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Chapter 5

ELEMENTS OF GROUP 5

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5.1 NITROGEN 262

- 5.1.1 Nitrogen and Nitrides 262
- 5.1.2 Bonds to Hydrogen 262
- 5.1.3 Bonds to Boron 264
- 5.1.4 Bonds to Carbon or Silicon 265
- 5.1.5 Bonds to Nitrogen 269
- 5.1.6 Bonds to Oxygen or Sulphur 274
- 5.1.7 Bonds to Halogens 282
- 5.1.8 Bonds to Phosphorus or Arsenic 284

5.2 PHOSPHORUS 284

- 5.2.1 Phosphorus, Polyphosphines and Phosphides 284
- 5.2.2 Bonds to Carbon or Silicon 288
- 5.2.3 Bonds to Halogens 305
- 5.2.4 Bonds to Nitrogen 310
- 5.2.5 Bonds to Oxygen 330
- 5.2.6 Bonds to Sulphur, Selenium or Tellurium 338

5.3 ARSENIC 340

- 5.3.1 Arsenic and Arsenides 340
- 5.3.2 Bonds to Carbon or Silicon 342
- 5.3.3 Bonds to Halogens 347
- 5.3.4 Bonds to Nitrogen 348
- 5.3.5 Bonds to Oxygen 349
- 5.3.6 Bonds to Sulphur or Selenium 351

5.4 ANTIMONY 351

- 5.4.1 Antimonides and Bonds to Carbon 351
- 5.4.2 Bonds to Halogens 352
- 5.4.3 Bonds to Oxygen 355
- 5.4.4 Bonds to Sulphur, Selenium or Tellurium 358

5.5 BISMUTH 359

REFERENCES 363

5.1 NITROGEN

5.1.1 Nitrogen and Nitrides

The photochemical reductive elimination of the nitrogen-containing ligands of cis-$(Ph_3P)_2Pt(N_3)_2$ at 77K in organic glasses generates $Pt(Ph_3P)_2$.[1] The absence of an e.s.r. signal from the photoproducts, the yellow colour (λ_{max} 380nm) and ready formation of N_2 at higher temperatures lead the authors to postulate the production of N_6, possibly in the form of hexaazabenzene.

The solid nitride chloride $Li_{1.8}N_{0.4}Cl_{0.6}$ has been studied in detail;[2] it functions as a solid ionic conductor. Transference and e.m.f. measurements confirm that the electrolytic flow is due to Li^+ and that there is negligible electronic conduction. The salt $(NH_4)_3[Ta_2NBr_{10}]$ has been synthesised from NH_4Br and $TaBr_5$ at 400°C;[3] the structure contains the D_{4h} symmetry anion, $[Br_5TaNTaBr_5]^{3-}$, in which the Ta-N distance, 1.85Å, is consistent with double bonding between these elements. A dinuclear μ-nitrido complex, $(Ph_4As)_2[N(WCl_5)_2]$, containing tungsten (IV) and (V) has been prepared.[4] The W-N-W bridge is also linear but apparently unsymmetrical, W-N distances 1.657 and 2.072Å; the conformation of the WCl_4 groups on each is eclipsed.

5.1.2 Bonds to Hydrogen

Ab initio m.o. calculation have been carried out to obtain an intermolecular potential function for $(NH_3)_2$.[5] Dimerisation energies for 250 orientations of these dimers were fitted to a 12-6-3-1 potential: Monte Carlo simulations of liquid NH_3 at its boiling point were then carried out. The calculated NN radical distribution functions are in better agreement with the results of X-ray studies than are earlier molecular dynamics simulations; however the experimental data are still more structured. The u.v. accelerated decomposition of dilute aqueous NH_3 by hypochlorite occurs over the pH range 2-12, where corresponding dark reactions are slow, and operates by enhancing the rate of decomposition of chloramines.[6] The irradiation also affects the formation of byproducts such as NO_2^- and NO_3^-.

Armor[7] has proposed the term ammoximation for the process described by equation (1). Typically the temperature for the

$$NH_3 + \tfrac{1}{2}O_2 + \text{ketone} \longrightarrow \text{ketoxime} + H_2O \qquad \text{...(1)}$$

28% conversion of cyclohexanone over silica gel was 194°C. Thermodynamic data have been obtained for the solution and protonation of NH_xMe_{3-x}, $x = 3,2,1$ or 0, $EtNH_2$ and $n\text{-}PrNH_2$ in Me_2SO or propylene carbonate at 25°C.[8] The authors compare their results with those for aqueous solutions and point out that the order of basicity in this family of amines cannot be rationalised in terms of one dominant thermodynamic parameter. Franz[9] discusses the preparation, handling and uses of tertiary amine trishydrofluorides. Not only are they non-corrosive towards borosilicate glass but also they are convenient agents for nucleophilic replacement of Cl or Br by F.

The nature of the products of the low temperature reactions between amines and ClO_2 depends on the availability of replaceable protons on carbon or nitrogen.[10] In the absence of such protons a 1:1 adduct is formed. When protons are available on the α-C atom they are abstracted and an azomethinium chlorite, $(RCH{=}NR'H)^+ClO_2^-$, results, among other products. In the absence of protons on the α-C those on N are attacked and amidochlorates, R_2NClO_2, are formed.

Some examples of N-H bond activation have been studied in detail.[11] The ammine complex $Os_3(CO)_{11}(NH_3)$ has been prepared by amine oxide induced carbonyl substitution of $Os_3(CO)_{12}$. Transfer of one H atom on to the metal cluster to give $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NH_2)$ was induced thermally. Reaction of the ammine with cyclohexanone gave the ketimine complex $Os_3(CO)_{11}(NHC_6H_{10})$ which rearranged thermally to $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NC_6H_{10})$.

