the solid state but ionic character in solution from n.m.r. spectroscopy. The molecular form has been identified by i.r. spectroscopy in the volatile products from thermolysis of Ph_4PF, but on trapping these vapours the dimeric, $Ph_4P^+Ph_4PF_2^-$, with trans-fluorine atoms is produced.

The new trichlorides, Ph_4MCl_3 for M = P or As, have been prepared at low temperature and investigated by Raman spectroscopy.[294] Related trihalides, rather than N-halogenated compounds, have been prepared by reaction of a free halogen or an interhalogen with triphenylphosphonium halides $(Ph_3PNHR)X$ carrying either an alkylamino or a cycloalkylamino group.[295]

5.2.4 Bonds to Nitrogen

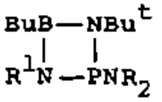
As in Section 5.2.2, the two oxidation states are treated separately and within each section compounds containing P-N double bonds are discussed first.

The +3 Oxidation State. Ab initio calculations have been reported for the model two coordinate phosphorus compound $HP{=}CH_2$.[213] Transamination reactions with highly hindered lithium amides, shown in equation (43), give good yields and provide an

$$(Me_3Si)_2N{-}P{=}NSiMe_3 + LiN(SiMe_3)Bu^t \rightarrow (Me_3Si)_2N{-}P{=}NBu^t + LiN(SiMe_3)_2 \qquad \ldots(43)$$

alternative preparative route to aminoiminophosphines.[296] Aminoiminophosphines will add methyl lithium to give $[(Me_3Si)_2N{-}P(Me){=}NR]^-Li^+$ but if the hindered lithium derivative, 2,4,6-tri-t-butylphenyl lithium, is used the product is the orange-red liquid, $Bu^t{}_3C_6H_2P{=}NSiMe_3$, the first stable two coordinate phosphorus compound to contain the C-P=N sequence of atoms.

Aminoiminophosphines $R_2NP{=}NR^1$, where $R = R^1 = SiMe_3$ and $R = Pr^i$, $R^1 = Bu^t$, undergo cycloaddition reactions with the iminoborane $BuB{=}NBu^t$ to give the new ring compounds (109).[297]



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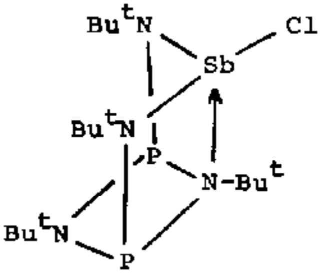

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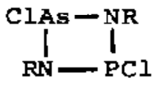
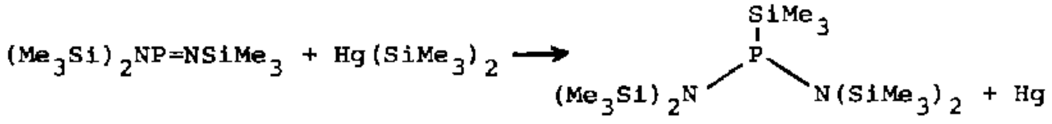


(111)

The related phosphine, $Bu^t(Me_3Si)NP{=}NBu^t$, reacts with $SbCl_3$ with elimination of Me_3SiCl to give the bicyclic compound (110) which has been examined crystallographically.[298] This behaviour is in contrast to that with arsenic trichloride which yields the four membered ring compound (111).

A novel compound containing an unusual P(III)-Si bond has been isolated from an aminoiminophosphine reaction with $Hg(SiMe_3)_2$ in $(Me_2N)_3PO$ (equation 44).[299] The compound is sensitive to oxygen

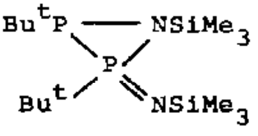


$(Me_3Si)_2NP{=}NSiMe_3 + Hg(SiMe_3)_2 \longrightarrow (Me_3Si)_2N{-}P(SiMe_3){-}N(SiMe_3)_2 + Hg$

...(44)

and moisture but appears to be stable to at least 200°C. The P-Si bond is labile and the compound reacts with acetyl chloride and methanol, for example, to give $MeC(O)P[N(SiMe_3)_2]_2$ and $HP[N(SiMe_3)_2]_2$ respectively.

Recently it has been shown that it is possible for $Bu^tP{=}NSiMe_3$, an intermediate in the formation of the azadiphosphorinane (112), to insert into the λ^3-PN bond of (112) to give two isomeric forms, (113) and (114), of a previously unknown azatriphosphetidine.[300]



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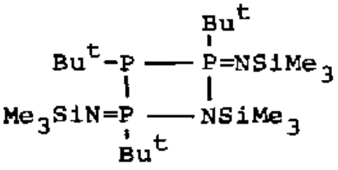

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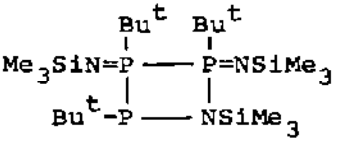
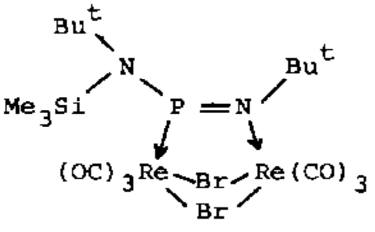


(114)

Compound (113) contains an almost planar four membered ring with the following angles: P-P-P 74.8, P-N-P 103.0 and P-P-N 87.7 and 89.4°. The P-P distances are 2.232 and 2.195Å and the P-N bonds 1.727 and 1.709Å.

Coordination of an amino-imino phosphine as a bridging group has been observed for the first time in the rhenium compound (115) prepared from $Bu^t(Me_3Si)NP{=}NBu^t$ and $[Re(CO)_3(THF)Br]_2$.[301] The N-P-N angle increases from 104.9° in the free ligand to 122.6° but the P-N bond lengths remain essentially unchanged. One ligand in the platinum complex, $Pt[P({=}NBu^t)(NBu^tSiMe_3)]_3$, is displaced on reaction with $Cl_2C{:}CCl_2$ and on treatment with water the two remaining ligands are coupled via a P-O-P linkage to give (116).[302]



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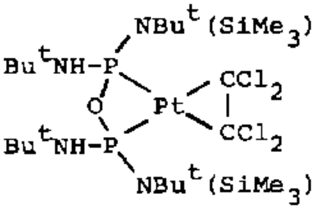

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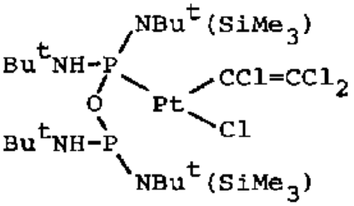


(117)

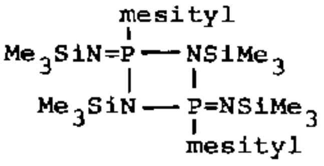
At room temperature, this compound isomerises to (117).

Aminophosphines of the type $(R_2N)_2PH$ are rare but it has recently been shown that the di-i-propyl derivative can be obtained as a low melting solid by the $LiAlH_4$ reduction of $(Pr^i{}_2N)_2PCl$.[172] A further secondary phosphine, $[(Me_3Si)_2N]_2PH$, together with $[(Me_3Si)_2CH]_2PH$, has been obtained by a similar reaction.[303]

Grignard reactions of Pr^iMgCl with $(Me_3Si)_2NPRCl$, where R = Pr^i, Bu^t, CH_2SiMe_3, $N(SiMe_3)_2$ or Ph, lead to both the expected products $(Me_3Si)_2NPRPr^i$ and the phosphine $(Me_3Si)_2NPR(H)$.[304] The latter is apparently produced by an excess of the Grignard behaving as a reducing agent; such phosphines can be more directly obtained by reduction of the corresponding chloride with $LiAlH_4$. Similar Grignard reactions have been used to produce $[(Me_3Si)_2N]_2PCH_2R$, where R = H, Me, $SiMe_3$ or Ph, and these compounds react with carbon tetrachloride, either neat or in dichloromethane solution, to give mixtures of the imino derivatives $(Me_3Si)_2NPCl(CHRSiMe_3)(:NSiMe_3)$ and $(Me_3Si)_2NPCl(CH_2R)(:NSiMe_3)$.[305] The two products arise as either $CHCl_3$ or Me_3SiCCl_3 can be eliminated in the reaction with carbon tetrachloride.

The thermally unstable aminophosphine, $(mesityl)PClN(SiMe_3)_2$, results from the reaction of $(mesityl)PCl_2$ with $LiN(SiMe_3)_2$ but more stable derivatives are produced on substitution of the remaining chlorine by either MeLi or Me_3SiCH_2MgCl.[306] Treatment of the methyl compound so obtained with CCl_4 leads via $CHCl_3$

elimination to the phosphinimine (mesityl)PCl(:NSiMe$_3$)(CH$_2$SiMe$_3$). This compound with trimethylsilylazide eliminates nitrogen to give the di-imide, (mesityl)P(=NSiMe$_3$)$_2$, as a probable intermediate to the cyclic compound (118) obtained in cis and trans forms as the stable product. In a similar fashion carbon tetrachloride reacts with the trimethylsilylmethyl derivative, (mesityl)P(CH$_2$SiMe$_3$)-N(SiMe$_3$)$_2$, giving the dimer (119), which on vacuum pyrolysis at 140°C, i.e. slightly below its melting point, yields the corresponding monomer (mesityl)P(=CHSiMe$_3$)(=NSiMe$_3$) as a colourless liquid stable for some hours at room temperature.[307] On heating at 145°C in a sealed system, both the monomer and dimer (119) are converted into the isomeric P$_2$CN ring compound (120).



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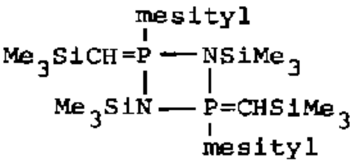

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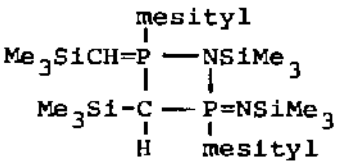
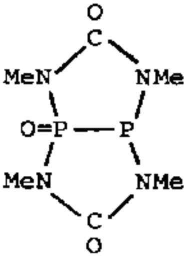


(120)

Two bicyclic P-N compounds (121) and (122), one containing a direct bond between phosphorus atoms in the +3 and +5 oxidation states have been synthesised by reactions between PCl$_3$ and the substituted urea OC(NMeSiMe$_3$)$_2$.[308] An interesting spirocyclic derivative (123) containing phosphorus(V) atoms in both four and five fold coordination results when (121) is treated with tetrachloro-o-benzoquinone.



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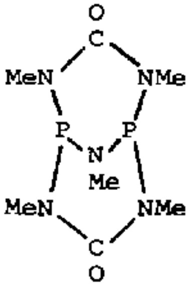

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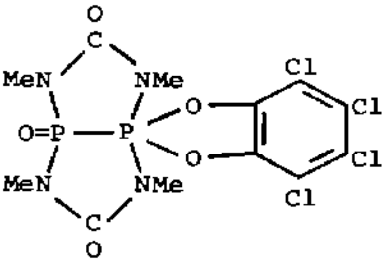
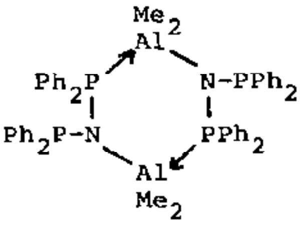


(123)

A molecule of an alkane is eliminated when the Group 3 alkyls, Me$_3$Al, Et$_3$Al, Me$_3$Ga and Et$_3$Ga, react with the diphosphinoamine, (Ph$_2$P)$_2$NH.[309] The products are cyclic compounds and a structure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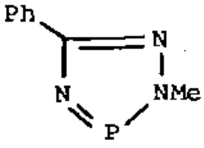
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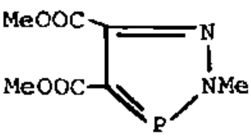
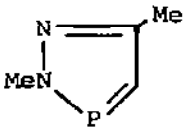

(126)

for the dimethyl aluminium derivatives (124) shows unsymmetrical coordination of the ligand. The lithium derivative of the diphosphinoamine gives an intensely yellow gold(I) complex on reaction with Ph_3PAuCl;[310] the product is formulated as $(Ph_2P)_2NAu$ for which a dimeric structure with an eight membered $Au_2P_4N_2$ is proposed.

The triazaphosphole derivative (125) reacts with acetylene dicarboxylic esters to give the diaza derivative (126) by loss of a nitrile,[311] and by a series of steps including cycloaddition and PhCN elimination, the reaction between N-phenyl benzohydrazonoyl chloride, PhCCl(=NNHPh), and the diazaphosphole (127) in the presence of base leads to compounds (128)-(130).[312] The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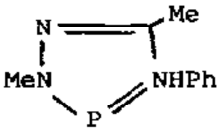
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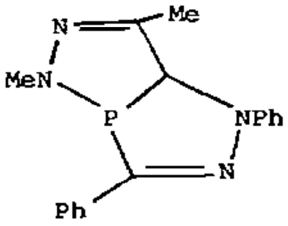
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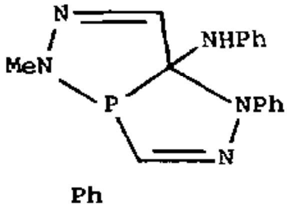
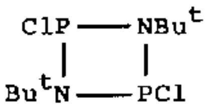

(130)

structures of (129) and (130) have been determined.

Cyclopentadine nickel compounds in which the ligand (131) is either unidentate, chelating or bridging have been isolated,[313] and the new four membered ring compounds (132) and (133, R = PhP(O) and SO_2) can be obtained by treating $P(NEt_2)_3$ with



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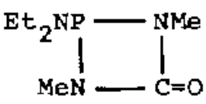

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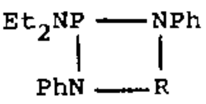
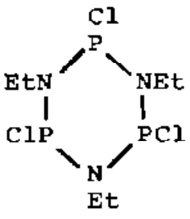


(133)

respectively, N,N'-dimethylurea, phenylphosphonic acid dianilide and N,N'-diphenyl sulphamide.[314]

A convenient route to the cyclophosph(III)azane (134) involves heating PCl_3 and $EtNH_3Cl$ in tetrachloroethane;[315] small quantities of other products such as $(ClPNEt)_2$ and the monoxides (135) and (136) are also produced. Under different conditions the reaction also yields the bicyclic product (137). In refluxing phosphorus trichloride solution, (137) is converted via (134) to $Cl_2PNEtPCl_2$, and with antimony trifluoride, both (134) and (137) give the corresponding fluorides.



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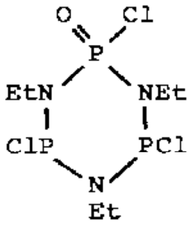

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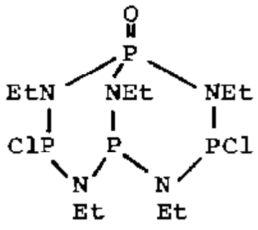

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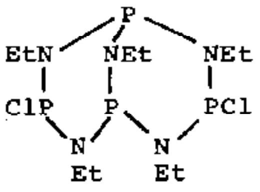
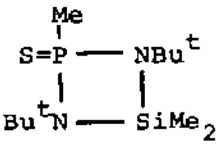


(137)

^{13}C n.m.r. and photoelectron spectra have been measured for compounds in the series $X_nP_4(NMe)_6$, where X = O or S and n = 0-4.[316] P.e.s. data for $S_nP_4(NMe)_6$ show a steady increase in the stability of the nitrogen pπ electrons with increase in n, which is interpreted as implying a small but real P-N π component to bonding.