The new compounds $C_2F_5NH_2$ and $CF_3CF{=}NH$ are readily prepared by the reaction of $C_2F_5NCl_2$ with MeSiH at -45^{o} and $-25^{o}C$, respectively.[12] The imine is formed from the amine by spontaneous dehydrofluorination (3min. at $25^{o}C$). Sulphur(IV) fluoride converts the amine to $C_2F_5N{=}SF_2$ whereas ClF produces $CF_3CF{=}NCl$ from the imine.

5.1.3 Bonds to Boron

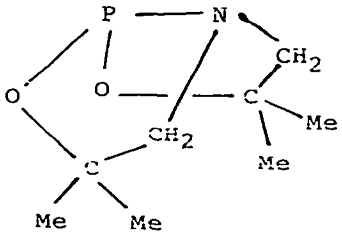
The molecular structures of $Me_3N.BX_3$, X = Cl or Br, have been determined from gas phase electron diffraction and vibrational spectroscopic data:[13] N-B distances are 1.652 ± 0.009 and 1.663 ± 0.013Å, respectively, and the potential barriers to rotation about these bonds were estimated to be higher than 18 and 12 kcal. mol^{-1} respectively. The adiabatic electron affinities of several boron trihalides, determined in a crossed molecular beam study of reaction (2), have been used to obtain

$$Cs + BX_3 \longrightarrow Cs^+ + BX_3^- \qquad ...(2)$$

B-N bond energies for the $Me_3N.BX_3$ adducts.[14] Values range from 33 to 48(±5) kcal mol^{-1} for BCl_3 and $BClBr_2$ respectively.

M.o. studies at the minimum basis set level for the known azaboranes, arachno-4-NB_8H_{13}, arachno-$B_9H_{12}NH^-$ and nido-10-N-7,8-$C_2B_{10}H_{11}$, as well as for the hypothetical closo-1,12-$NCB_{10}H_{11}$ have been described by Bicerano and Lipscomb.[15] The most characteristic feature of the bonding in these compounds is the tendency of nitrogen to form polar and, whenever possible, two-centre bonds.

The isolation of crystals of a stable bis(borane) adduct of the aminophosphorane (1) has enabled Grec et al.[16] to obtain detailed



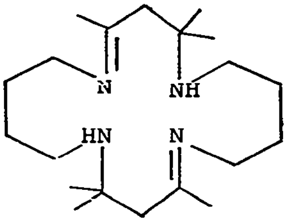
(1)

structural information on a P-bound N atom coordinated to BH_3. The N-B bond length, 1.655(8)Å, is comparable with that in $Me_3N.BH_3$ (1.638Å) and the P-N bond, 1.757(4)Å is indicative of no π bonding. It was proposed that the bicyclic structure and the pyramidal nature of phosphorus in (1) force the N atom to remain pyramidal and, hence, to show strongly basic character. Legzdins and coworkers[17] have obtained a number of products from the reaction between $Li(Et_3BH)$ and $[CpCr(NO)_2]_2$: $[Cp_2Cr_2(NO)_3(EtNBEt_2)]$ was isolated in 6% yield and contains the novel $EtNBEt_2$ ligand which is bonded through N symmetrically to both Cr atoms (Cr-N, 2.069(4)Å. The N-B distance, 1.459(5)Å, is compatible with some π bond character, however, the coordination of boron is approximately tetrahedral.

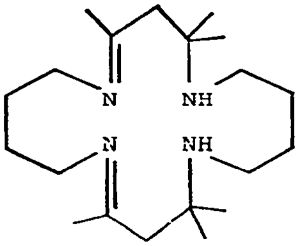
5.1.4 Bonds to Carbon or Silicon

Natural abundance ^{15}N n.m.r. spectra of nitrogen-containing crown ethers, cryptands, and other compounds with pyridine-type ligands and of their complexes with alkali, alkaline earth metal ions, Ag^+ and Tl^+ have been reported.[18] Downfield shifts on complexation were observed and these increase as cationic charge and ionic character increase: however, increasing polarisability of the cation produces an upfield shift. Nitrogen-silver and -thallium couplings were sizeable for some cryptate complexes.

A transition metal complex $[\mathrm{WBrdppe_2(N_2CCl_2)}]^+\mathrm{PF_6}^-$ of dichlorodiazomethane has been prepared by the reaction of the analogous N_2H_2 complex with $CXCl_3$ (X = Br or H) in the presence of a Ph_2I^+ salt and aqueous base.[19] Novel 18-membered tetraza macrocyclic ligands (2) and (3) have been prepared by the condensation of acetone with bis(1,4-diaminobutane)copper(II) perchlorate.[20a] The X-ray crystal structure of both complexes was also reported.[20b]



(2)

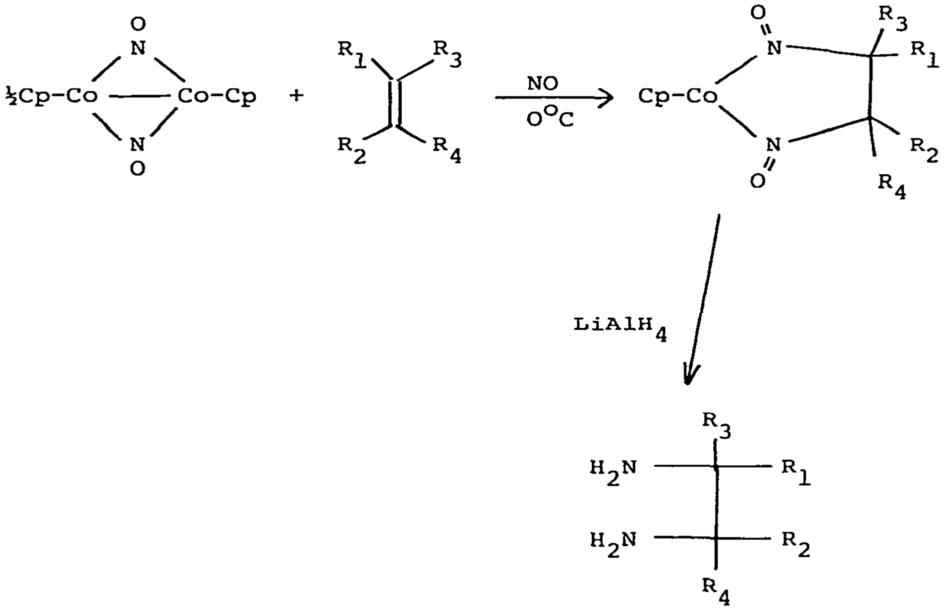


(3)