The +5 Oxidation State. During the initial stages of the reaction with $Re(CO)_5Br$, the three coordinate thiophosphorane, $Bu^t(Me_3Si)NP(:S)(:NBu^t)$, isomerises to the cyclic PN_2Si compound (138) before forming a dimeric complex.[317] A derivative of the nitrogen analogue of the monomeric metaphosphate anion, i.e. $(Me_3SiN=)_2P(NSiMe_3)^-$, has been stabilised in the rhenium carbonyl complex (139) which results when $(Me_3Si)_2NP(=NSiMe_3)_2$ reacts with $[Re(CO)_3(THF)Br]_2$.[318]

High yields of the P-N-S compound, $Cl_3P=N-SF_3$, which is unstable



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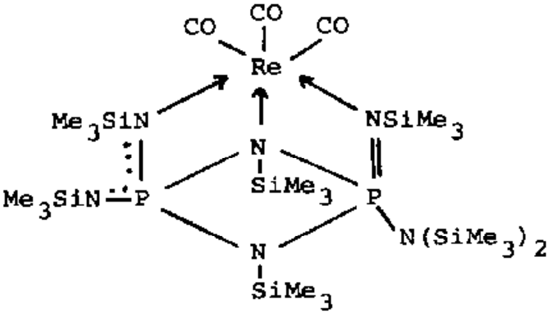


(139)

at room temperature, are obtained together with PCl_5 when phosphorus trichloride reacts with F_5SNCl_2.[319]

^{31}P n.m.r. line shape analysis has been used to study pseudorotation processes in a range of aminophosphoranes including F_4PNHMe, $F_4PNMe(CH_2Ph)$, $F_3(CF_3)PNMe_2$, $(CF_3)_3PF(NHMe)$.[320] Insertion of carbon dioxide into the P-N bond of $Me(CF_3)_3PNMe_2$ gives the neutral six coordinate carbamate $Me(CF_3)_3P(O_2CNMe_2)$, which unusually, is fluxional in solution in contrast to the static geometry of the related mono- and di-thio analogues.[321]

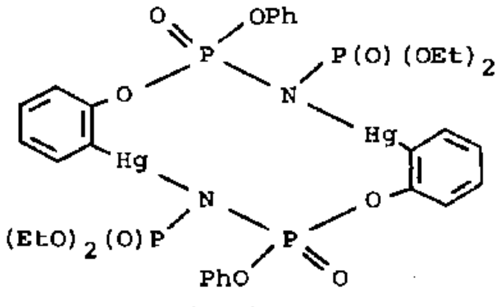
An X-ray structure for the imidodiphosphinic acid, $Ph_2P(S)NHP(S)Ph_2$, shows that the proton is located on the nitrogen atom with the sulphur atoms in trans positions with respect to the central PNP group.[322] The P-N bonds (1.678Å) have some π character and the molecules are linked in pairs by N-H---S bonds.

O-nucleophiles such as Me_2SO, $Me_2NC(O)H$ and $(Me_2N)_2CO$ on reaction with the phosphoryl phosphazene $Cl_3P{:}N{\cdot}P(O)Cl_2$ give respectively $[Cl_2P(O)]_2NH$, $[Me_2NC(Cl)H]^+[Cl_2P(O)]_2N^-$ and $[Me_2NC(Cl)NMe_2]^+[Cl_2P(O)]_2N^-$,[323] and the related alkoxy derivatives $(R'O)_3P{:}N{\cdot}P(O)(OR)_2$ can be obtained in high yield by the single step process in equation (45).[324] Azide esters are

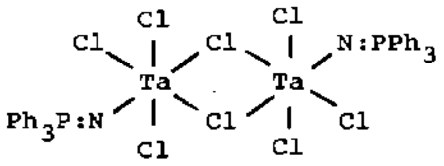
$$(R'O)_3P + (RO)_2P(O)H + CCl_4 + NaN_3 \rightarrow (R'O)_3P{=}N{-}P(O)(OR)_2 + N_2 + CHCl_3 + NaCl \qquad \ldots(45)$$

initially formed but these react further; among the byproducts is $(RO)_2P(O)CCl_3$.

An improved preparative route has been obtained for tetraphenylimidodiphosphate, $(PhO)_2P(O)NHP(O)(OPh)_2$, which has been converted into a number of metal derivatives;[325] the structure of the copper complex has been determined. Mixed phosphinic-phosphoric analogues have also been isolated; for example, $Et_2P(O)NHP(O)(OPh)_2$ can be obtained by HCl abstraction from a mixture of $Et_2P(O)Cl$ and $(PhO)_2P(O)NH_2$.[326] The product reacts with mercury(II) oxide to give the 12-membered ring compound (<u>140</u>). THF is known to be polymerised when treated with the imidodophosphoryl chloride, $Cl_2P(O)NHP(O)Cl_2$, but in the presence of smaller amounts of THF, the chloride yields short chains of THF molecules, end stopped with diphosphoryl chloride, $H[O(CH_2)_4]_nN[P(O)Cl_2]_2$.[327]



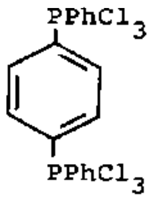
(<u>140</u>)



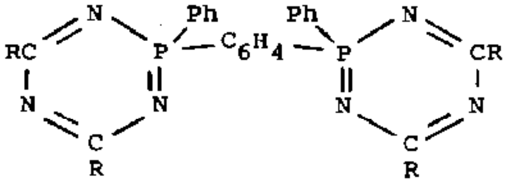
(<u>141</u>)

A series of new five coordinate amine substituted compounds, i.e. $R_3M(NR^1{}_2)_2$, where R = Ph or p-tolyl, M = P, As or Sb and R^1 = benzimidazole, succinimide, phthalimide, etc, has been prepared from the dibromide, R_3MBr_2.[328] The products are non-ionic and with M = As or Sb, the bonds to nitrogen are cleaved by Br_2, IBr, $HgBr_2$ etc.

A Staudinger reaction of $(TaCl_4N_3)_2$ with triphenylphosphine leads to the centrosymmetric dimer (<u>141</u>) as the major product, together with $TaCl_5$ and $TaCl_4(NPPh_3)(NHPPh_3)$.[329] The latter arises from reaction of an intermediate with the 1,2-dichloroethane solvent. The 1,4-bis(phosphino)benzene (<u>142</u>) has been synthesised as an intermediate in the formation of the bridged phosphabenzene (<u>143</u>).[330]

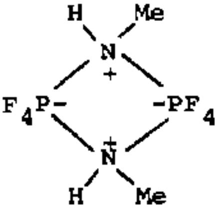


(<u>142</u>)



(<u>143</u>)

Organometallic reagents such as PhLi, $ZnEt_2$ or MeMgBr react with the internal salt (144) to give the neutral analogue (145), which depending on the specific reagent, may react further to substitute one or two of the P-F bonds.[331] With DABCO, 1,8-bis(dimethylamino)naphthalene or an alkali fluoride, compound (144) is converted into salts of the anion (146). A range of derivatives can be produced using the spiro bis(triazaphosphole) (147) which has been synthesised recently.[332] The unusual tetradentate ligand $(Pr^i_2NPO)_4$ occurs in the complex (148) obtained when $(Pr^i_2N)_2P(O)H$ reacts with molybdenum hexacarbonyl.[333] A phosphinous acid derivative is thought to be formed first, which loses di-i-propylamine; attention is drawn to the similarity between the P_4O_6 framework and that of the $P_4O_4Mo_2$ skeleton in (148)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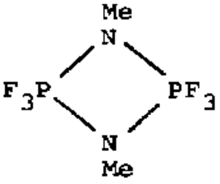
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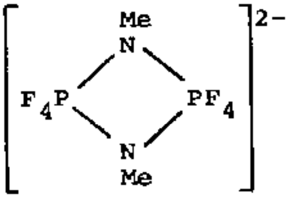
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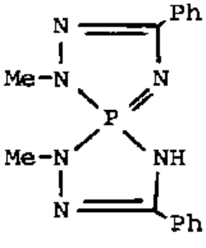
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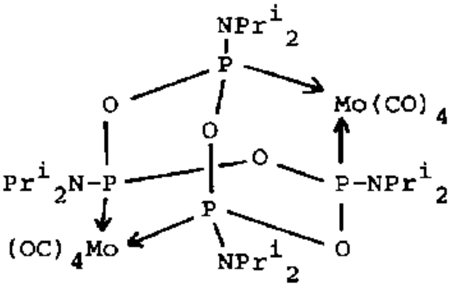
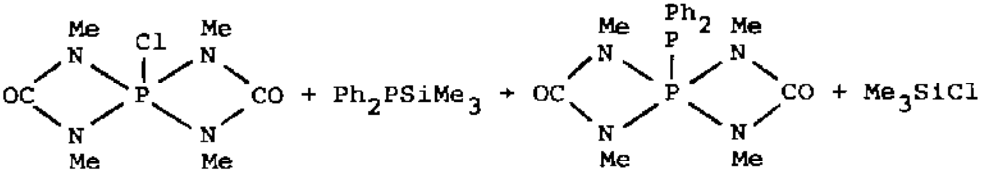

(148)

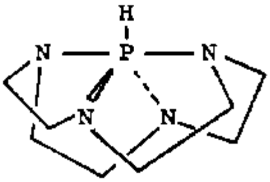
A new compound (149) containing phosphorus atoms in both three and five fold coordination has been synthesised by the reaction in equation (46).[334] The central phosphorus is in highly distorted trigonal bipyramidal coordination with the axial angle (N-P-N) being 163.9°; the P-P distance is 2.214Å and as the angles at the Ph_2P group are similar to those in triphenylphosphine (p-d)π bonding is unlikely.



...(46)

(149)

The cyclen phosphorane (150) forms a bis(borine) adduct on reaction with diborane which is a little unusual as here there are two nitrogen atoms attached to a phosphorus(V) centre showing donor properties.[335] The monomer-dimer equilibrium in chloroform solution shown by the related cyclen phosphine oxide (151) has been investigated by i.r. and ^{31}P n.m.r. spectroscopy.[336] Dimerisation occurs via intermolecular P=O···HN hydrogen bonds.



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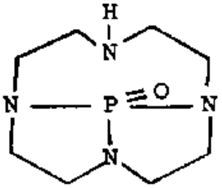
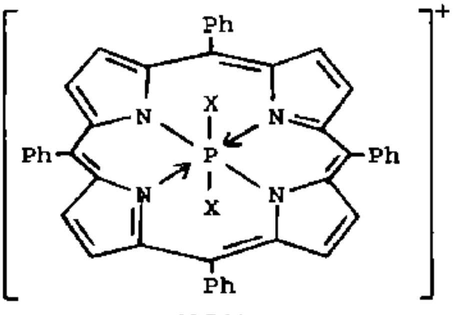


(151)

The phosphorus atom in the hydrated dihydroxy(porphinate) cation (152, X = OH) is displaced 0.09Å from the plane of the four nitrogen atoms, leading to P-O distances of 1.545 and 1.644Å.[337] The porphin system, which is markedly non-planar, shows S_4 symmetry. The corresponding dichloride (152, X = Cl) has also been synthesised and characterised.[338] Structural data are now available for (153), the first compound to be investigated



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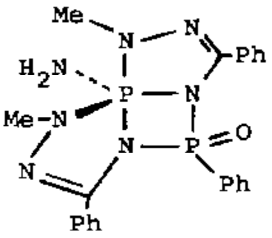
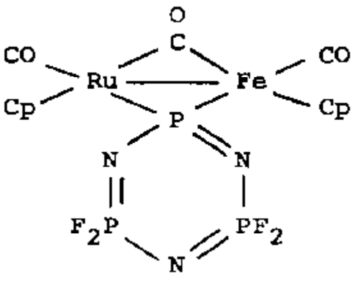


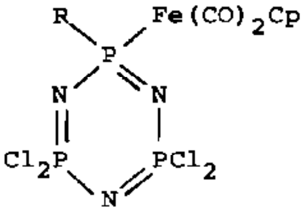
(153)

containing a PN_5 unit.[339] The geometry is basically trigonal bipyramidal, but distorted some 26% along the Berry coordinate, with axial P-N distances of 1.728 and 1.826Å. The equatorial distances to the heterocyclic rings are 1.700 and 1.710Å while the short (1.625Å) P-NH_2 distance, together with the observation that the plane of the NH_2 group is almost perpendicular to that of the equatorial PN_3 plane, supports the presence of P-N π bonding.

New cyclotriphosphazenes, mono- or geminally di-substituted with organometallic groups have been synthesised using either $N_3P_3F_6$[340] or the phosphazene anions[341] $(N_3P_3Cl_4Me)^-Li^+$ or $(N_3P_3Cl_4PhBEt_3)^-Li^+$ as starting materials. The hexafluoride, for example, reacts with both $Fe(CO)_2Cp^-$ and $Ru(CO)_2Cp^-$ to give monosubstituted $N_3P_3F_5[M(CO)_2Cp]$ derivatives and the ruthenium compound yields the mixed metal complex, $N_3P_3N_5[Ru(CO)_2Cp]$-$[Fe(CO)_2Cp]$, when treated with $KFe(CO)_2Cp$. Carbon monoxide is lost on photolysis to produce (<u>154</u>). The phosphazene anions, on the other hand, react with $CpFe(CO)_2I$ to generate the new complex species (<u>155</u>, R = Me or Ph) and an X-ray structure has been carried out on the methyl compound.



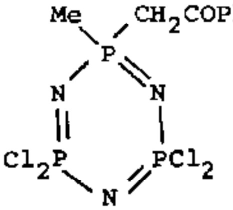
(<u>154</u>)



(<u>155</u>)

In contrast to reactions with phenyl lithium, treatment of $N_3P_3F_6$ with 1-lithioalkoxyethylenes, $LiC(OR){:}CH_2$ where R = Me or Et, proceed smoothly to give the mono- and geminally disubstituted derivatives $N_3P_3F_{6-n}[C(OR){:}CH_2]_n$.[342] Reactions of the corresponding hexachloride, $N_3P_3Cl_6$, with the lithium salts of the enolates of acetaldehyde[343,344] acetone[344] and acetophenone,[344] on the other hand, give O-alkyl derivatives, e.g. $N_3P_3Cl_{6-n}(OCH{:}CH_2)_n$ for n = 1-6, by a predominantly non-geminal route with comparable quantities of the cis and trans isomeric forms. A C-substituted compound (<u>156</u>) has however been obtained in low yield when

$N_3P_3Cl_4MeLi$ is treated with α-bromoacetophenone and a further



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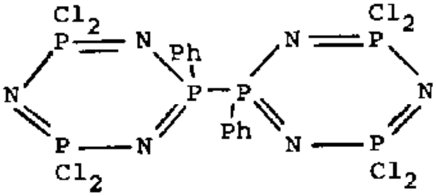


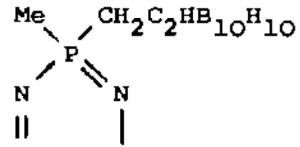
(157)

C-substituted compound in high yield results when the copper phosphazene complex, $(N_3P_3Cl_4Me)_2Cu$, is treated with 2-methoxyallyl bromide.[344]

A series of new cyclotriphosphazenes, $N_3P_3Cl_4PhR$ where R = Cl, Br, I, Me, Et, Pr^i and Bu, has been synthesised from the biphosphazene (157) by the initial cleavage of the P-P bond with $LiBEt_3H$ followed by treatment with either an alkyl halide, a free halogen or a proton releasing agent.[345] A full crystal structure for $N_3P_3Cl_5Ph$, one of the compounds obtained by this method, has been determined.

Trimethylaluminium in refluxing toluene reacts with $N_3P_3Cl_6$ in an unusual reaction to give good yields of the geminally tetrasubstituted derivative, $N_3P_3Cl_2Me_4$;[346] there is strong n.m.r. evidence for a completely geminally reaction path. The corresponding reaction with methyl lithium has been reinvestigated showing formation of small quantities of $N_3P_3Cl_5Me$ or $N_3P_3Cl_4Me_2$ together with low molecular weight acyclic species.[347] It is concluded that reaction occurs via nucleophilic attack at phosphorus rather than by the metal halogen exchange that occurs in reactions of both organo-copper and Grignard reagents.

On treatment with the acetonitrile adduct of decaborane, the propynyl-phosphazene, $N_3P_3Cl_4Me(CH_2C{\vdots}CH)$, gives the o-carboranyl derivative (158), which with piperidine gives an anionic nidocarborane (159) by chlorine substitution and opening



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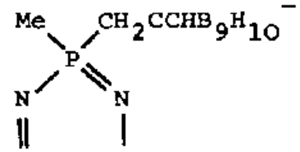
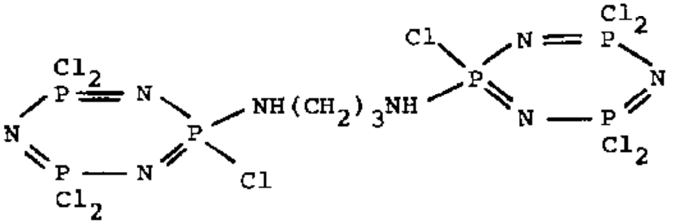


(159)

of the borane cage.[348] From an X-ray study the P-N bonds distant from the carborane substituted phosphorus atom are long (1.68Å) pointing to protonation at these nitrogens. Compound (158) reacts with bases to give mono- and di-anions which can subsequently form complexes with metal carbonyls.

The anti-cancer ethyleneimine derivative, $N_3P_3Cl_2(NC_2H_4)_2$, has been examined by single crystal X-ray diffraction.[349] In addition to producing the expected spiro derivative, $N_3P_3Cl_4[NH(CH_2)_3NH]$, the reaction between $N_3P_3Cl_6$ and propylaminediamine gives two by-products, one of which from X-ray crystallography is the bridged compound (160).[350] ^{31}P n.m.r. spectra for a series of 68 geminally disubstituted triphosphazenes have been analysed, allowing the calculation of group shift contributions.[351]



(160)

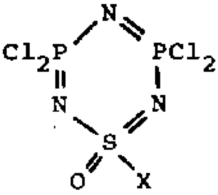
Thermal polymerisation of $N_3P_3Cl_6$ in the ion chamber of a mass spectrometer has been observed[352] and, perhaps far more unusually, species up to $[NP(OPh)_2]_{12}$ have been identified in similar mass spectrometric measurements on $N_3P_3(OPh)_6$.[353] The experiments require temperatures of 200°C and sample pressures up to 5 x 10^{-1} torr; fragmentation causes loss of a phenoxy group and polymerisation is initiated by the cation $N_3P_3(OPh)_5^+$. Polymeric aryloxyphosphazenes, which have side chains carrying pendant phosphine groups, e.g. $[NP(OC_6H_4PPh_2)_x(OPh)_{2-x}]_n$ where x = ca. 0.3, have been synthesised for assessing the value of such systems in carrying transition metals in catalyst systems.[354] Data are reported for the model trimeric compounds, $N_3P_3(OPh)_5(OC_6H_4PPh_2)$, $N_3P_3(OPh)_6$ and $N_3P_3(OC_6H_4PPh_2)_6$.

A nitridophosphate, formulated as $Na_4P_4O_9N_2$, has been obtained by heating the trimetaphosphimate, $Na_3P_3O_6(NH)_3.H_2O$ to ca. 450°C;[355] further heating yields $Na_6P_6O_{15}N_2$. A number of new cobalt, nickel and zinc tetrametaphosphimates have been isolated from reactions between the metal chloride and hydrated sodium or potassium tetrametaphosphimate, $M_4[P(NH)O_2]_4$.[356] Among the compounds isolated are $Co_2(P_4O_8N_4H_4).9H_2O$ and the corresponding nickel and zinc salts with respectively 12 and 7.5 molecules of water, and $K_2M(P_4O_8N_4H_4).8H_2O$ and $Na_2M(P_4O_8N_4H_4).6H_2O$ where M = Co, Ni and Zn.

Mixtures of the completely substituted tetraphosphazene, $N_4P_4(NHR)_8$, and the bicyclic $N_4P_4(NHR)_6(NR)$ are produced on reaction of $N_4P_4Cl_8$ with an excess of either i-propyl or butyl amine in chloroform solution.[357] The compounds were characterised by a detailed i.r. and ^{31}P n.m.r. investigation and n.m.r. data have been collected for a number of asymmetrically substituted bridged compounds, $N_4P_4(NMe_2)_5(NHR')(NR')$.

Bromine n.q.r. data for both $N_3P_3Br_6$ and $N_4P_4Br_8$[358] and ^{31}P and ^{15}N n.m.r. spectra for a series of aniline substituted tetrameric phosphazenes[359] and for the higher phosphazenes, $(NPX_2)_{5\text{ and }6}$ for X = F, OMe and NMe_2 are now available.[360] New separation methods have been devised for the chlorophosphazenes, $(NPCl_2)_{5-7}$.[361]

An n.m.r. investigation of the reactions of the two mixed ring compounds (161) and (162), where X = F, Cl or Ph, with ammonia in ether or acetonitrile as solvent points to reaction occurring only at the phosphorus centres with replacement following a geminal path.[362] The spirocyclic derivative (163) in both cis and trans isomeric forms can be prepared from (162, X = Ph) by reaction successively with NH_3, PCl_5 and $(Me_3Si)_2NMe$.[363]



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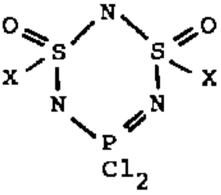

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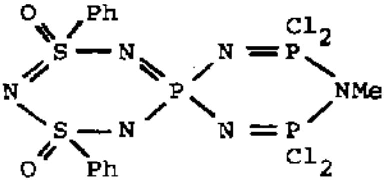
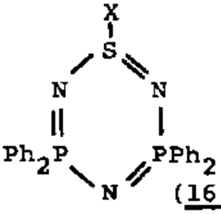


(163)

A mixed P-N-S ring compound (164, X = I) containing an exocyclic S-I bond has recently been obtained by treating the corresponding chloride with potassium iodide in acetonitrile.[364] The structure



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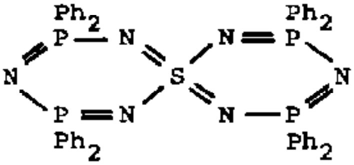

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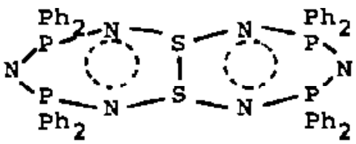
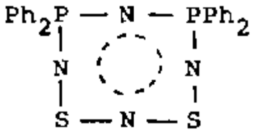


(166)

has been confirmed X-ray diffraction, which shows planarity for the P_2N_3 segment of the ring, and although the compound is unusually stable, on heating to ca. 150°C it decomposes to the spirocyclic species (165). Reaction of triphenylantimony with (164, X = Cl) gives a new bicyclic P-N-S compound (166), together with small amounts of two isomeric mixed ring compounds (167) and (168).[365] The major product (166) has a structure based on a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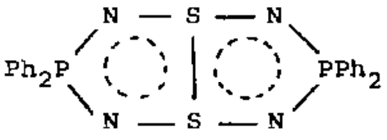
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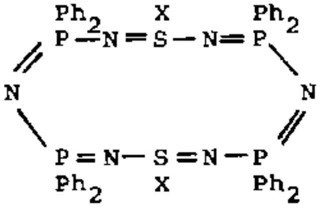

(169)

twelve membered ring bridged by a transannular S-S bond; the mean S-N distance is 1.598 with internal and terminal P-N distances of 1.582 and 1.619Å respectively. Compounds (167) and (168) have also been isolated from the very complex reactions which occur when S_4N_4 in refluxing toluene is treated with the diphosphines, P_2Me_4 or P_2Ph_4.[366] In addition the reactions give the known compounds $R_2PS_2N_3$ and $(NPR_2)_{3\text{ and }4}$. Thermolysis of (164, X = Cl or I) to the spirocyclic (165) probably proceeds via a twelve membered ring intermediate (169) which can then lose SX_2. Evidence to support this has been obtained by the isolation of (169, X = NMe_2) which is formed when (164, X = NMe_2) stands in acetonitrile solution.[367] From an X-ray structure, compound (169, X = NMe_2) is centrosymmetric thus the dimethylamino groups occupy trans positions; the S-N(endo) bonds (1.590Å) are shorter than the exo bonds (1.703Å) and on heating the compound is indeed converted to the spiro-derivative (165).

5.2.5 Bonds to Oxygen

The +3 Oxidation State. The chemistry of the phosphorus chalcogenides with an adamantane structure has been reviewed.[368] The synthesis of three members of the oxide series, P_4O_n for n = 7-9, from either elemental phosphorus or P_4O_6 has been reexamined, and the reactions of P_4O_7 and P_4O_8 with methanol in benzene shown by paper chromatography and ^{31}P n.m.r. spectroscopy to follow the reactions in equations (47) and (48).[369]

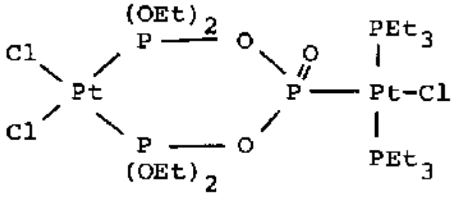
$$P_4O_7 + 6MeOH \rightarrow (MeO)_2PHO + (MeO)(HO)PHO + (MeO)_3P + H_3PO_4 \quad ...(47)$$

$$P_4O_8 + 5MeOH \rightarrow H_4P_2O_7 + (MeO)_2PHO + (MeO)_3P \quad ...(48)$$

Hydrogen bonding between phosphorous acid and the fluoride ion is assessed at 61 kJ mol^{-1} from ab initio calculations,[370] but attempts to show the presence of this species in aqueous solution led to the isolation of the 1:1 adduct $KF.HPO_3H_2$. This is however not the same species as that obtained in non-aqueous systems which is known to contain strong hydrogen bonds.

As expected, hydrogen bonding (O---O separations 2.529 and 2.547Å) plays an important role in the structure of KH_2PO_3.[371] The X-ray powder data for $NaH_2PO_3.H_3PO_3$ has been indexed.[372]

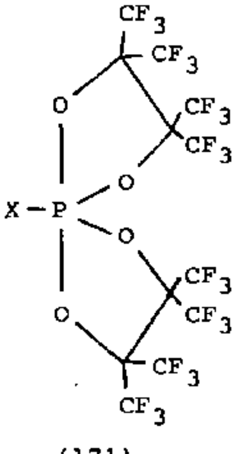
A platinum complex (170) of the unknown triphosphorous acid, $H_5P_3O_7$, as a bridging group has been identified from the reaction



(170)

of trans-$Pt_2Cl_4(PEt_3)_2$ and tetraethyldiphosphate;[373] the compound can also be obtained by hydrolysis of $PtCl_2[PCl(OEt)_2]PEt_3$ with hydrochloric acid in acetone. Reaction of the phosphonite, $R^1R^2POCH(CF_3)_2$ where $R^1 = R^2$ = Me or Bu^t or R^1 = Me, $R^2 = Bu^t$, with methyl iodide yields thermally stable iodides $[R^1R^2MePOCH(CF_3)_2]^+I^-$.[374] Among the new compounds obtained using the mercury or xenon fluorotellurates, $M(OTeF_5)_2$, are $M(OTeF_5)_3$ where M = P or As, $OPF_2(OTeF_5)$, $OP(TeF_5)_3$ and $As(OTeF_5)_5$.[375]

The +5 Oxidation State. The hydrogen atom in the hydrophosphorane (171, X = H) can be replaced by a variety of other groups without changing the basic structure.[376] For example halogen derivatives (171, X = Cl or Br) result with the free halogen and the hydroxy analogue from a reaction with DMSO; water hydrolyses the compound to phosphorous acid and perfluoropinacol but the organo



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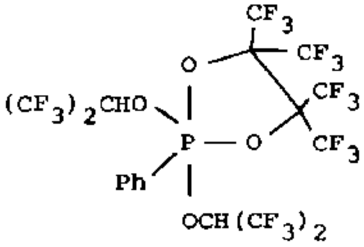
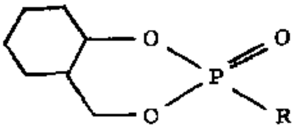


(172)

derivatives, (171, X = $PhCH_2$ and MeC(O)) can be prepared from the hydrogen starting material by reactions with $PhCH_2Br$ in the presence of tertiary amine and acetyl chloride respectively. Reaction with trimethylamine alone converts (171, X = H) to the salt, Et_3NH^+ $P[O_2C_2(CF_3)_4]_2^-$, in which the phosphorus atom is in distorted pseudo-trigonal bipyramidal coordination with a lone pair of electrons in the equatorial site.[377] P-O axial distances are 1.772 and 2.019Å with equatorial distances of 1.675 and 1.687Å.

The dioxaphospholane (172) shows a 27% deviation from trigonal bipyramidal geometry[378] and structures for two related dioxaphosphorinanes (173, R = 2,4-dinitrophenyl and p-methoxyphenoxy)[379] and the ammonium salt of the dioxaphosphorinane



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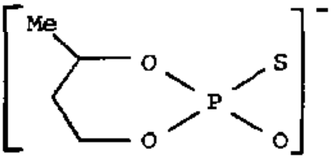
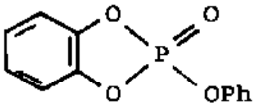


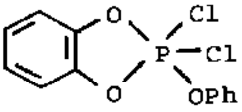
(174)

sulphide (174) have also been determined.[380]

Reactions between PCl_5 and o-phenylene phosphates (175) and phosphonates are similar and lead to five coordinate species.[381] Products such as (176) are formed initially and on further treatment with (175) are converted to di-chelated species (177, X = Cl) by loss of $(PhO)_2POCl$. The related compound (177, X = OPh)



(175)



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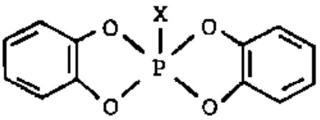
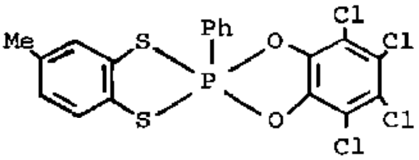


(177)

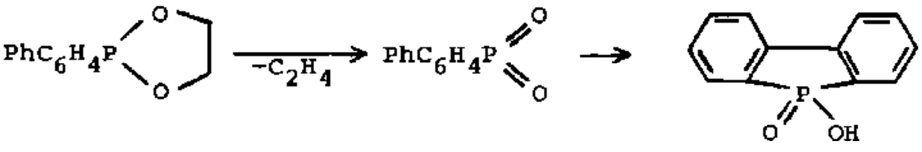
can be obtained by treating the chloride with (175). The least distorted square pyramidal phosphorane thus far noted is the di-chelated derivative (178) where the geometry about phosphorus is 93% along the Berry coordinate from ideal trigonal bipyramidal geometry.[382] The basal positions are occupied by the



(178)

Group 6 atoms.

Monomeric phosphonates, RPO_2 where R = PhC_6H_4[383] or 2,4,6-tri-(t-butyl)phenyl,[384] have been unambiguously identified as the initial products of flash vacuum pyrolysis at 600-800°C of the cyclic phosphonites shown in equations (49) and (50) (see ref. 478 for the sulphur analogue). The final products, isolated in



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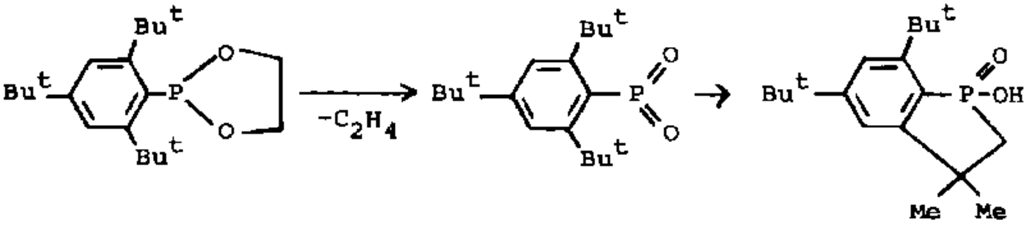
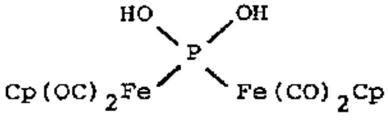


...(50)

good yields, result from insertion reactions into C-H bonds.