Chlorine thiocyanate, whose preparation has been described by Frost et al.,[21a] equation (3), has been shown by a microwave study to be Cl-S bonded.[21b] Stoll and Röllgen have provided mass spectrometric evidence for the thermal evaporation of intact positive ions from quaternary ammonium salts.[22] No negative ion evaporation was detected and the ratio of intact cations to those from neutral products was 10^{-5}:1 for n-Bu_4NI.

$$\mathrm{AgNCS} + \mathrm{Cl_2} \longrightarrow \mathrm{AgCl} + \mathrm{ClSCN} \qquad \ldots(3)$$

The first general method for vicinal diamination of alkenes has been reported by Bergman et al.[23] The method works satisfactorily for substituted alkenes including at least some tetrasubstituted ones. The reaction sequence (4) shows the intermediate cobalt



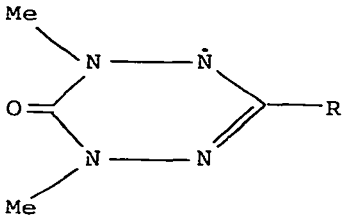
...(4)

complex which does not need to be isolated. Homogeneous catalytic activation of C-N bonds in tertiary amines has been reported by Shvo and Laine.[24] Thus process (5) occurs in the presence of

$$Et_3N + Pr_3N \rightleftharpoons Et_2PrN + EtPr_2N \qquad \text{...(5)}$$

a variety of Group 8 metal carbonyls, especially $M_3(CO)_{12}$, M = Ru or Os, at 125°C. This should be compared with the earlier report by Murahashi et al. of heterogeneous catalysis on Pd black under more vigorous conditions.

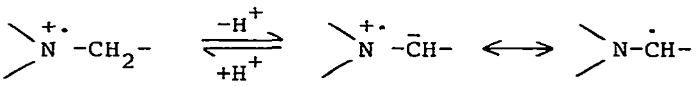
6-Oxoverdazyls (4) have been synthesised, R = H or Ph;[25] they are stable, crystalline free radicals which are sufficiently soluble in water for e.s.r. studies. The electrochemical



(4)

oxidation of a number of aromatic amines, e.g. Ph_3N, has been investigated in the low-temperature molten salt system $AlCl_3$-n-butylpyridinium chloride.[26] In acidic melts Ph_3N is oxidised reversibly to its radical cation, which at more positive potentials undergoes a further, chemically irreversible oxidation to the dication. The one-electron oxidation of pentafluoropyridine has been achieved by means of O_2AsF_6 in SO_2ClF solution at -45°C.[27] The $[C_5F_5N]AsF_6$ salt decomposes at 0°C to give a 1:1 mixture of $C_5F_5N.AsF_5$ and $C_5F_7N.AsF_5$, on the basis of their Raman and mass spectra.

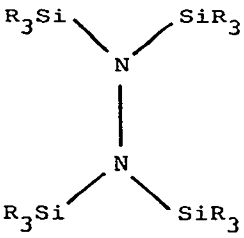
Gardini and Bargon[28] have presented evidence from CIDNP experiments for fast proton exchange between the α-carbons of tertiary aliphatic aminylium radical cations, $R_3N\cdot^+$, and protic species (e.g. water). With hindsight this is plausible on account of the resonance structure, see equation (6), of their conjugate bases. The aminylium radicals were generated by

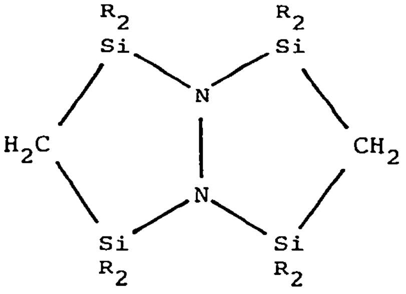


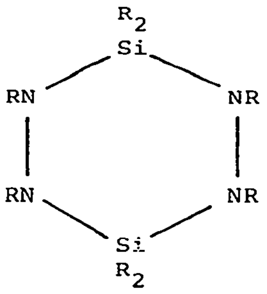
...(6)

photoinduced electron transfer from the tertiary amine to an acceptor (e.g. MeCN or naphthalene) having a suitable reduction potential. The e.s.r. spectra of the previously unreported aminyl π-radicals, RR'N·, obtained by the photolysis of $M(NRR')_2$, M = Ge or Sn, are reported:[29] typically the groups R and R' are $GeMe_3$, $SiEt_3$ and CMe_3.

Cleavage of the N-Si bond in $Me_3SiN(t\text{-}Bu)PF_2E$, E = lone pair or $(CF_3)_2COCO(CF_3)_2$, can be effected by PF_5:[30] the intermediate, $F_4PN(t\text{-}Bu)PF_2E$, was unstable but $F_3P{=}NPF_2E$, the product of t-BuF elimination, could be isolated. The vertical ionization energies (7.9, 7.15 and 7.5eV, respectively) of three permethylsilylhydrazines, (5a - c) have been measured in the gas phase.[31]


(5a)


(5b)


(5c)

Oxidation of the parent compounds is effected by $AlCl_3$ in CH_2Cl_2 solution to give the radical cations whose e.s.r. spectra have been interpreted. The radical cation derived from (5a) has the Si_2N moieties twisted towards a planar structure; the chair conformation of the monocyclic radical cation is converted to a half-chair by the flattening of one SiNNSi group. These and other observations in the literature can be rationalised by consideration of the parent $N_2H_4^{\cdot +}$ radical ion for which calculations suggest that the one-electron oxidation should have made the $>N{\equiv}N<$ skeleton planar and have shortened the N-N bond by~25pm. In the course of a study of some reactions of Cp_2V with silyl azides Wiberg et al.[32] have characterised a silylnitrene derivative, $Cp_2VNSiMe_3$ with the V-N-Si angle 178°, and the V-N and N-Si distances 1.665 and 1.736Å, respectively.