Irradiation of the cationic complex (179) leads to CO loss and formation of the phosphido-bridged complex (180),[385] the first example of a complex containing a P(O)OH group. X-ray crystallography points to a cis arrangement of cyclopentadiene groups with P-O bond distances of 1.514 and 1.587Å.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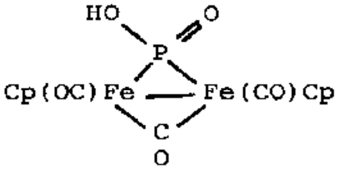
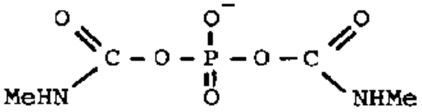

(180)

Carbamoylphosphates (181) and (182) can be obtained readily from reactions between hydrogen and dihydrogen phosphates and methyl isocyanate in a range of solvents, including acetonitrile, chloroform, DMF and, rather surprisingly, water.[386] On treatment with amines in aqueous solution, these compounds lead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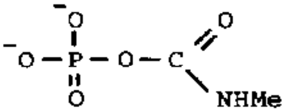

(182)

to a variety of amidophosphates, among which $NH_4[O_2(HO)PNH_2]$ and $Ca[O_2(HO)PNHMe]_2.4H_2O$ have been isolated.[387] A hydrated calcium phosphoramidate, $Ca(HPO_3NH_2)_2.1{\cdot}5H_2O$, has been isolated from calcium chloride and $NaHPO_3NH_2$ in aqueous solution, but even at room temperature it decomposes to $Ca_2P_2O_7.H_2O$.[388] Ammonolysis of the 2:1 adduct, $py_2.P_2O_5$, with liquid ammonia yields a mixture of $(NH_4PO_3)_x$ and $(NH_4)_2P_2O_5(NH_2)_2$.[389]

An X-ray structure for the steel corrosion inhibitor, $ZnPO_3F.2{\cdot}5H_2O$, shows two independent PO_3F^{2-} groups and zinc ions in both tetrahedral and octahedral coordination.[390]

Phosphonate and arsenate complexes, $Me_2Sn(PhEO_3)$ where E = P or As, can be obtained in two isomeric forms, based probably on two dimensional sheets (α-form) and infinite chains (β-form), according to i.r. and variable temperature Mössbauer data.[391] Polymeric chains with octahedrally coordinated calcium atoms bridged by diethylphosphate groups are present in the structure of

$Cd[O_2P(OEt)_2]_2$.[392]

N.m.r. spectra for the substituted ethylenediamine, $(^{2-}O_3PCH_2)_2NCH_2CH_2N(CH_2PO_3{}^{2-})_2$, and its metal complexes point to preferential protonation of nitrogen in the free ligand but oxygen in the complexes.[393] The lanthanide complexes show ABX ^{31}P spectra consistent with long lived Ln-N but short lived Ln-O bonds. Complex formation between phosphoryl ligands such as R_3PO, where R = NMe_2, morpholino, Bu or Ph, and $(Me_2N)_2P(O)NMeP(O)(NMe_2)_2$ with a range of 3d metal trifluoromethane sulphonates has been studied.[394] Tin(IV) complexes with the bis(phosphoryl) ligand, $Ph_2P(O)CH_2CH_2P(O)Ph_2$, have the formula R_2SnCl_2L, but from X-ray crystallography the ligand is essentially unidentate for R = Pr (Sn-O 2.24 and 2.58Å) while for R = Bu it behaves as a cis chelating group (Sn-O 2.27 and 2.27Å).[395]

Conformational isomerism in $MeP(O)(OMe)_2$ and $Me_2P(O)OMe$ has been investigated by matrix studies at 20K, i.r. investigations on the compounds in the vapour and condensed phases and by deuteration experiments.[396-398]

Spectra of the Group 1 monomeric phosphates MPO_3 and phosphites MPO_2, obtained by matrix isolation methods, suggest that they all have C_{2v} structures with bidentate phosphorus groups as mentioned in previous work in this area.[399]

Dehydration of NaH_2PO_4 to cyclotrimetaphosphate and Maddrell's salt is controlled, according to recent experiments, by nucleation and crystallisation of the two products.[400] If the monophosphate is seeded with either of the pure products, the reaction is structure controlled and yields either pure trimetaphosphate or pure Maddrell's salt. Dehydration of $Cs_2HPO_4.1{\cdot}5H_2O$ on heating first gives the 0·5 hydrate, then the anhydrous salt and at 220-320°C, it is converted to β-$Cs_4P_2O_7$.[401] The magnesium phosphate complex, $Mg(H_2PO_4)_2.4$ urea has been characterised[402] and i.r. data have been collected for $Sr(H_2PO_4)_2.H_2O$ and its deuterated analogue.[403] Amorphous calcium phosphate and hydroxylapatite have been characterised by ^{31}P n.m.r. spectroscopy (magic angle spinning, cross polarisation, variable temperature) and by comparison with other calcium phosphates the amorphous material is probably not a mixture of protonated and unprotonated phosphates.[404]

The Na_3PO_4-$Sr_3(PO_4)_2$-$EuPO_4$ system has been investigated by d.t.a. and X-ray diffraction[405] and these techniques have been used in a study of $Ge(OH)EO_4$ where E = P or As.[406] The phosphorus compound is converted to $Ge_5O(PO_4)_6$ and GeO_2 at 710°, a similar reaction occurs with the arsenic derivative at a much lower temperature.

The sparingly soluble solids, $Pb_2(NO_3)PO_4.2H_2O$, $PbHPO_4$ and $Pb_5(OH)(PO_4)_3$, together with precipitates of variable composition, have been obtained from reactions between $Pb(NO_3)_2$ and $Me_2NH_2(HPO_4)$.[407] Conditions for the formation of mixed zinc cobalt phosphates, $Zn_{3-x}Co_x(PO_4)_2 4H_2O$, from mixtures of the metal sulphates and $(NH_4)_2HPO_4$ have been determined[408] and thermolysis of the species for x = 0.5 to 1000°C has been studied.[409]

Hydroxyphosphates, $M(OH)PO_4$ where M = Zr or Hf, can be obtained from $MO(NO_3)_2.2H_2O$, H_3PO_4 and water in the ratio of 1:1:20 in a sealed ampoule at 250°C.[410]

Among the monophosphate structures determined in 1983 are: Na_2HPO_4 (with almost hexagonally close packed HPO_4^{2-} ions, orientationally disordered),[411] $RbH_5(PO_4)_2$ (containing a framework of PO_4 tetrahedra linked by strong hydrogen bonds),[412] $Na_3PO_4.8H_2O$,[413] $NaMg_4(PO_4)_3$ (obtained by heating a $MgCO_3-(NH_4)_2HPO_4$ mixture to 1173K),[414] the low temperature form of $NaCaPO_4$,[415] $CaK_3H(PO_4)_2$ (with a glaserite-type structure),[416] α-$NaCuPO_4$ (from Na_3PO_4 and $Cu_3(PO_4)_2$ on heating to 1023K),[417] $K_3Fe_2(PO_4)_3$,[418] $Co(H_2PO_4)_2.2H_3PO_4$ (contains hydrogen bonded PO_4 groups in layers parallel to the yz plane, two neighbouring layers are linked by further hydrogen bonds and Co^{2+} ions into sheets)[419] and $LnPO_4$ (for Ln = Tb,[420] Dy,[420] Ho,[420] Er,[421] Tm[421] and Yb;[421] the compounds were prepared from the appropriate oxide and $PbHPO_4$ at ca. 1360°C and have the zircon structure).

A sodium salt containing both mono- and di-phosphate groups, $Na_5H_2(PO_4)(P_2O_7)$ has been prepared by a solid state reaction between $(NaPO_3)_4.H_2O$ and Na_2O at 623K.[422] The two phosphate anions are connected by hydrogen bonds to give a three dimensional network.

Conditions leading to the different forms of hydrated $Ti(HPO_4)_2$, an inorganic ion exchanger, have been defined showing, for example, that the monohydrated α-form can be obtained by heating the amorphous phosphate at 110-165°C with phosphoric acid.[423] The $H^+-Co(NH_3)_6^{3+}$ exchange on α-zirconium phosphate leads to an increase in the interlayer separation from 7.6 to 11.2Å.[424]

Lithium exchange has been studied using α-$Hf(HPO_4)_2.H_2O$,[425] and the synthesis and exchange properties of γ-$Zr(HPO_4)_2.2H_2O$ have been investigated.[426] The use of different substituents at phosphorus in mixed species of the type, $Th(O_3PPh)_n(O_3PC_6H_4Ph)_{2-x}$ for x = 0-2, has been investigated as a means of introducing microporosity into layered structures.[427] X-ray data show an apparent linear increase in the interlayer spacing with increasing incorporation of biphenylphosphonate groups but an alternative explanation is possible in terms of bonding of these groups from normal as a result of strain imposed by incipient voids. Similar Th and Zr layered structures containing p-terphenyl groups have also been synthesised with layer spacings of ca. 33Å;[428] when a terphenyl group bridges between two layers separations are in the order of 18.6Å.

Two mixed oxide layer hydrates, $VOPO_4.2H_2O$[429] and $NbOPO_4.3H_2O$,[430] have been synthesised. The vanadium compound will intercalate species such as pyridine and can be reduced by mild reagents such as iodide ion to products formulated as $Mx_{/n}VOPO_4.(2+y)H_2O$, where M = Li, x = 1.0 and y = 2.1, for M = NH_4, x=0.48 and y = 2.0. The niobium compound will intercalate alkylamines but other species such as DMSO, ethyleneglycol and formamide, which are suitable guest molecules in other layer phosphates, are not incorporated and the compound is partially dehydrated to the monohydrate.

V_2O_5 reacts with a mixture of aqueous H_3PO_3 and H_3PO_4 to give an intermediate, which can be converted by heat treatment to the crystalline diphosphate, $V_4(P_2O_7)_3$;[431] an isostructural chromium compound has also been obtained during the thermal decomposition of the polyphosphate, $Cr(PO_3)_3$.

The hydrolysis of $Na_4P_2O_7$ and $Na_5P_3O_{10}$ at 100°C has been followed by ^{31}P n.m.r. spectroscopy;[432] the reaction of the diphosphate is catalysed by urea but surprisingly the triphosphate hydrolysis is inhibited. It is suggested that the presence of different hydrogen bonding systems with the two phosphates accounts for this different behaviour (see also ref. 456).

Symmetrically substituted diacetyl di- and tri-phosphates can be obtained following the reactions in equations (51) and (52),[433] but when ammonium triphosphate is the starting material, the

$$Na_2H_2P_2O_7 + 2Ac_2O \rightarrow Na_2[P_2O_5(OAc)_2] + 2HOAc \qquad \ldots(51)$$

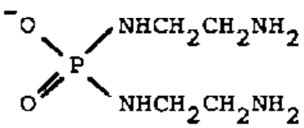
$$Na_3H_2P_3O_{10} + 2Ac_2O \rightarrow Na_3[(AcO)PO_3PO_2PO_3(OAc)] + 2HOAc \qquad ...(52)$$

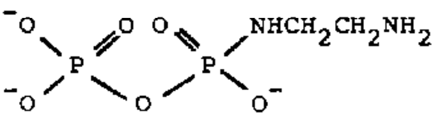
product is a new modification of ammonium trimetaphosphate.

Mixtures of copper(II) oxide and a dihydrogen phosphate on heating to ca. 700°C give $M_2CuP_2O_7$, where M = Li,[434] Na[434] and K[435] and a further double diphosphate, $Na_2UO_2P_2O_7$, has been observed in $Na_4P_2O_7$-$(UO_2)_2P_2O_7$ system.[436] Anhydrous $K_2H_2P_2O_7$ shows a bridging P-O-P angle of 131.0° with bridge and terminal P-O bond distances of 1.618 and 1.565Å respectively.[437] Crystals of $K_3HP_2O_7.Te(OH)_6.H_2O$ can be isolated by evaporation of a 1:1 mixture of the components and, as in other compounds of this type, there is no interaction between the two species[438] (see also ref. 443).

Structures have been reported for the isostructural erbium[439] and neodymium[440] hypophosphates, $MHP_2O_6.4H_2O$; the $P_2O_6^{4-}$ anions [P-P distance 2.196 (Er) and 2.188Å (Nd)] are linked by hydrogen bonds into infinite chains.

Three new species, (<u>183</u>)-(<u>185</u>), have been identified as products in the reaction of sodium trimetaphosphate and ethylenediamine in the 8-12 pH range.[441] The reaction however does not take place in acid solution nor does ethylenediamine react with mono-, di- or triphosphate. The structures of $Na_2HP_3O_9$[442] and $2(NH_4)_3P_3O_9.Te(OH)_6$[443] have been determined by single crystal X-ray methods and data for $PbNa_4(P_3O_9)_2$[444] show that the compound is best represented as $(Pb,Na)Na_3(P_3O_9)_2$, where there is a statistical occupancy of the lead position.


(<u>183</u>)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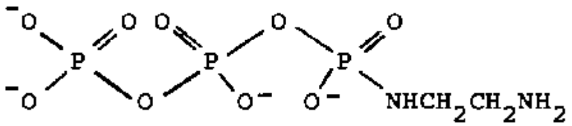

(<u>185</u>)

The vanadium triphosphate, $VH_2P_3O_{10}.2H_2O$, which can be prepared from the metal and phosphoric acid at 463-573K, is isomorphous with the aluminium, gallium, chromium and iron compounds.[445] Thermal analysis and detailed vibrational spectroscopy suggest the presence of four different water environments in the double triphosphate, $Na_2Al(P_3O_{10}).4H_2O$.[446]

A reinvestigation of the $Na_4P_4O_{12}$-H_2O system has confirmed the existence of a monohydrate, stable in the 100-120°C temperature range, in addition to the well known tetrahydrate and anhydrous materials.[447] An X-ray determination shows that the anion structures (D_{2d}) in the monohydrate and anhydrous forms differ only slightly. On heating in a moist atmosphere, a single crystal of $K_2Pb(P_4O_{12})$ is converted at 537°C to crystallographically orientated $Pb_2P_2O_7$ and an amorphous phase;[448] this behaviour is in contrast to the reaction in anhydrous conditions which leads to polyphosphate.

Full structures have been determined for the following tetrametaphosphates: $Ca_2(P_4O_{12}).4H_2O$,[449] $Zn_2(P_4O_{12})$,[450] $Ce(NH_4)(P_4O_{12})$,[451] $Ni_2(P_4O_{12})$ (obtained from NiO and $NH_4H_2PO_4$ at 1200K; the anion is centrosymmetric),[452] $SrNa_2(P_4O_{12})$ (prepared by treating the two metal carbonates with phosphoric acid at 623K; the anion has $\bar{4}$ symmetry),[453] $SrNa_2(P_4O_{12}).6H_2O$ (obtained from concentrated aqueous solutions of $Sr(NO_3)_2$ and $Na_4P_4O_{12}.4H_2O$; the anion has mm symmetry).[454]

The linear tetraphosphates, $Sr_3P_4O_{12}$ and $Ba_3P_4O_{13}$, prepared from the metal chloride and the acidified phosphate solution obtained when $Na_4P_4O_{12}$ is hydrolysed with NaOH, are amorphous to X-rays.[455]

Hydrolysis of two higher cyclic metaphosphates, $P_6O_{18}{}^{6-}$ and $P_8O_{24}{}^{8-}$, with hydrochloric acid can be followed by anion exchange chromatography,[456] showing a decrease in rate from tri- to hexametaphosphate but an increase with the octaphosphate. The latter is possibly due to its stronger proton affinity.

Infinite chains in $Zn(PO_3)_2$ have a period of two tetrahedra[457] while in $LiK(PO_3)_2$, obtained from a mixture of $LiPO_3$ and KPO_3 heated to 833K, the repeating unit is 8 PO_4 units.[458] The mixed polyphosphate, $KCe(PO_3)_4$, is isostructural with the neodymium compound;[459] neutron diffraction data for $UO_2H(PO_3)_3$ indicate P-O-H angles of 119.4 and 116.0° with O-H distances of 0.98 and 0.99Å.[460] Single crystals of two vanadium polyphosphates, α-$VO(PO_3)_2$ and $V(PO_3)_3$, have been isolated from mixtures of V_2O_5, H_3PO_4 and H_2SO_4 in the ratio 1:16:2 after heating to 300°C for two weeks.[461] The structure of the latter is based on a mixed framework of VO_6 octahedra and PO_4 tetrahedra linked via their apices which leads also to polyphosphate chains with a repeating unit of six PO_4 groups.