5.1.5 Bonds to Nitrogen

Yamabe and coworkers[33a] have reported the results of their m.o.

calculations on coordinated dinitrogen, diazirine, and diazomethane. Their results agree with the ab initio calculations of Veillard[33b] about the preference for end-on coordination of N_2. They disagree about the importance of M-N σ bonding in weakening the N-N bond: the Japanese workers conclude that only M-N π backbonding is significant here. Dinitrogen complexes of Os(III) have been characterised by Buhr and Taube.[34] The complexes were prepared by the reductive diazotisation of Os(IV) ammines by NO or, for the conversion of $[Os(NH_3)_5(N_2)]^{2+} \rightarrow [Os(NH_3)_4(N_2)_2]^{2+}$, via an Os(III) intermediate. The acidity of NH_3 coordinated to Os(III) is enhanced by a factor of approximately ten in the presence of coordinated N_2. A binuclear Ta complex with an unusual, linear dinitrogen bridge, N-N = 1.298(12)Å, also shows short Ta-N bonds, 1.837 and 1.842(8)Å. Schrock, Churchill and coworkers[35] have described the complex as a "diimido type", i.e. Ta=N-N=Ta. Furthermore, analogous complexes, (6) and (7), react quantitatively

$$[(PEt_3)_2Cl_3Ta{=}N{-}N{=}TaCl_3(PEt_3)_2]$$

(6)

$$[Cl(PMe_3)_3(C_2H_4)Ta{=}N{-}N{=}Ta(C_2H_4)(PMe_3)_3Cl]$$

(7)

with acetone to give dimethylketazine, $Me_2C{=}N{-}N{=}CMe_2$. Reactions of coordinated dinitrogen in $[Mo(N_2)_2(dppe)_2]$, dppe = $Ph_2P(CH_2)_2PPh_2$, with alkyl bromides generate the 2-alkyldiazenido-N derivative, $[MoBr(N_2R)(dppe)_2]$, with loss of N_2.[36] That the analogous reaction of 6-bromo-1-hexene produces the cyclopentylmethyldiazenido complex provides evidence for a pathway involving an alkyl radical. Treatment of $[MoBr(N_2C_4H_9)(dppe)_2]$ with $NaBH_4$ or NaOMe produces nearly equal quantities of NH_3 and $C_4H_9NH_2$, with yields of 60%.

Little is known about the ligand behaviour of the unsubstituted N-iminopyridine, $C_5H_5\overset{+}{N}-\overset{-}{N}H$. The X-ray structure of an adduct of this compound with bis(dimethylglyoximato)methylcobalt(III) shows that the imino nitrogen is the coordinating atom and has sp^2 character:[37] the N-N bond length is 1.350(9)Å. The neutral diazo molecules $N_2C_5X_4$, X = Cl or Br, replace coordinated N_2 in

$[IrCl(N_2)(PPh_3)_2]$ to form the four-coordinate $[IrCl(N_2C_5X_4)(PPh_3)_2]$.[38a] The geometry of the η^1 diazo ligand in the compound with X = Cl has been shown to be bent.[38b] However, in the M(O) complexes, M = Ni, Pt or Ru, the same ligand is π bonded, e.g. Figure 1.[39]

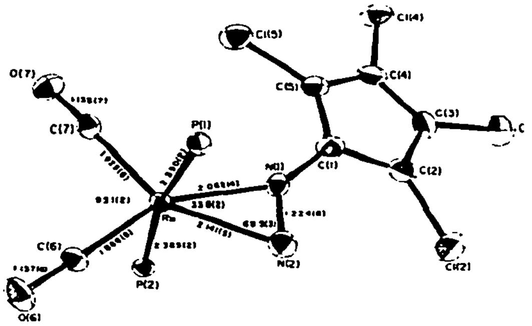


Figure 1. Molecular structure of $[Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2]$ showing some bond distances (Å) and angles (°). (Reproduced by permission from Inorg. Chem. 19(1980)2441).

The aryldiazenido complex $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)]BF_4$ and a rhenium analogue have been synthesised and investigated by X-ray diffraction.[40] The geometry of the diazenido ligand is interesting because of the short Mn-N bond, 1.693(7)Å, and the nearly linear Mn-N-N arrangement (angle 171.8°).

Sisler et al.[41] have investigated the reaction between methylamine and chloramine under a number of different reaction conditions. Their results show that reaction occurs only in the presence of a base, such as KOH or NaOMe, and that under these conditions a mixture of N_2H_4 and MeN_2H_3 are formed. Amination of primary and secondary amines by hydroxylamine-O-sulphonic acid is a known reaction. The same workers[42] have shown that 1,1-dimethylhydrazine can be made in this way from Me_2NH in diglyme; the reported yield is 35% based on the sulphonic acid used. The known, analogous conversion of $MeNH_2$ to MeN_2H_3 is 55% efficient. Tungsten complexes containing the arylhydrazido(2-) ligand have been prepared by the reaction of Cp_2WH_2 with ArN_2^+ below $-20^\circ C$.[43] The complex cation, $[Cp_2WH(NNHAr)]^+$, rearranges in solution (and also in the solid state), especially at temperatures near 0^oC, to an isomeric product, $[Cp_2W(H_2NNAr)]^+$, containing the arylhydrazido(1-) ligand bound side-on through both N atoms to W. The crystal structure of one of these isomerised products has been determined (Figure 2).[44]

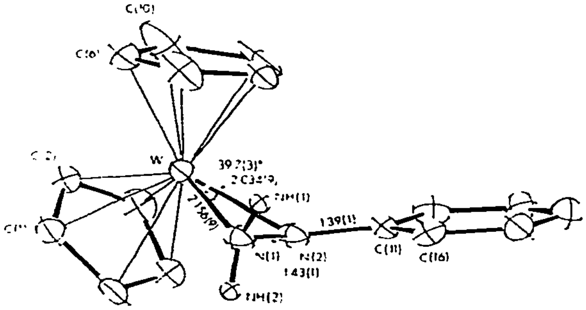
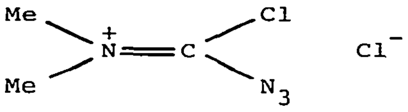


Figure 2. Perspective view of the $[(\eta^5-C_5H_5)_2W(H_2NNPh)]^+$ cation showing some key parameters (Reproduced by permission from Inorg. Chem., 19(1980)3142).

The thermochemistry of trans-, cis-diimide, 1,1-diazene and the diazenyl radical, HN=N·, has been calculated using ab initio GVB and CI methods.[45] The following ΔH_f^o values were obtained 56.9, 61.6, 86.3, and 76.2 kcal mol^{-1}, respectively. The authors compared their results with other calculations and used them to interpret conflicting experimental data. Imino ligands, particularly the 1,2-diimines, are known to stabilise metal ions in a variety of low and high oxidation states. Jeffery et al.[46] have explored the coordination chemistry of two diiminodiphosphines, N,N'-bis[o-(diphenylphosphino)benzylidene]ethylenediamine ($en=P_2$) and the corresponding 1,3-diaminopropane derivative ($tn=P_2$), with nickel, copper and silver. The ligands function as tetradentate chelating agents, as inferred from spectroscopic data and as proved by the X-ray structure of $[Cu(en=P_2)]ClO_4.CH_2Cl_2$, in which the metal has a highly distorted tetrahedral environment. Van der Poel et al.[47] have reported the isolation of stable metal α-diimine, R-dim, complexes, e.g. [trans-$PdCl_2(R\text{-}dim)_2$], in which the ligand is monodentate. Certain complexes, e.g.

$[PtCl_2(PBu_3)(t\text{-}Bu\text{-}dim)]$ generate d.n.m.r. spectra in the presence of excess (t-Bu-dim) which are consistent with a fluxional behaviour of the ligand involving a symmetrical 5-coordinate metal intermediate.

The photolyses of nine secondary and tertiary azides have yielded imine products without any evidence of nitrene processes.[48] Azidochloromethylenedimethylammonium chloride (8) has been



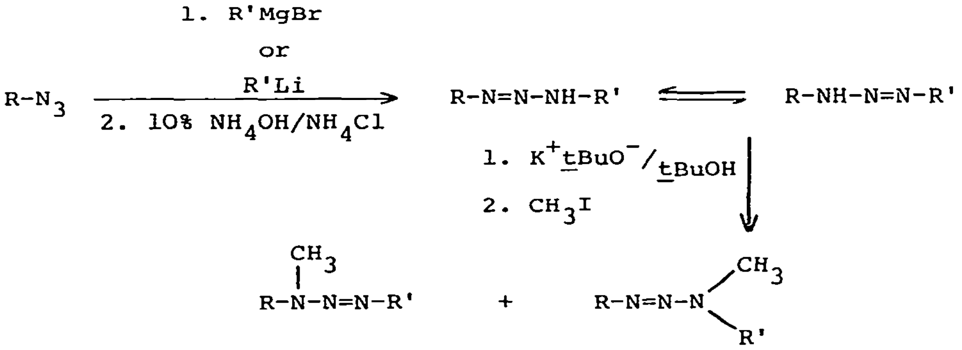
(8)

reported as useful in the conversion of primary amines to aminotetrazoles. Kokel and Viehe[49] have now shown that it reacts with certain acidic CH groups to transfer a diazo or diazonium group.

Alkylaryltriazenes, R-N=N-NHAr, decompose when Ar contains electron withdrawing substituents, according to equation (7), a heterolysis of the single N-N bond, in aqueous solution at

$$RN_2NHAr \longrightarrow RN_2^{+} + ArNH^{-} \qquad ...(7)$$

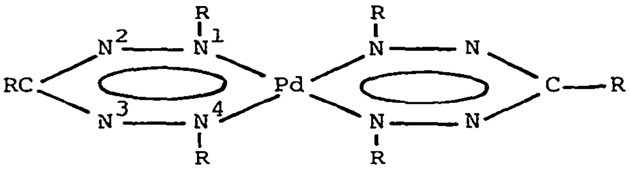
25°C.[50] A facile high-yield (85-95%) preparation of trialkyltriazenes has been reported.[51] Benzyl or n-butyl azide was treated with a Grignard or alkyl lithium reagent, R' = Me or n-Bu, and the resulting dialkyltriazene, after removal of the proton on nitrogen by t-BuOK was alkylated with MeI, reaction sequence (8).



...(8)

Since both terminal nitrogen atoms were methylated an isomeric mixture was produced which required chromatographic separation. The barrier to rotation about the nominally single N-N bond, a measure of the contribution of the 1,3-dipolar resonance form, was measured by ^{13}C d.n.m.r. spectroscopy: values in the range 10.5 - 11 kcal mol^{-1} were obtained.