5.2.6 Bonds to Sulphur or Selenium

Precise bond distances have been obtained from X-ray and neutron diffraction data on α-P_4S_3 and further data show that librational amplitudes about the three-fold axis predominate as the $\alpha \rightarrow \beta$ transition is reached.[462]

Metal complexes containing coordinated P_4S_3 or P_4Se_3 units are little known, but the nickel and palladium derivatives $LNi(P_4S_3).2PhH$, $LNi(P_4Se_3).2PhH$, and $LPd(P_4S_3)$, where L is the tetradentate ligand, tris(diphenylphosphino)ethylamine, $N(CH_2CH_2PPh_2)_3$, have been recently characterised.[463] A structure for the P_4Se_3 derivative shows coordination via the apical phosphorus atom.[464] An iridium complex, $Ir(P_4S_3)(PPh_3)(CO)Cl$, on the other hand has a dimeric structure (see Figure 7), but here one of the P-P bonds of the basal triangle is broken and the two modified P_4S_3 groups bridge between the metal centres.[465] The compound is obtained by treating $Ir(PPh_3)_2(CO)Cl$ with P_4S_3 in benzene. P_4S_3 and P_4Se_3 behave in yet a different fashion on reaction with $[RhCl(cod)]_2$ when complexes of the type $[MeC(CH_2PPh_2)_3.Rh(P_3X_3)].PhH$ can be isolated.[466] The structure

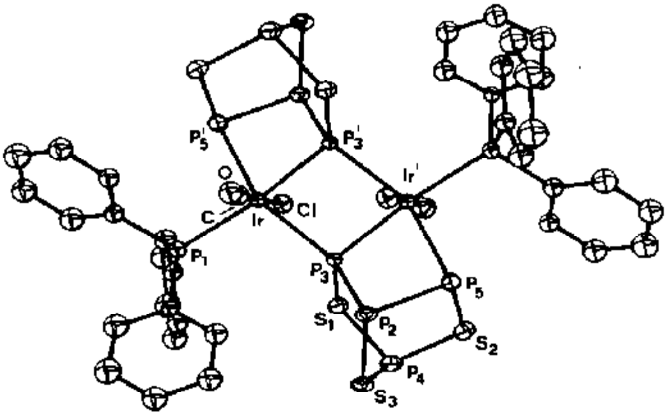
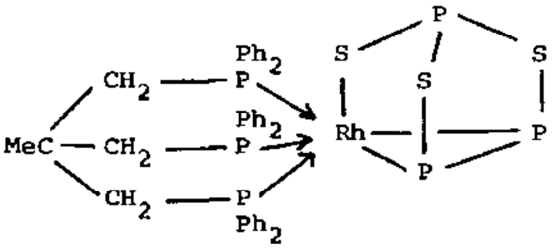


Figure 7. The structure of $[Ir(P_4S_3)(PPh_3)(CO)Cl]_2$ (reproduced by permission from Angew. Chem., Int. Ed. Engl., 22(1983)790).

of the P_4S_3 product (186) shows that the rhodium atom occupies one of the phosphorus positions in the base of the original P_4S_3 cage.



(186)

The heats of formation of a range of phosphorus sulphides, calculated by M.O. bond index methods, agree well with known data and it has been possible to establish useful P-P and P-S bond energy terms and to use them to predict which isomeric form of a particular compound will be stable.[467]

Pure samples of mixed species in the two systems $P_xAs_{4-x}S_3$ for x = 1-3 and $P_4S_xSe_{3-x}$ for x = 1-2 have been isolated by h.p.l.c.[468] In the P_4S_3-P_4Se_3 system there is no change in the number of phosphorus-chalcogen bonds and the reaction is entropy controlled but in the P_4S_3-As_4S_3 system there is, for example, preferential formation of PAs_3S_3 from a 1:3 mixture of P_4S_3 and As_4S_3. This follows from the fact that the P-S bond energy is substantially higher than that of an As-S bond and the product, 4 mols of PAs_3S_3, contains 12 P-S bonds compared with 6 P-S bonds in the starting material.

The monothiophosphates, $NH_4H_2PO_3S$ and $(NH_4)_2HPO_3S$, have been prepared from P_4S_{10} and unit cell data determined,[469] and the previously unknown symmetrical monothiodiphosphate, $(O_3PSPO_3)^{4-}$, has been isolated as the lithium or barium salt via the tetramethyl ester $(MeO)_2P(O)SP(O)(OMe)_2$.[470] The products are however contaminated by a variable amount of the corresponding carbonate. A crystal structure of the μ-disulphidebis(phosphate), $(C_6H_{11}NH_3^+)_4(O_3PSSPO_3)^{4-}$, shows P-S bonds with a mean distance of 2.14Å and a P-S-S-P torsion angle of 93.3°.[471]

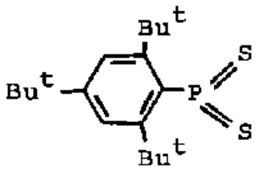
Hydrogen bonding in $Na_3PS_4.8H_2O$ has been studied by i.r. spectroscopy and single crystal X-ray diffraction[472] and the structure of $Pd_3(PS_4)_2$, prepared from the elements at 600°C, shows extensive distortion of the PS_4^{3-} anion (S-P-S angles 97.5 and 119.8°) from the expected tetrahedral geometry.[473]

Mixtures of thiophosphates containing different oxidation state phosphorus atoms can be produced by oxidising either white or red phosphorus or P_4S_3 with aqueous solutions of alkali polysulphides.[474] Among the compounds isolated during this study were: $Na_6P_6S_{12}.16H_2O$, $K_5P_5S_{10}.5H_2O$, $Na_5P_3OS_7.8H_2O$, $Na_5P_3S_8.10H_2O$ and $Na_4P_2S_6$. Partial hydrolysis of $Na_5P_3S_8$ yields the hydridothiodiphosphate $(S_3PPS_2H)^{3-}$, which is also the major product when PCl_3 reacts with aqueous sodium sulphide.[475] The latter also yields oxo-, thio- and oxothio-phosphates.

The $P_2S_6{}^{2-}$ ion in $Tl_2P_2S_6$, obtained from the elements at 930°C, has D_{2h} symmetry with terminal and bridging P-S distances of 1.969 and 2.132Å respectively.[476] The bridging P-S-P angle is 86.9°. The isomeric P-P bonded structure is present in the $P_2S_6{}^{4-}$ ion of a new, orthorhombic $(P2_12_12_1)$, modification of $Ag_4P_2S_6$.[477] The molecular parameters are very similar to those in the previously described monoclinic $(P2_1/b)$ form but the three dimensional packing differs.

A member of the previously unknown dithiooxophosphorane series (187) has been isolated, as shown in equation (53), as orange crystals soluble in acetonitrile.[478] Structures for the dimethyl-

$$Bu^t{}_3C_6H_2P(SiMe_3)_2 + S_2Cl_2 \rightarrow$$



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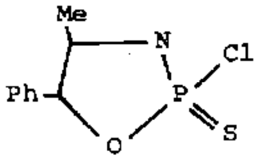
and dicyclohexyl-thiophosphinic acids, $R_2P(S)OH$, show the presence of centrosymmetric dimers with almost linear O-H---S hydrogen bonds (O---S 3.12Å for R = Me).[479] Almost quantitative yields of the pyridinium dithiophosphates, $PS_2X_2{}^-$ where X = Cl or Br, have been obtained by treating the dithiophosphoric acid chloride - pyridine betaine, $py.PS_2Cl$, with the appropriate anhydrous hydrogen halide.[480] The corresponding $PS_2F_2{}^-$ salt can be obtained from the betaine with a saturated aqueous solution of NH_4F; reactions of $PS_2Cl_2{}^-$ with alcohol and amines, R^1R^2NH where R^1 = alkyl and R^2 = H or alkyl, yield respectively $(RO)_2PS_2H$ and amine salts of the $[(R^1R^2N)_2PS_2]^-$ anion.

Crystal structures have been determined for the 2S,4S,5R[481] and 2R,4S,5R[482] forms of the oxazaphospholidine sulphide (188). I.r. and Raman data for $MeP(S)F_2$ have been assigned and a normal

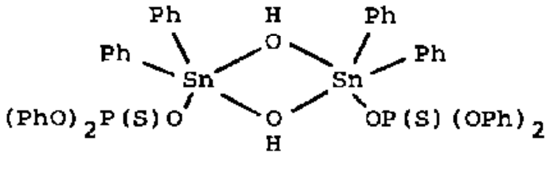


(188)

coordinate analysis carried out; the following bond distances have been obtained from microwave data: r(P–C) 1.809, r(P–F) 1.547 and r(P=S) 1.878Å).[483]

There is Cl–CF_3S exchange when thiophosphoryl chloride, $PSCl_3$, and $CF_3SP(O)Cl_2$ react giving a 50% yield of $CF_3SP(S)Cl_2$.[484] Analysis of the n.m.r. spectra of a series of dialkylthiophosphoryl bromides has revealed a correlation between the ^{31}P chemical shift and the number of β-methyl groups.[485]

There is continuing interest in the structures of dithiophosphate and phosphinate complexes. Studies on the zinc complexes, $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]^-$ and $[Zn(S_2PPh_2)_3]^-$, shows that in each case the zinc atom is in slightly distorted tetrahedral coordination to two unidentate and one chelating ligand.[486] Eight fold dodecahedral coordination is found for the lanthanides in both the bis(dimethylacetamide) adduct of $La[S_2P(OPr^i)_2]_3$[487] and the anions in $Ph_4As[Ln(S_2PR_2)]_4$, whereas Ln = Ce or Er, R = OMe and Ln = Nd or Ho, R = OPr^i.[488] In the latter, the arrangement of sulphur atoms has almost perfect D_{2d} symmetry. The structure of $Ph_2Sn[OP(S)(OPh)_2]OH$, an intermediate in the hydrolysis of $Ph_2Sn[OP(S)(OPh)_2]_2$, is dimeric (189) with distorted trigonal bipyramidal coordination about the tin atoms.[489] Neutral dimeric products with formulae such as $[Pr(OSPMe_2)_3.EtOH.PrOH]_2$, $[Pr(OSPMe_2)_3(H_2O)_3]_2.4H_2O$ and $[Er(OSPMe_2)_3(H_2O)_2]_2$ have also been isolated from reactions between Me_2POS^- and La^{3+}, Pr^{3+}, Nd^{3+} and Er^{3+}.[490] Structures of all three compounds have been determined



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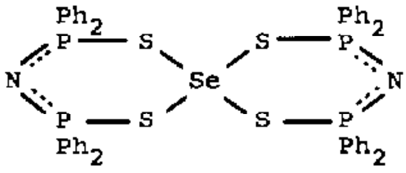


(190)

(see Figure 8 for the erbium derivative) showing that the ligand is present both as a unidentate group and as a simultaneous chelating-bridging group. The four unidentate groups are coordinated via the oxygen atom while the sulphur atoms are involved in hydrogen bonding interactions with the coordinated water molecules. The related dicyclohexyl ligand gives a similar

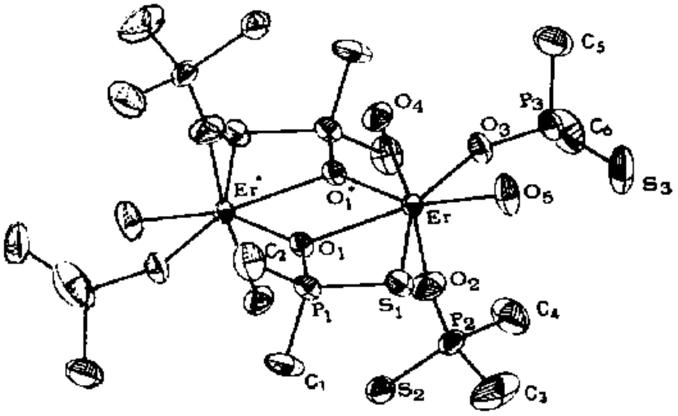


Figure 8. The structure of $[Er(OSPMe_2)_3(H_2O)_2]_2$ (reproduced by permission from Z. Anorg. Allg. Chem., 506(1983)115).

dimeric neodymium complex $[Nd(OSPR_2)_3(H_2O)_2]_2$ but with Er^{3+} the product is the ammonium salt $NH_4^+[Er(OSPR_2)_4(H_2O)_2]^-$,[491] where erbium is in six-fold coordination to four oxygens of the ligands and two water molecules.

A new selenium(II) species $(SPh_2P.N.PPh_2S)_2Se$ (190) has been isolated for structure determination by treating $Se[S_2P(OEt)_2]_2$ with $NH_4[N(Ph_2PS)_2]$ in methanol.[492]

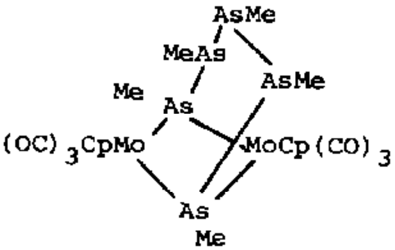
5.3 ARSENIC

5.3.1 Polyarsines

A diarsene, RAs=AsR', incorporating the bulky substituents R = 2,4,6-$Bu^t{}_3C_6H_2$ and R' = $CH(SiMe_3)_2$, has been synthesised from $RAsH_2$ and $R'AsCl_2$ in the presence of DBU in THF solution (see ref. 171 for the corresponding RP=AsR').[493] As with related compounds, the geometry is trans about the double bond which is 2.224Å. As-As-C angles are 99.9 and 93.6° at the arsenic atoms carrying the alkyl and aryl substituents respectively. The compound reacts with

$Cr(CO)_5$.THF to give the adduct $RAs{=}AsR'Cr(CO)_5$ in which the carbonyl is attached via the the alkyl arsenic lone pair of electrons thus yielding the first complex containing an unsupported As-As double bond.[494] The arsenic-arsenic separation (2.246Å) changes little from the value in the uncomplexed diarsene.

New metal carbonyl complexes have been isolated using both $(MeAs)_5$ and $(PhAs)_6$ as starting materials. With the penta-arsine, reaction with $[CpMo(CO)_3]_2$ leads to ring opening and the two ends of the five membered chain bridge between both molybdenum atoms.[495] The compound formulated as $[CpMo(CO)_3]_2(MeAs)_5$ has the structure (191), the terminal arsenic atoms behave as three electron donors. Under mild conditions, the cyclohexaarsine with $Co_2(CO)_8$ gives a black solid, identified by X-ray diffraction as



(191)

$[Co_8(\mu_6\text{-}As)(\mu_4\text{-}As)(\mu_4\text{-}AsPh)_2(CO)_{16}]_2$.[496] Each half of this complex species contains four distorted tetrahedral units, i.e. three $AsCo_3$ and one As_2Co_2, connected to give a cluster of clusters. The heavy atom framework is shown in Figure 9.

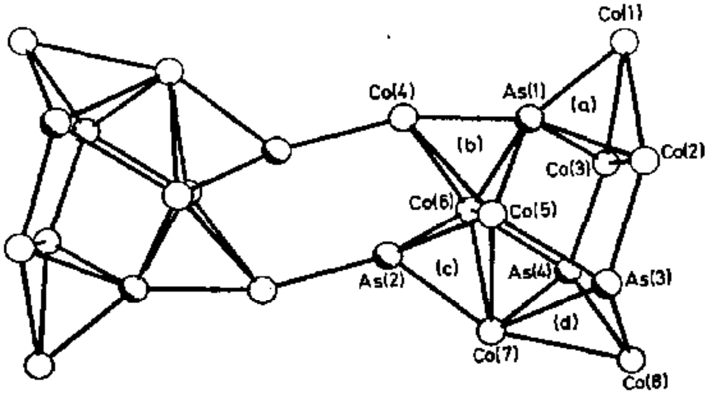
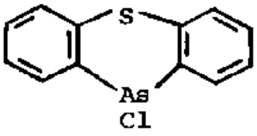


Figure 9. The structure of $[Co_8(\mu_6\text{-}As)(\mu_4\text{-}As)(\mu_4\text{-}AsPh)_2(CO)_{16}]_2$ (reproduced by permission from J. Chem. Soc., Chem. Commun., (1983)39).

The $(PhAs)_6$ structure has been redetermined to obtain a standard for the As-As single bond length.[497] There are three independent distances in the range 2.456-2.464Å; the ring has the chair conformation with phenyl groups in equatorial positions.

5.3.2 Bonds to Carbon

Organoarsenic chemistry for 1981 has been surveyed.[498] Arsenic-(III) cations carrying two η^5-pentamethylcyclopentadienyl groups, i.e. $(Me_5C_5)_2E^+ \; BF_4^-$ where E = As or Sb, have been isolated from reactions between $(Me_5C_5)_2EF$ and boron trifluoride in hexane at $-20^\circ C$.[499] An X-ray structure has been determined for the arsenic compound; both compounds show dynamic n.m.r. behaviour in solution. The 10-chlorophenothiarsenin (192) structure consists of two almost planar C_6H_4AsS groups which form a dihedral angle of 152.7°;[500] the chlorine atom occupies a quasiaxial position.

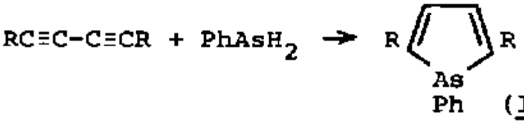


(192)

The ligands 2-dimethylarsino-[501] and 2-methylarsino-ethanol[502] have been synthesised, and metal carbonyl complexes incorporating one and two molecules of the former have been isolated. The former also reacts with alkyl halides giving, for example, $(Me_3AsCH_2CH_2OH)I$ and $[CH_2(Me_2AsCH_2CH_2OH)_2]Br_2$ with respectively methyl iodide and dibromomethane.[501] Reactions of the monomethyl derivative with acrylates, $CH_2{:}CHX$, lead to $MeAs(CH_2CH_2OH)(CH_2CH_2\text{-}X)$.[502]

Electron diffraction data for Me_3As and Me_3Sb give the M-C distances as 1.968 and 2.163Å with bond angles of 96.1 and 94.1° respectively.[503] The mean As-C distance in Ph_3As is 1.957Å with a C-As-C bond angle of 100.1° from X-ray diffraction;[504] the asymmetric unit contains four independent Ph_3As molecules.

A range of substituted arsoles (193, R = Me, Et, Ph, p-MeC_6H_4, p-ClC_6H_4, etc. has been synthesised, see equation (54), and their



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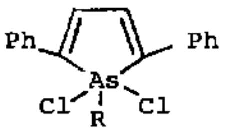
conversion to radical anions with lithium or potassium studied.[505] Reaction of (193, R = Ph) with $PhICl_2$ leads to the arsenic(V) derivative (194) which decomposes under mild conditions with loss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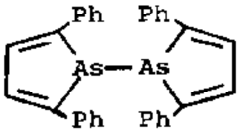

(195)

of RCl.[506] The resulting monochloride can then be converted to the diarsine (195) by treatment with NaMe.

Pyrolysis of the dibromide, $(Me_3SiCH_2)_3AsBr_2$, under reduced pressure proceeds with loss of Me_3SiBr via the ylid, $Br(Me_3SiCH_2)_2As{=}CH_2$, to the new tertiary arsine $(Me_3SiCH_2)_2AsCH_2Br$.[507]

5.3.3 Bonds to Halogens

Arsenic, antimony and bismuth(III) oxides on heating with an ammonium halide to 635K are converted to the ammine complexes $MX_3.NH_3$, where M = As, Sb or Bi and X = Br or I;[508] the compound $SbCl_3.2NH_3$ has also been isolated. Related complexes with mono-, di- and tri-methylamine can also be prepared.

The ternary compounds, Cd_2As_3I, $Cd_4As_2I_3$, Cd_5As_3I and Cd_3AsI_3, the first two in single crystal form, have been identified in the CdI_2-AsI_3-Cd_3As_2 system.[509]

Following the phosphorus reactions mentioned earlier,[286,287] high temperature experiments between $AsCl_3$, oxygen and silver lead to AsOCl, which can be detected either mass spectrometrically[510] or trapped in an argon matrix.[511] Bands are observed 980 and 380 cm^{-1} in the i.r. spectrum. Mass spectrometry also confirms the formation of SbOCl by a similar method[510] but the matrix isolation approach is complicated as SbOCl appears to be stable only in the presence of Sb_4O_6 and i.r. bands of the latter interfere with identification.[511]

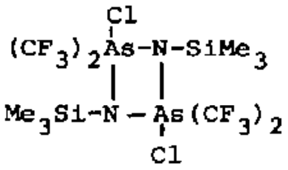
Black crystals of $I_4(AsF_6)_2$ result when elemental iodine is oxidised with an excess of AsF_5 in sulphur dioxide at room temperature;[512] the corresponding reaction with SbF_5 gives a dark green solution from which $I_4(SbF_6)(Sb_3F_{13})$ can be isolated. Both products have been analysed by X-ray crystallography which shows that the rectangular I_4^{2+} cation consists of two weakly interacting

I_2^+ cations.

The vapour species over $AsCl_4^+AsF_6^-$ have been investigated by mass spectrometry and matrix isolation - i.r. methods.[513] The primary products are AsF_5 and a new mixed halide, $AsFCl_4$, but a second new halide, $AsCl_2F_3$, melting at ca. -75°C, has been isolated following pyrolysis of $AsCl_4^+AsF_6^-$ at 100°C.[514] This compound however rapidly isomerises in the liquid phase to the ionic starting material; vibrational spectroscopy on the covalent form points to a C_{2v}, trigonal bipyramidal monomeric structure with two fluorine atoms in axial positions.

5.3.4 Bonds to Nitrogen

As-N bond formation occurs when $(CF_3)_2AsCl$ or CF_3AsCl_2 reacts with $LiN(SiMe_3)_2$ and, in the presence of chlorine, the former product $(CF_3)_2AsN(SiMe_3)_2$ is converted to monomeric $(CF_3)_2AsCl{=}NSiMe_3$.[515,516] On removal of solvent, the compound dimerises to (<u>196</u>), which contains a planar As_2N_2 ring with



(<u>196</u>)

trigonal bipyramidal geometry about arsenic. Axial positions are occupied by chlorine and one of the nitrogen atoms (As-N 1.933Å); the distance to the equatorial nitrogen atom is 1.768Å. On heating in a hydrocarbon solvent, compound (<u>196</u>) is converted to a mixture of the cycloarsazanes $[(CF_3)_2AsN]_3$ and 4.[516]

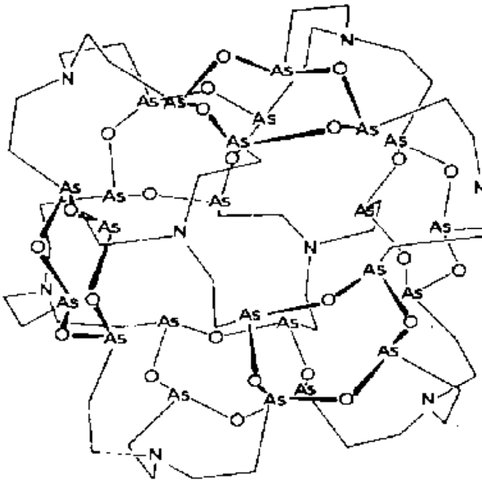
A number of monosubstituted metal carbonyl complexes have been formed by reacting $M(CO)_6$, where M = Cr, Mo or W, with the aminoarsines $Me_nAs(NMe_2)_{3-n}$ for n = 0-2.[517] On treatment with protonic reagents such as HCl, EtOH or EtSH, the As-N bonds are cleaved to give $M(CO)_5AsMe_nX_{3-n}$ where X = Cl, OEt or SEt.

5.3.5 Bonds to Oxygen

The spectra of matrix isolated alkali metal arsenites $MAsO_2$ and antimonites $MSbO_2$, for M = Na-Cs, have been interpreted in terms of cyclic C_{2v} structures with O-As-O and O-Sb-O angles of 115 and 106° respectively.[518] Crystals of a mixed arsenic-antimony oxide, $AsSbO_3$, result on heating a 1:1 mixture of As_2O_3 and Sb_2O_3 to 670K.[519] The compound is isostructural with claudetite and shows no evidence of arsenic-antimony disorder. Mean As-O and Sb-O distances are 1.80 and 1.95Å respectively with As-O-Sb angles of 132.3°.

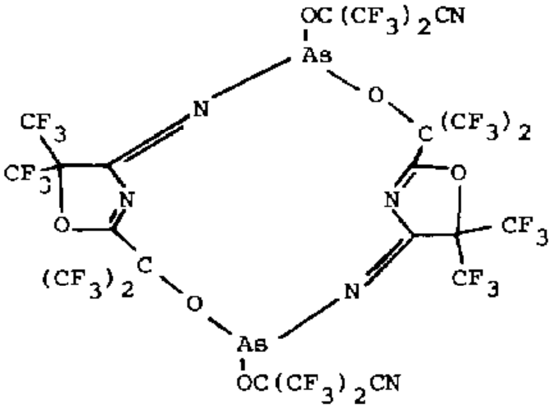
Both cis and trans forms of the arsenic(III) methoxytetrafluorotellurate, $As(OTeF_4OMe)_3$, have been isolated and characterised from reactions between arsenic trifluoride and the appropriate boron derivative.[520]

The triarsine, $N(CH_2CH_2AsPh_2)_3$, prepared by reaction between $NaAsPh_2$ and $[HN(CH_2CH_2Cl)_3]Cl$ in liquid ammonia, can be converted to the iodide on treatment with HI in CH_2Cl_2.[521] The iodide is the starting material for a series of new cryptands, e.g. $[N(CH_2CH_2)_3]_8(As_4O_4)_6$ and $[N(CH_2CH_2)_3]_8(As_4S_4)_6$, which result by reaction with respectively aqueous ammonia or hydrogen sulphide in the presence of triethylamine. The As-N-O derivative has the structure shown in Figure 10, andcontains six eight-membered As_4O_4 rings interlinked by $N(CH_2CH_2)_3$ groups. A new 14-membered macrocycle (<u>197</u>) has been prepared from $As(CN)_3$ and hexafluoracetone;[522] from the structure, it is clear that all the initial As-C bonds are cleaved during reaction.

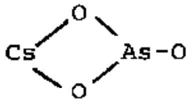


<u>Figure 10</u>. The structure of $[N(CH_2CH_2)_3]_8(As_4O_4)_6$ (reproduced by permission from J. Organomet. Chem., 252(1983)153).

Matrix isolation of vaporised samples of MH_2AsO_4, where M = K, Rb or Cs, give in addition to bands characteristic of the monomeric arsenites $MAsO_2$, extra absorptions that can be assigned



(<u>197</u>)



(<u>198</u>)

to molecular arsenates.[523] For $CsAsO_3$, the fundamentals at 978, 923, 880, 368 and 335 cm^{-1} can be associated with the C_{2v} structure (<u>198</u>). As_4 species containing from six to ten oxygen atoms have been identified in the mass spectra of As_2O_5 at temperatures between 862 and 933K.[524] The data also yield the following standard heats of formation: As_4O_7 -1209.5, As_4O_8 -1361.9, As_4O_9 -1495.4 and As_4O_{10} -1618.8 kJ mol^{-1}. Vibrational spectra of As_2O_5 and the isostructural $AsSbO_5$ have been analysed.[525]

Reaction of the bidentate ligand, $Ph_2As(O)CH_2CH_2As(O)Ph_2$, with Ph_3SnCl gives a 1:2 adduct in which each tin atom is in trigonal bipyramidal coordination with an oxygen atom from the ligand and the chlorine atom in axial positions.[526]

The structures of two secondary arsenic minerals, phaunouxite $Ca_3(AsO_4)_2.11H_2O$ and rauenthalite $Ca_3(AsO_4)_2.10H_2O$ (members of the extensive series of hydrated calcium arsenates) have been determined and the topotactic dehydration of the former to the latter has been investigated.[527] The mixed species, $Ca_9(Ca_xMg_{1-x})(AsO_4)_6(AsO_3OH)$ with x = ca. 0.5 is an isotype of $Ca_9Mg(PO_4)_6(PO_3OH)$ and has the whitlockite structure.[528]

Three nickel arsenates, $Ni(H_2AsO_4)_2.H_2O$, $Ni(HAsO_4).2H_2O$ and $Ni_3(AsO_4)_2.8H_2O$ have been isolated from reactions between $Ni(OH)_2$ and arsenic acid.[529] The first compound dehydrates at 500°C to give the cyclic trimetaarsenate, $Ni_3(As\ O_9)$, which on further heating to 730°C loses As_2O_5 to generate the diarsenate, $Ni_2As_2O_7$. The diarsenate can also be prepared by heating

$Ni_3(AsO_4)_2$ to 700°C. The basic arsenate $Cu_2(AsO_4)OH$ and two forms of $Cu(HAsO_4).1\frac{1}{2}H_2O$ have been isolated from similar reactions between arsenic acid and copper hydroxide.[530] Powder neutron diffraction data have been collected for $DUO_2AsO_4.4D_2O$.[531]

5.3.6 Bonds to Sulphur or Selenium

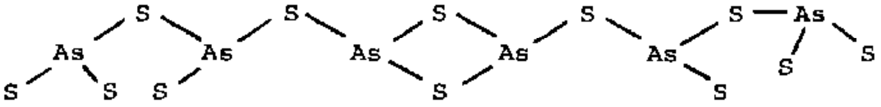
The crystal structure of tris(phenylthio)arsine shows the presence of discrete molecules (C_3 symmetry) with the arsenic lying on a three fold axis.[532] The As-S distances are 2.243Å and the S-As-S angles 96.38°. Arsenic, antimony and bismuth selenoates, $M(SePh)_3$ have been synthesised by reacting the appropriate thiophenolate with PhSeH in chloroform solution.[533] Redistribution reactions between $M(SPh)_3$ and $M(SePh)_3$ have been monitored by n.m.r. spectroscopy showing that for M = As the reaction occurs over a period of several hours at room temperature.

The α-form of arsenic tri(methylxanthate), $As(S_2COMe)_3$, and the corresponding ethyl derivative are isostructural, with the heavy atom lying on a three fold axis.[534] In the methyl compound the distorted octahedron of sulphur atoms about arsenic fall into two groups with bond distances of respectively 2.298 and 2.992Å. There is further weak S---S interaction (3.650Å) to give loosely bound dimers. The dithiocarbamates, $M(S_2CNR_2)_3$ and $M(S_2CNR_2)_2X$ where M = As or Sb, X = Cl or Br and $R_2 = -(CH_2)_2S(CH_2)_2-$, have been investigated by mass spectrometry.[535]

Arsenic(III) and the corresponding antimony and bismuth complexes with 2-mercaptoaniline have low solubility but from i.r. spectroscopy the ligand appears to be involved in only weak M-N bonding.[536]

Dialkyl dithiophosphates of the type $MCl_{3-n}[S_2P(OR)_2]_n$, for M = As and Sb, R = Et, Pr, Pr^i and Bu^i and n = 1 and 2, can be obtained either from the trihalide and the sodium salt of the dithiophosphoric acid or by comproportionation reactions between MCl_3 and $M[S_2P(OR)_2]_3$.[537] I.r. and n.m.r. data for the dithioarsinates, $Ph_{4-n}M(S_2AsR_2)_n$ where M = Si, Ge and Pb and R = Me and Ph, point to unidentate arsinate groups when M = Si or Ge but bidentate coordination appears to be present in the lead compounds.[538] Reactions of the sodium dithioarsinates, NaS_2AsR_2 for R = Me and Ph, with Ph_2PCl leads to the arsenic(III) derivative $R_2AsSP(S)Ph_2$ rather than the expected diphenylphosphinyl product $Ph_2PSAs(S)R_2$;[539] migration of sulphur from As(V) to P(III) has been confirmed by i.r. and n.m.r. spectroscopy.

The two, dark red sulpho-salt, $PbTlAs_3S_6$, obtained by hydrothermal synthesis in the Tl_2S-PbS-As_2S_3 system, contains both lead and thallium in seven fold coordination to sulphur.[540] Each arsenic atom is in pyramidal coordination to three sulphur atoms which are interconnected to give As_6S_{12} groups (199) containing an unusual As_2S_2 ring.



(199)

5.4 ANTIMONY

5.4.1 Polystibines

I.r. and Raman spectra for R_2SbSbR_2, where R = Me, Me_3Si and Ph, and data for $(Me_3Si)_4As_2$ have been assigned and force constants calculated for the methyl and trimethylsilyl antimony compounds.[541] These two compounds are thermochromic and their Raman spectra show strong lines at ca. 50 cm^{-1} which are assigned to the long itudinal acoustic mode of an infinite chain of antimony atoms. This assignment is supported by the absence of such bands in the spectra of the non-thermochromic compounds Ph_4Sb_2 and $(Me_3Si)_4As_2$.