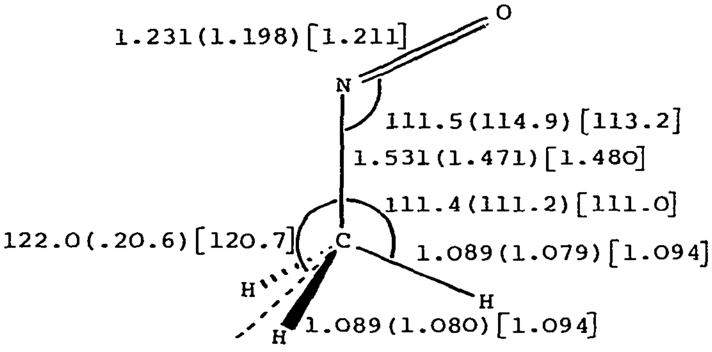
The formazanyl palladium ring CN_4Pd in bis(1,3,5-tri-p-tolylformazanyl)palladium, (9), is non-planar being folded about the N^1-N^4 axis:[52] the non-metal ring atoms are evidently sp^2 hybridised and the average bonded interatom distances (N-N, 1.307(7); C-N, 1.343(8)Å) reflect significant double bond character. The first example of a bis(tetraazadiene)metal complex, $[Ni(ArN_4Ar)_2]$, has been reported by Overbosch et al.[53] The ligand, ArN=N-N=NAr, does not exist in the free state and must be generated at the metal centre. The diamagnetic Ni(O) complex was obtained in ca. 4 mols of ArN_3 at room temperature: the N-N distances are all similar and close to 1.32Å.



R = p-tolyl (9)

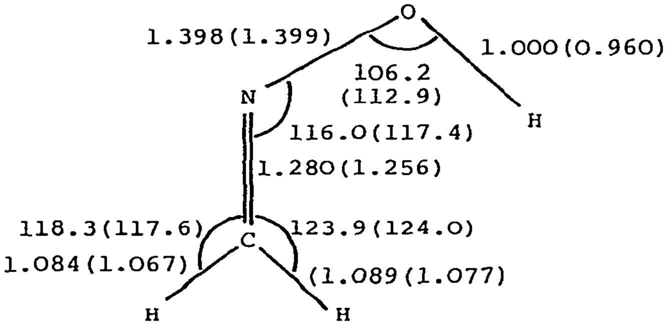
5.1.6 Bonds to Oxygen or Sulphur

Radom et al.[54] have investigated the potential energy surface relating to the 1,2- and 1,3 intramolecular hydrogen shifts for the interconversion of nitrosomethane (10), syn-formaldoxime (11), anti-formaldoxime (12), and formaldonitrone (13) by a number of ab initio m.o. methods. The optimised structural parameters are shown, compared with the 4-31G values (in parentheses) and, where available, experimantal data [in square brackets].



∠ HCH = 108.8(108.2)[109.2]

(10)



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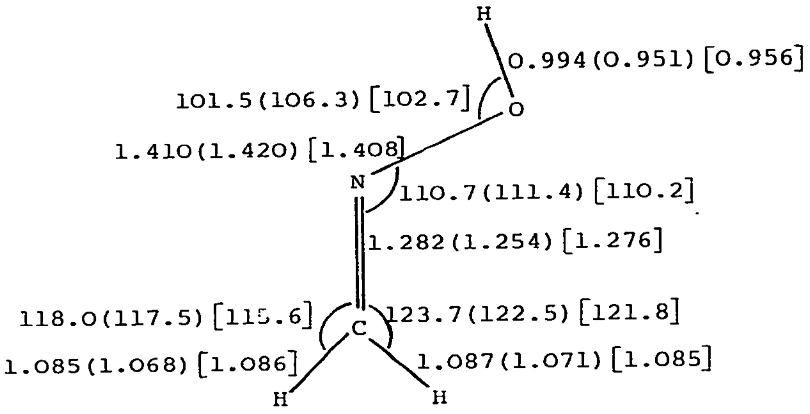
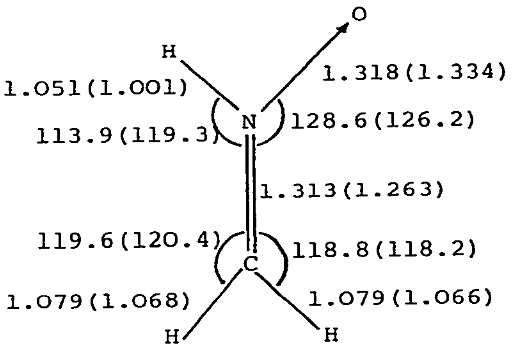

H
0.994(0.951) [0.956]
101.5(106.3) [102.7]
O
1.410(1.420) [1.408]
N
110.7(111.4) [110.2]
1.282(1.254) [1.276]
118.0(117.5) [115.6]
123.7(122.5) [121.8]
C
1.085(1.068) [1.086]
1.087(1.071) [1.085]
H
H

(<u>12</u>)


O
H
1.318(1.334)
1.051(1.001)
N
128.6(126.2)
113.9(119.3)
1.313(1.263)
119.6(120.4)
118.8(118.2)
C
1.079(1.068)
1.079(1.066)
H
H

(<u>13</u>)

Some reactions of N_2O with a range of titanium complexes have been investigated by Bottomley and coworkers.[55] They found that $(Cp_2TiCl)_2$ and (Cp_2Ti) are oxidised to $(Cp_2TiCl)_2O$ and $(Cp_2Ti)_2O$, the latter being further oxidised to a Ti(IV) polymer: $Cp_2Ti(CO)_2$ is oxidised more slowly to give $[(Cp_2Ti)_4(CO_3)_2]$ and eventually, with excess N_2O, a Ti(IV) polymer. In all instances the reduction product is N_2.