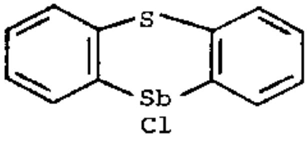
The Sb-Sb bond in Me_4Sb_2 is cleaved by an equimolar quantity of either bromine or iodine to give the appropriate dimethyl monohalide in high purity.[542] Reaction with methyl iodide, on the other hand, gives Me_3Sb and Me_2SbI at a 1:1 ratio but with an excess of MeI, the 1:2 addition compound $MeSbI_2.2Me_4SbI$ is the product. With $(4\text{-}MeC_6H_4)_2Te_2$, tetramethyldistibine is quantitatively converted to the telluro-stibine, $4\text{-}MeC_6H_4TeSbMe_2$, a yellow liquid and the first compound to be synthesised with a direct antimony-tellurium bond.[543]

Dehalogenation of Bu^tSbCl_2 with magnesium in THF solution has now been shown to give the cyclopentastibine $Sb_5Bu^t{}_5$ in addition to $Sb_4Bu^t{}_4$.[544]

5.4.2 Bonds to Carbon

The 1981 annual survey of organo-antimony chemistry has been published.[545] The organo-antimony halides, Ph_2SbX and $PhSbX_2$ where X = Cl or Br can be obtained readily in high purity by redistribution reactions between Ph_3Sb and SbX_3 in mole ratios of respectively 2:1 and 1:2.[546] The reactions which take place in the melt at, or slightly above, room temperature can be extended to other substituted aryl derivatives. The methyl derivatives, $MeSbX_2$ where X = Cl or Br, can be obtained in good yield by treating the antimony(III) halide with either $PbMe_4$, $SnMe_4$ or $SbMe_3$.[547]

The structure of thioantimonin (200), obtained by treating the corresponding Me_2Sn substituted heterocycle with antimony(III) chloride, differs from that of the arsenic analogues as here the chlorine atom is in a quasi-equatorial position.[548] Sb-Cl and Sb-C distances are 2.390 and 2.141Å with C-Sb-C and Cl-Sb-C angles of 89.8 and 94.6° respectively. Vibrational spectra of



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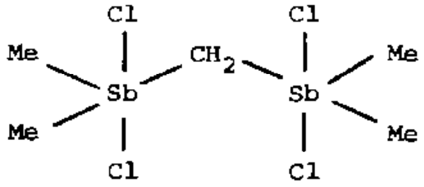


(201)

$(Me_2Sb)_2CH_2$ are consistent with the presence of two rotamers with C_{2v} and C_s symmetry while only one form is present in the related antimony(V) derivative $(Me_2SbCl_2)_2CH_2$.[549] From X-ray crystallography the structure of the latter (201) is based on two trigonal bipyramids linked through equatorial positions by the CH_2 group.

The hindered Grignard reagent, $(Me_3Si)_2CHMgCl$ replaces only one of the chlorine atoms in $SbCl_3$ while with the lithium derivative, $(Me_3Si)_2CHLi$, both $[(Me_3Si)_2CH]_2SbCl$ and $[(Me_3Si)_2CH]_3Sb$ can be obtained;[550] even with the lithium salt, however, only monosubstitution is possible with the more highly hindered derivative $(Me_3Si)_3CLi$.

The reaction between antimony(III) chloride and sodium cyclopentadienide in THF, originally thought to give $Cp_2SbSbCp_2$, on reexamination[551] has been shown to yield the sodium salt of a tetrastiba-adamantane. As shown in Figure 11, the basic unit contains three μ_3-C_5H_3 groups with the addition of μ_2-$C_5H_3^-$ and

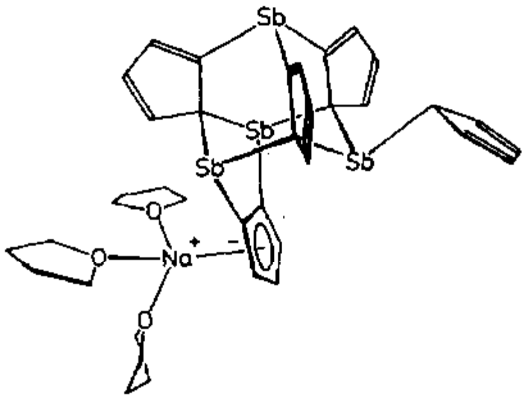
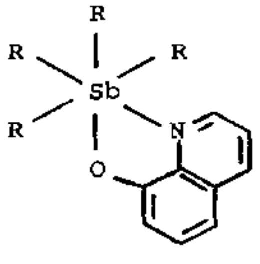


Figure 11. The structure of $Na(THF)_3[Sb_4(C_5H_3)_4(C_5H_5)]$ (reproduced by permission from Z. Anorg. Allg. Chem., 496(1983)58).

σ-C_5H_5 groups as further substituents; the structure is completed by a $Na(THF)_3^+$ cation located above the C_5H_3 anionic ring. A mechanism is given for the formation of this unusual compound.

Reactions of R_5Sb, where R = Me or Ph, with 8-hydroxyquinoline and anthranilic acid lead to the tetrasubstituted derivatives (202) and (203) respectively.[552] The six coordinate structure for



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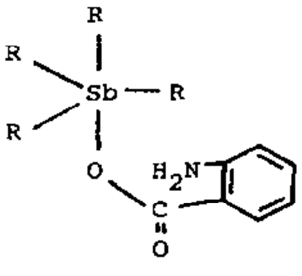


(203)

(202) follows from Mössbauer data and a full X-ray structure for the methyl derivative (Sb-O 2.187, Sb-N 2.463Å); a five coordinate covalent structure is suggested by Mössbauer spectroscopy for (203).

5.4.3 Bonds to Halogens

Thermal analysis and X-ray diffraction have shown the formation of $Sb_3O_2F_5$, SbOF and Sb_3O_4F in the SbF_3-Sb_2O_3 system.[553] The possibility of forming fluoroantimonates by solid phase reactions has been confirmed by isolation of the following species (melting points in ^{o}C are given in parentheses): Rb_2SbF_5 (585), $RbSbF_4$ (240), $Rb_3Sb_4F_{15}$ (210), $RbSb_2F_7$ (190), $RbSb_3F_{10}$ (215), $RbSb_4F_{13}$ (230), Cs_2SbF_5 (555), $CsSbF_4$ (215), $Cs_3Sb_4F_{15}$ (175), $CsSb_2F_5$ (205) and $CsSb_4F_{13}$ (195).[554] In addition Na_2SbF_5, Rb_2SbF_5 and $RbSb_2F_7$ can also be obtained from the alkali fluoride and SbF_3 in acetic acid solution.[555]

Crystals of $[M(H_2O)_6](SbF_4)_2$ for M = Ni or Cu are isostructural with the anion consisting of infinite layers of pseudotrigonal bipyramidally coordinated antimony atoms (Sb-F_{eq} 1.921, 1.941; Sb-F_{ax} 2.066, 2.127, F_{ax}-Sb-F_{ax} = 152.4^{o}); in addition for M = Ni there are longer contacts to three symmetry related fluorines at distances ranging between 2.778 and 3.073Å.[556]

Mixed phosphate salts containing SbF_2^+ and SbF^{2+} [558] cations have been isolated from reactions between SbF_3 and a dihydrogen phosphate. The SbF_2^+ cation occurs in $KSbF_2(HPO_4)$ where the Sb-F distances are 1.902 and 1.955Å and the F-Sb-F angle is 85.2^{o}. The antimony does however make contacts to three oxygen atoms of different HPO_4^{2-} anions at 2.144, 2.169 and 2.501Å raising the coordination to pseudo-octahedral; the lone pair is located trans to the fluorine atom with the shorter Sb-F distance.[557] The compounds $NH_4(SbF)PO_4.H_2O$ and $Na(SbF)PO_4.nH_2O$, where n = 2-4, have highly symmetrical layer structures in which each oxygen of the phosphate anion is bonded to a different SbF^{2+} group (Sb-F ca. 1.92Å).[558] Again the antimony is in pseudo-octahedral coordination with a stereochemically active lone pair.

$SbCl_3$ and a two fold excess of oxalic acid in hydrochloric acid solution yield $Sb(C_2O_4)OH$,[559] while in 1,2-dichloroethane solution complex formation occurs between SbX_3, where X = Cl, Br or I, and DMF, DMA or tetramethylurea.[560] Both 1:1 and 1:2 adducts are present in the complex $2SbCl_3.3$(4-phenylpyridine) according to an X-ray investigation.[561] The former contains a pyramidal $SbCl_3$ unit (mean Sb-Cl 2.427, Sb-N 2.473Å) while the latter is square pyramidal with the two nitrogen atoms (Sb-N 2.390Å) occupying trans positions; the $SbCl_3$ unit here is T-shaped.

A reexamination of the $SbCl_5$-CS_2 reaction at 5^{o}C has shown that the product is $SbCl_3.S_8$, which decomposes slowly to the components at room temperature rather than $SbSCl_3$.[562] Its structure is based on pyramidal $SbCl_3$ and S_8 rings with pairs of $SbCl_3$ molecules loosely associated into dimeric units; Sb---S distances fall in the range 3.33 - 3.73Å.

Among the chloroantimonate structures determined during 1983 are those for $Et_3NHSbCl_4$,[563] $(MeNH_3)_3SbCl_6$,[563] and the 2,2'- and 4,4'-bipyridinium salts of the $SbCl_5^{2-}$ anion.[564] The tetrachloroantimonate contains chains of $SbCl_3$ molecules bridged by chloride ions, giving antimony a coordination number of five (square pyramidal geometry Sb-Cl(bridging) 2.825, 2.897; Sb-Cl(terminal) 2.381 - 2.468Å). Octahedral $SbCl_6^{3-}$ ions are not found in the structure of the second compound but there are chains of $SbCl_5$ units giving six fold coordination to antimony; the sixth chloride makes no contact to antimony. Antimony in the two bipyridinium salts is also in six fold, distorted octahedral, coordination but in the 2,2'-isomer there are centrosymmetric tetrameric $Sb_4Cl_{20}^{8-}$ ions while the 4,4'-salt consists of infinite chains. In each, two of the chlorine atoms at antimony are bridging.

The neutron powder diffraction profile of the mixed oxidation state anion, Cs_2SbCl_6, has been interpreted as showing a super lattice ordering at low temperatures;[565] each $Sb(III)Cl_6^{3-}$ ion is surrounded by 8 $SbCl_6^-$ and 4 $Sb(III)Cl_6^{3-}$ groups.

One mol of Me_3P readily adds to the iron-antimony complex, $Cp(CO)_2FeSbBr_2$, giving the Sb-P bonded adduct $Cp(CO)_2FeSbBr_2PMe_3$.[566] The compound contains antimony in very distorted pseudo-trigonal bipyramidal coordination; the bromine atoms occupy the axial positions but the Br-Sb-Br is closed to 149.1° largely as a result of the steric demands of the Cp and Me_3P groups. In addition the Sb-P distance, 2.596Å, is long.

The red crystalline adduct $SbI_3.AlI_3$ can be obtained by heating the components in carbon disulphide solution.[567] An X-ray structure shows tetrameric $Al_2Sb_2I_{12}$ units containing SbI_6 octahedra and AlI_4 tetrahedra sharing common edges as shown in Figure 12; terminal Sb-I distances are 2.708Å with bridging Sb-I distances of 3.123 and 3.589Å.

Antimony(III) halides with the exception of the iodide give 1:1 adducts with 1,10-phenanthroline, which from i.r. and Mössbauer data are considered to be halogen bridged polymers.[568] The stereochemical activity of the antimony lone pair varies with the halogen and is greatest for the fluoride. Phenylantimony diiodide also forms 1:1 complexes with 1,10-phenanthroline and 2,2'-

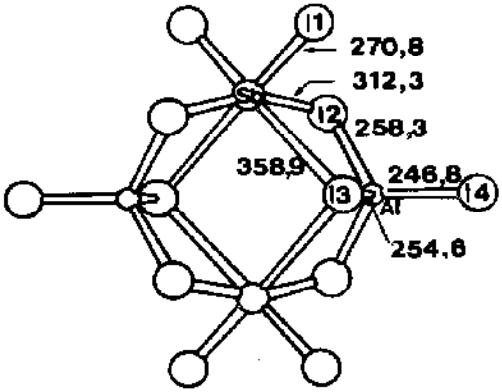


Figure 12. The structure of $Al_2Sb_2I_{12}$ (reproduced by permission from Z. Naturforsch., Teil B, 38(1983)1539).

bipyridyl with suggested pseudooctahedral structures in which the phenyl group and lone pair occupy trans positions.

A solution of SbF_5 in arsenic(III) fluoride can be reduced by PF_3 to yield $(SbF_3)_3SbF_5$, a product which also results when SbF_5 and iodine react in the same solvent.[569] From a single crystal investigation the compound comprises SbF_6^- anions and infinite chains of $Sb_3F_8^+$ units lying along the b axis (see Figure 13). If

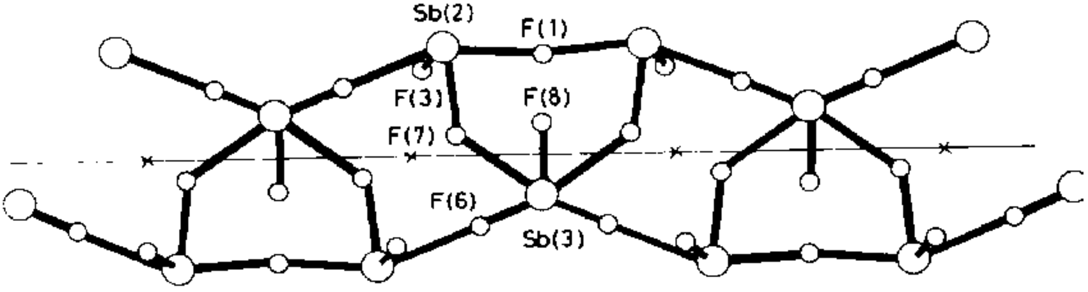


Figure 13. The structure of the $(Sb_3F_8^+)_\infty$ strands in $(SbF_3)_3SbF_5$ (reproduced by permission from J. Chem. Soc. Dalton Trans., (1983)619).

contacts ≤2.15Å only are considered, the chain consists of fluorine bridged (2.270 and 2.414Å) SbF_3 and $Sb_2F_5^+$ units. A large excess of SbF_5 has also been shown to convert graphite fluorosulphate, C_8SO_3F, to $C_8^+SbF_6^-$ in which there is an increase in the interlayer spacing from 7.81 to 8.19Å.[570] The former anion is converted to $Sb_2F_9SO_3F$.

In carbon tetrachloride solution, $SbCl_5$ and acetic anhydride react to give in addition to the previously observed compound, $SbCl_4(OAc)$, a second species formulated as $MeCO(SbCl_5)_2OAc$.[571]

Octahedral adducts of $SbCl_5$ with donors such as PhCOCl, PhCN, CCl_3CHO, Et_2O, etc. have been investigated by ^{35}Cl and ^{121}Sb and ^{123}Sb n.q.r. spectroscopy.[572] In some cases it has been possible to assign resonances to equatorial and axial chlorine atoms but there is no systematic difference between these frequencies and the differences are often marked by crystal field effects.

Synthetic routes to the mixed chlorobromoantimony(V) anions have been discussed in general and preparative routes described to the new salts $Et_4N[SbCl_4Br_2]$ and $Et_4N[SbCl_2Br_4]$.[573] The methods involve oxidative addition of a halogen to an antimony(III) species, reaction of Et_4NX with SbX_5 or substitution in $(SbCl_4OEt)_2$ or $[SbCl_3(OEt)_2]_2$. I.r. spectroscopy points to a cis geometry for the new compounds while ^{121}Sb n.m.r. spectroscopy in acetonitrile indicates halogen exchange.

Oxidation of Ph_3Sb in a non-donor solvent such as carbon tetrachloride with $SbCl_5$ leads to the weak 1:1 addition compound, $Ph_3SbCl_2.SbCl_3$, but even in weakly donating solvents such as toluene the product is uncomplexed Ph_3SbCl_2.[574] A structure for the addition compound shows that there are weak Sb---Cl interactions (3.262Å) between the axial chlorine atoms of Ph_3SbCl_2 and $SbCl_3$ giving polymeric chains parallel to the a axis. Further treatment of Ph_3SbCl_2 with antimony(V) chloride also gives a 1:1 adduct for which the ionic structure $Ph_3SbCl^+SbCl_6^-$ is proposed on the basis of an X-ray crystallographic study. There is a residual weak Sb---Cl interaction (3.231Å) between one chlorine of the anion and the antimony of the cation; the cation geometry as expected is intermediate between the tetrahedral and trigonal bipyramidal extremes.

5.4.4 Bonds to Oxygen

Vibrational data for $Sb(OEt)_nX_{3-n}$ for n = 1 - 3 and X = Cl or Br have been assigned on the basis of the known structures of

$Sb(OEt)_2Cl$ and $Sb(OEt)Cl_2$;[575] data for the related compounds $Sb(OEt)Br_2$ and $Sb(OEt)_2I$ however point to polymeric structures. Assignments of the mass spectra of $Sb(OMe)_3$, $Sb(OMe)_2Cl$ and $Sb(OMe)Cl_2$ are also reported together with that of $(CD_3CH_2)_3Sb$;[576] the origin of Sb-H containing fragments is considered.

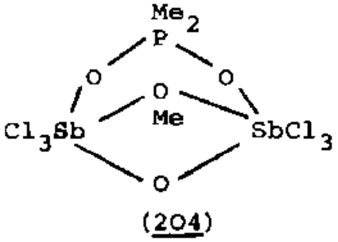
Reactions of the trifluoroacetates of antimony(III) and bismuth(III) with an excess of trifluoromethanesulphonic acid lead to the corresponding $M(O_3SCF_3)_3$ derivatives,[577] while the dicarboxylato species $MeM(O_2CR)_2$, where M = Sb or Bi and R = Me, Ph or Bu^t, can be obtained either by treating the corresponding dibromide with the appropriate sodium carboxylate in methanol or by reactions between $MeM(OEt)_2$ and the free carboxylic acid.[578]

Structures have been reported for the hydrated antimony tartrates, $M[Sb_2\{(+)-C_4H_2O_6\}_2].nH_2O$ where M = Ca, n = 2,[579] M = Ba, n = 3,[579] and M = Sr, n = 2.[580] All three compounds contain a binuclear Sb_2 unit bridged by two tartrate groups with mean Sb-O distances to the carboxylate oxygens of 2.17Å and to the hydroxy oxygens of 1.99Å. The structure is also reported for the oxonium antimony sulphate, $(H_3O)_2Sb_2(SO_4)_4$ obtained by treating Sb_2O_3 with 17M sulphuric acid.[581] This compound, which is only obtained in a small sulphuric acid concentration range, reverts to the anhydrous sulphate, $Sb_2O(SO_4)_2$, on removal from the acid. Its structure is based on sheets arising by the linking of Sb-O-S chains by sulphate groups; there are two distinct antimony environments.

The reaction between equimolar quantities of Sb_2O_3 and V_2O_5 in the temperature range 600 to 800°C is markedly dependent on the presence of oxygen, but in an oxygen-free nitrogen atmosphere the product is an antimony deficient rutile type compound formulated as $VSb_{1-y}O_{4-3/2y}$, where $0 < y < 0.1$.[582] However, biphasic mixtures containing Sb_2O_4 and a non-stoichiometric phase containing less oxygen, i.e. $VSb_{1-y}O_{4-2y}$ where $0 < y < 0.1$, are produced in the presence of commercial nitrogen or when the reactions are carried out in sealed tubes. The structural properties of these phases and the changes produced by further heat treatment are discussed[583] together with e.s.r. data for these types of products.[584]

The previously reported defect pyrochlore $CeSbO_3$ obtained from CeO_2 and Sb_2O_3 has been investigated with a suggestion that the product is, in fact, a mixture of crystalline CeO_2 embedded in a matrix of glassy Sb_2O_3.[585] Single crystals of $M_{11}Sb_9O_{30}$, for M = La or Pr, produced by hydrothermal methods, crystallise in the tetragonal space group, P4/ncc.[586]

Two new dinuclear antimony(V) compounds (204) and (205) containing dimethylphosphinate bridges have been prepared, the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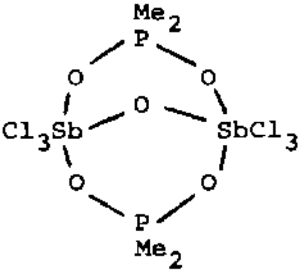
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former by treating $(Me_2PO_2SbCl_4)_2$ with a 1:1:1 mixture of $SbCl_5$, H_2O and MeOH in dichloromethane.[587] The latter, for which a full crystal structure is available, can be obtained by a number of methods including the reaction of $Cl_3Sb(EtCOO)(OH)SbCl_3$ with dimethylphosphinic acid in dichloromethane.

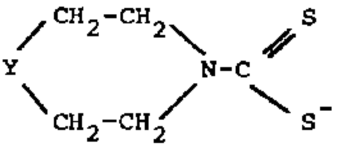
Two "hydrates" of Sb_2O_5, i.e. $HSb_3O_8(Sb_2O_5.{}^1/3H_2O)$[588] and $H_3O[Sb_5O_{13}](Sb_2O_5.{}^3/5H_2O)$,[589] have been synthesised for structure determination. The former consists of distorted SbO_6 octahedra linked through vertices and edges into a three dimensional framework. In addition to the latter the alkali metal derivatives $NaSb_5O_{13}$ and KSb_5O_{13} have also been isolated via a hydrothermal method under an oxygen pressure using Sb_2O_3 and either Na_2O_2 or KO_2.[589] The structures again are based on a polymeric framework of edge and vertex sharing SbO_6 octahedra with cations occupying holes in the structure.

The cyclohexyl substituted antimony(V) compounds, $(C_6H_{11})_3Sb(OH)X$, where X = Cl, Br, OAc or NO_3, have been prepared by hydrolysis of the oxygen bridged compounds, $[(C_6H_{11})_3SbX]_2O$ in an acetone-water mixture.[590] Although the hydroxy-chloride and -bromide readily dehydrate to the μ-oxo starting material, both the acetate and nitrate are stable.

5.4.5 Bonds to Sulphur

The mixed xanthate-halide complexes, $M(S_2COEt)_2X$, where M = Sb, X = Cl, Br or I and M = Bi, X = Cl or Br, can be prepared either by treating the tris(xanthate) with a free halogen or by reorganisation reactions of MCl_3-$M(S_2COEt)_3$ mixtures.[591] The structure of $Sb(S_2COEt)_2Br$ shows the antimony atom in six-fold coordination to four sulphur atoms (2.493-2.993Å) and two bromine atoms (2.780, 3.269Å) which bridge antimony atoms to give zig-zag chains. The methyl derivatives, $MeSb(S_2COR)_2$ where R = Me, Et, Pr^i, Ph or CH_2Ph, can be obtained either from the dibromide and the corresponding sodium xanthate or by insertion of CS_2 into the Sb-O bonds in $MeSb(OR)_2$ for R = Me, Et or Bu^t.[592] Similar methods have been used to prepare $PhSb(S_2COR)_2$ where R = Me, Et, Pr, Pr^i, Bu or allyl.[593] The structure of $MeSb(S_2COEt)_2$ contains a central antimony atom in distorted pentagonal pyramidal coordination to methyl in the axial position and four sulphur atoms in equatorial positions (Sb-S, 2.581, 2.617, 2.834 and 2.904Å); the fifth equatorial position is occupied by a symmetry related sulphur atom at 3.353Å.[592]

Related antimony(III) and bismuth(III) dithiocarbamates with formulae such as $Sb_2L_3X_3$, $SbLX_2$ and $BiLX_2$, where L is the dithiocarbamate group (206) and X is a halogen, are polymeric with bidentate dithiocarbamate groups according to i.r. spectroscopy.[594] Complex formation occurs between antimony hydrogen bis(thioglycolate) and a range of transition metals in aqueous solution.[595]



(206, Y = CH_2, O or S)

A series of antimony(III) dithiophosphates, $Sb[S_2P(OR)_2]_3$ where R = Me, Et, Pr^i, Bu, Bu^i or Bu^s, has been prepared from the trichloride and either the ammonium or sodium salt of the corresponding dithiophosphoric acid.[596] The compounds have been characterised by ^1H and i.r. spectroscopy and the structures of the compounds with R = Me and Pr^i have been determined. The latter shows that in both compounds antimony is in distorted octahedral coordination to six sulphur atoms with three short (2.528Å) and three longer (3.010Å) Sb-S distances.

$TlSbS_2$, which can be prepared by heating Tl_2S and Sb_2S_3 to 873K in a sealed tube, has a structure based on sheets of linked SbS_4E, pseudo-trigonal bipyramidal units; Sb-S bonds fall in the range 2.41 to 2.96Å.[597] The structure has also been determined for $Pb_2Sb_2S_5$, a member of the $Sb_2S_3.nPbS$ homologous series,[598] and three new lanthanum derivatives, $LaSbO_2S_2$, $La_6Sb_8S_{21}$ and $La_3Sb_3S_{10}$ have been synthesised.[599] Investigations in the $FeSe-Sb_2Se_3$ system show the formation of two ternaries, $FeSb_2Se_4$ and $2FeSe.Sb_2Se_3$; but there are no analogous ternaries in the corresponding NiSe system.[600]

5.5 BISMUTH

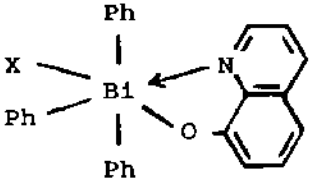
One of the alkyl groups in R_3Bi can be cleaved by sodium in liquid ammonia to yield the bismuthides $NaBiR_2$ Where R = Et, Pr, Pr^i or Bu;[601] on further reaction with 1,2-dibromoethane they are converted to dibismuthanes R_4Bi_2. The compounds are red liquids and were characterised by n.m.r. and mass spectrometry. A similar series of reactions occurs when triphenylbismuth is treated successively with potassium in THF solution and 1,2-dichloroethane.[602] The resulting Ph_4Bi_2 is an orange solid, soluble in toluene, with a staggered trans conformation according to X-ray data.[603] The Bi-Bi distance is 2.990Å with Bi-Bi-C angles of 90.9 and 91.6° and C-Bi-C angles of 98.3°.

The annual survey of organo-bismuth chemistry for 1981 has been published.[604] The preparation of the trisubstituted, highly hindered alkyl bismuth, $Bi[CH(SiMe_3)_2]_3$ from $BiCl_3$ and $[(Me_3Si)_2CH]Li$ is noteworthy as in similar reactions with phosphorus, arsenic and antimony only two substituted alkyl groups can be incorporated.[605] The geometry at bismuth is pyramidal but both the Bi-C distances (mean 2.328Å) and the C-Bi-C angles (mean 102.9°) are, greater than usual as a consequence of the bulk of the substituents. This also leads to severe distortion of the angles at the carbons attached to bismuth (Bi-C-Si 106.4, 121.2°). Triorganobismuthines with a chiral centre at the metal have been synthesised by the reactions outlined in equation (55).[606]

$$BiAr_2Ar' \xrightarrow{HBr} BiArAr'Br \xrightarrow{Ar''MgX} BiArAr'Ar'' \qquad \ldots(55)$$

Ar = 4-chlorophenyl
Ar' = 2-methylphenyl or 2,4,6-trimethylphenyl
Ar" = α-naphthyl or 2-i-propoxyphenyl

The 2-methyl-8-quinolinate (207, X = Cl or Br) has distorted



(207)

octahedral geometry with Bi-O and Bi-N distances of 2.19 and 2.71Å respectively.[607]

Structures have been determined for both $LiBi(SiMe_3)_2.DME$ and $(Me_3Si)_4Bi_2$, the latter a green compound with a metallic lustre.[608] The bismuthide consists of chains of alternating lithium and bismuth with both atoms in four fold coordination. The dibismuth compound is centrosymmetric (Bi-Bi 3.035Å, Bi-Bi-Si 97.4°) but zig-zag chains are formed by short intermolecular contacts (Bi---Bi 3.804Å, Bi-Bi---Bi 169°).

He(I) and (II) photoelectron spectra for BiX_3, where X = F, Cl, Br or I, and SbF_3 have been recorded and correlated with the spectra of related molecules.[609] The anhydrous complexes, Cs_2BiF_5, $CsBiF_4$ and $CsBi_2F_7$ can be isolated from the $CsF-BiF_3-HF-H_2O$ system[610] and five discrete oxide fluoride phases have been observed in the 20-35 mol% Bi_2O_3 range of the $BiF_3-Bi_2O_3$ system.[611] Intermediate crystalline phases formulated as BiOCl, $Bi_{12}O_{15}Cl_6$, $Bi_{24}O_{31}Cl_{10}$, BiOBr and $Ni_{24}O_{31}Br_{10}$ have been detected in the solid state analysis of the $BiCl_3$- and $BiBr_3-Bi_2O_3$ systems.[612] $BiCl_3$ complexes with 1-phenyl-3-(2-pyridyl)-2-thiourea and N,N'-diethylimidazolidine-2-thione have been isolated and their structures determined; in each case the bismuth atom is in six fold coordination.[613] N-methyl and N,N-dimethyl-O-ethyl thiocarbamates, MeRNC(S)OEt where R = H or Me, also form complexes with bismuth(III) halides and among the compounds isolated are $BiX_3.2[Me_2NC(S)OEt]$ and $BiX_3.2[MeHNC(S)OEt]$, where X = Cl or Br.[614]

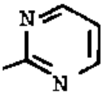
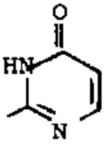
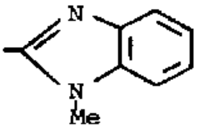
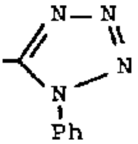
Bismuth(III) bromide and ferrocene in the presence of molecular oxygen and sunlight give a new bromobismuthate salt together with BiOBr as a byproduct.[615] X-ray crystallography showed the salt to be $(Cp_2Fe)_4Bi_4Br_{16}$, where the centrosymmetric anion has a novel structure based on four edge sharing $BiBr_6$ octahedra.

BiF_5 and its addition compounds with ClF_3 and RbF have been synthesised and characterised by vibrational spectroscopy,[616] n.q.r.[616] and variable temperature ^{19}F n.m.r. spectroscopy.[617] An excess of BiF_5 in anhydrous hydrogen fluoride gives a 2:1 adduct with UOF_4 in contrast to the lack of reactivity of AsF_5;[618] its structure is considered to be similar to that found for $UOF_4.2SbF_5$ and $UOF_4.3SbF_5$, i.e. basically fluorine bridged but with some ionic character.

X-ray and neutron diffraction data for $Bi_6O_4(OH)_4(ClO_4)_6.7H_2O$, obtained from a solution of bismuth(III) oxide in $3MHClO_4$, show the presence of hexanuclear $[Bi_6O_4(OH)_4]^{6+}$ cations.[619] The bismuth atoms are at the corners of a slightly distorted octahedron with triply bonding oxygen atoms above each of the faces; Bi-O distances to oxygen are shorter (2.154Å) than those to OH (2.402Å).

The double formate, $K_2Bi(HCOO)_5$, previously isolated from a formic acid solution of the two simple formates can also be obtained from aqueous systems if the potassium formate concentration is in the range 45.6 to 79.5 mass %.[620]

Evidence for the formation of Bi_5PO_{10}, Bi_3PO_7, $Bi_4P_2O_{11}$ and $BiPO_4$ comes from a d.t.a. and X-ray investigation of the Bi_2O_3-P_2O_5 system between 0 and 50 mol% P_2O_5;[621] in addition there are two further phases at the ratios of 25:1 and 12:1 for which the sillenite structures, $Bi_{24}(Bi,P)O_{40}$ and $Bi_{24}P_2O_{41}$ are proposed. Single crystals of further sillenite phases, $Bi_{38}CrO_{60}$ and $Bi_{16}CrO_{27}$, have been obtained by hydrothermal methods in the Bi_2O_3-Cr_2O_3 system in the presence of atmospheric oxygen.[622] Bismuth molybdate and tungstate phases, e.g. $M(I)Bi(EO_4)_2$ for M = Ag or Tl and E = Mo or W, have been obtained and shown to have scheelite structure;[623] phase equilibria in the $Bi_2(MoO_4)_3$-$M(II)MoO_4$ (M = Ni, Co or Mn) and $Bi_2(MoO_4)_3$-$M(III)_2(MoO_4)_3$ (M = Al, Cr, Fe or In) systems have been investigated by d.t.a., t.g.a. and X-ray diffraction.[624]

Metatheses have been used to prepare a range of substituted bismuth xanthates, $Me_2Bi(S_2COR)$ where R = Me, Et, Pr, Pr^i, Bu and Bu^i; the compounds decompose in solution to give $MeBi(S_2COR)_2$.[625] Similar reactions using Me_2BiBr as a starting material have given the thiolates, $Me_2Bi(SR)$,[626] where R =  ,  ,  or 

The substituted ethylenedithiol, $Na_2[S_2C_2(CN)_2]$, reacts in acetone solution with bismuth(III) chloride in the presence of Ph_4AsCl to give a mixture of products from which $Ph_4As[Bi\{S_2C_2(CN)_2\}_2]$ can be isolated.[627] X-ray diffraction shows a chain structure where the ligands are simultaneously bridging and chelating. Coordination about bismuth can be described as either distorted octahedral if the lone pair of electrons is inactive or distorted pentagonal bipyramidal if the lone pair occupies an equatorial position.

Two forms of $BaBi_2S_4$, both crystallising in the space group $P6_3/m$, can be obtained by heating mixtures of BaS and Bi_2S_3 at 640°C; the bismuth atom is in nine fold tricapped trigonal prismatic coordination.[628] The structure of $Pb_{1.6}In_8Bi_4S_{19}$, prepared by vapour transport with iodine from a Pb:4In:2Bi:10S mixture, contains InS_6 octahedra and both mono- and bi-capped Bi-S trigonal prisms; Bi-S distances fall in the range 2.69 to 3.33Å.[629]

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