The catalytic conversion of NO, by the action of a $Co\text{-}La_2O_3\text{-}Pt$ catalyst supported on active carbon, to N_2 and CO_2 has been investigated:[56] the process operates efficiently at about $400^{\circ}C$. The kinetics of the oxidation of Fe^{2+} by aqueous nitric acid, with overall stoichiometry shown in equation (9), have been studied by spectrophotometric and potentiometric techniques at

$$3Fe^{2+} + 4H^{+} + NO_3^{-} \longrightarrow 3Fe^{3+} + 2H_2O + NO \qquad \text{...(9)}$$

high nitric acid concentration (0.6 - 2.0M) at $23\pm1^{\circ}C$.[57] The results of earlier equilibrium and kinetic studies were incorporated into a reaction scheme consisting of seven principal reactions; three for the reduction of nitrate to NO by Fe^{2+}, one for the formation of $FeNO^{2+}$, and three for the chemistry of oxonitrogen species in nitric acid. The conclusion is that the forward reaction (10) between NO and NO_3^-, is the rate-determining

$$NO + NO_3^{-} + H^{+} \rightleftharpoons NO_2 + HNO_2 \qquad \text{...(10)}$$

step and that the rate of this reaction can be assessed to within a factor of two. The X-ray photoelectron spectra of a series of iron complexes of the type $[Fe(NO)X(das)_2]^{n+}$, das = o-phenylenebis(dimethylarsine) and X = Cl, I or NCS, show a linear relationship between ν(NO) and the N 1s binding energy.[58a] This correlation shows less scatter than that reported by Finn and Jolly,[58b] who included data for a variety of central metals and associated ligands. The Lewis basicity of coordinated nitric oxide towards tricyclopentadienylsamarium has been investigated by i.r. spectroscopy;[59] the terminal nitrosyl ligand was found to be more basic than either μ_2 or μ_3 bridging groups. The alkyl nitrito complexes $[Ru(bipy)_2pyN(O)OR]^{2+}$, R = Me, Et, n-Bu or i-Pr, have been prepared by reactions involving attack of OR^- on the nitrosyl complex $[Ru(bipy)_2pyNO]^{3+}$.[60] It appears that the alkyl nitrite group is a better π-acceptor than nitro, pyridyl or acetonitrile ligands attached to Ru(II). However, once formed the alkyl nitrite complexes undergo an irreversible one-electron oxidation yielding $[Ru(bipy)_2pyNO]^{3+}$ and ROH, as the major products. The structure of an iron nitrosyl complex $[Fe(NO)(i\text{-}Prdtc)_2]$, dtc = dithiocarbamate, has been solved:[61] it contains an unambiguously linear Fe-N-O arrangement, with Fe-N and N-O distances 1.676(3) and 1.161(3)Å respectively.

An improved gas chromatographic method for the determination of nitrite ion, at concentrations in water as low as 0.5ng ml^{-1}, has been developed.[62] The method is based on the Sandmeyer reaction and the resulting p-bromochlorobenzene is determined with an electron capture detector. The characteristic electronic spectrum of the NO_2^- ion survives when the ion is bonded to metal ions through the oxygen atoms.[63] Walker et al. have examined the vibrational fine structure associated with the n→π* transition in the near uv for $K_3[Hg(O_2N)_4]NO_3$ at 10K and for a series of nickel complexes. Nitrate-free samples of $Ca(NO_2)_2.H_2O$ and $Ca(NO_2)_2$ have been characterised by Brooker and DeYoung.[64] The monohydrated Mg salt could not be prepared free of nitrate. The dark red salts M_3NO_3, M = K or Rb, have been prepared by solid state reactions of equimolar mixtures of M_2O and MNO_2 at ca. 300°C/2 days.[65] Structurally these compounds resemble the previously characterised sodium analogue; namely they are of the anti-perovskite type, $(NO_2)OM_3$. The Rb salt has antiferro-electrically ordered NO_2^- groups.

The action of 0.1 wt% $NaNO_2$ solution on Al at room temperature is initially slow but after an induction period the corrosion rate is catastrophic.[66] Ammonia, hydrogen, and bayerite ($\beta\text{-}Al(OH)_3$) were identified as the corrosion products. Emeish[67] has studied the kinetics of the reaction between NO_2^- and ClO_3^- in water and in water-dioxan mixtures and has proposed the following rate equation (11). Decreasing the dielectric constant increases the

$$\text{rate} = k[HNO_2][ClO_3^-][H^+] \qquad \ldots(11)$$

reaction rate which is in accord with the accepted role of H_2NClO_5 as the key intermediate. A spectrophotometric study of the kinetics of the reaction between HNO_2 and ClO_2^- has identified both a chloride ion-catalysed pathway as well as an uncatalysed one.[68]

A mechanism involving peroxonitrite and HOCl as intermediates was said to be consistent with the observations.

Nitro complexes of bis(dipyridyl)ruthenium(III), $[Ru(bipy)_2LNO_2]^{2+}$, where L = py etc., have been shown to be unstable with respect to oxidation of the nitro group:[69] the products were found to consist of the corresponding nitrosyl and nitrato compounds in a 1:1 ratio. Although much effort has been given to the study of the spontaneous intramolecular isomerisation of coordinated nitrito to nitro groups in transition metal complexes, Sargeson et al.[70] have noticed that there is also a base-catalysed pathway for this conversion, for Co, Rh and Ir(III) pentammines.

The standard enthalpies of formation of crystalline NO^+X^-, X = ClO_4 or HSO_4, and $(NO)_2S_2O_7$ have been determined:[71] the results are +59.0, -680.3 and -1041.0 kJ mol^{-1}, respectively, based on the enthalpies of reaction with aqueous base. The authors discuss the likely sources of the discrepancies with previous data. A new general synthesis of trifluoromethylamines of the type CF_3NXH has been reported by Sekiya and DesMarteau.[72] Excellent yields of these amines were obtained by the hydrolysis of compounds of the type $CF_3NXC(O)F$, which are readily available from the reaction of the oxaziridine $CF_3\overline{NCF_2O}$ with a range of nucleophiles. In this way six new amines have been prepared and characterised, namely with X = CF_3O, $(CF_3)_2CFO$, MeO, EtO, Me_2CHO and Me_3CO. The same workers[73] have synthesised $SF_5\overline{NCF_2O}$, the second member of the class of perfluorinated three-membered heterocycles based on the $-\overline{NCF_2O}$ unit. This SF_5 derivative has a different chemistry to that of $CF_3\overline{NCF_2O}$; thus, nucleophilic attack, by CsF at 22°C, occurs not only at nitrogen but also at carbon to give a 30% yield of CF_3NO. A number of mixed methyl and trifluoromethylarsines and stibines have been converted to the di[bis(trifluoromethyl)nitroxy] compounds by the action of $(CF_3)_2NO$.[74] The new derivatives $Me_n(CF_3)_{3-n}M(ON(CF_3)_2)_2$, M = As or Sb, are extremely moisture-sensitive and yield $(CF_3)_2NOH$ on hydrolysis or treatment with HCl.

Irradiation of $NaNO_3$ at low temperatures[75] produces NO_2^-, N^{3-}, N_2, O_2, NO and two other intermediates, which are thermally unstable and have been tentatively identified as NO^- and N^-. These assignments are based on X-ray p.e.s. studies in which unmonochromatised $A\ell\text{-}K_\alpha$ radiation was used both to induce the radiation damage and to excite the spectrum.

Campbell et al.[76] have reported that there is evidence for the formation of a new intermediate, a peroxy NO_3 radical, formulated as ONOO, in the decomposition of gaseous N_2O_5. Chlorine(I) nitrate, $ClONO_2$, has been produced in a high degree of purity by the single stage reaction of the type (12).[77]

$$M(NO_3)_2 + 2ClF \xrightarrow{\leq 0^{o}C} MF_2 + 2ClONO_2 \qquad ...(12)$$

The yield is highest when the metal nitrate (anhydrous) used is $Pb(NO_3)_2$ (92%) and lower yields are obtained from the alkaline earth nitrates (Ca, 63%; Sr, 44%; Ba, <10%).

The products of reaction of dry HNO_3 and the fluorides of Na and Cs have been characterised by Gillard et al:[78] CsF generates one unstable product containing the hydrogen-bonded $FHONO_2^-$ anion, which loses HF readily. Low energy (<22eV) photoelectron spectra have been recorded for the gaseous transition metal nitrates: Ti(IV), Co(III), Cu(II) and $OV(NO_3)_3$.[79] The interpretation of these spectra has been achieved with the help of ab initio m.o. and scattered wave Xα calculations. The ionization energies of electrons in nitrate orbitals are essentially the same for the Ti, V and Co compounds but are lower for Cu(II). This is readily correlated with the greater number of d orbitals into which electron donation can take place for the earlier transition metals as compared with copper.

The facile synthesis of the bis(chlorosulphur)nitrogen cation, $N(SCl)_2^+$ by means of reaction (13), has been reported, where M = As or Sb.[80] The crystal structure of the AsF_6^- and $AlCl_4^-$ salts have been determined by X-ray methods; the cation was found to have an essentially planar cis structure, Figure 3, as had been concluded from the previously reported but less accurate X-ray data for the BCl_4^- salt. Herberhold and Haumaier[81] have reported that a nitromethane solution of $N_3S_3Cl_3$ and $2AgPF_6$ behaves as a source of $NS^+PF_6^-$; thus it reacts with $C_6H_6Cr(CO)_3$ in acetonitrile to give a thionitrosyl metal complex $[Cr(NS)(NCMe)_5](PF_6)_2$. $(NSCl)_3$ reacts with Rh(I) complexes and with $RhCl_3.3H_2O$ in the presence of Ph_3E, E = P or As, to give thionitrosyl complexes;[82] these were characterised by analysis,

$$SCl_2 + NS^+MF_6^- \xrightarrow{SO_2} N(SCl)_2MF_6 \qquad ...(13)$$

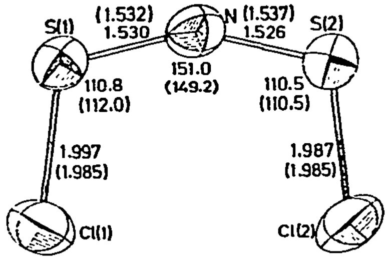


Figure 3. The structure of the $N(SCl)_2^+$ ion in the lattice of the $AlCl_4^-$ salt; bond lengths and angles in parentheses are for the BCl_4^- salt. (Reproduced by permission from Z. Naturforsch., 35b(1980)657).

i.r. spectra and magnetic studies. The recently synthesised $[Ni(NSF)_6](AsF_6)_2$[83] is isostructural with the Co(II) analogue, in which the S-N (1.40_3Å) and S-F (1.57_1Å) distances are shorter than those in free NSF.[84]

An improved synthesis of 1,1,1-trimethyl-N-sulphinylsilanimine, $Me_3Si-N=S=O$, has been claimed:[85] it involves the direct and facile reaction between SO_2 and hexamethyldisilazane. The authors suggest that this reaction may be valuable in detecting atmospheric SO_2, in the absence of moisture, by means of the fluorescence characteristics of the product.

The crystal structure of $K_3[N(SO_3)_2].H_2O$ has been determined by X-ray methods.[86] The N-S bond length (1.609(2)Å) in the approximately C_{2v} symmetry anion is significantly shorter than the corresponding bonds in sulphamate ($NH_2SO_3^-$), hydroxylamine-N,O-disulphonate ($O_3SONHSO_3^{2-}$),[87] imidosulphonate ($NH(SO_3)_2^{2-}$) or nitrilosulphonate ($N(SO_3)_3^{3-}$). The SNS angle (121.0°) is marginally smaller than in the imidosulphonate ion.

The low-temperature study by X-ray diffraction of thiotrithiazyl nitrate has been used to calculate the electron distributions.[88] The experimental and theoretical electron densities in the $S_4N_3^+$ ring are in good qualitative agreement except in the region of the lone pairs on the chemically equivalent pair of N atoms. On the other ligand the unique N atom, opposite the disulphide group, evidently bears a well-defined lone pair according to the electron density plots.

5.1.7 Bonds to Halogens

Münch and Selig[89] have observed that the first stage AsF_5-graphite compound, $C_{10}AsF_{5+x}$ $(0<x<0.5)$ converts N_2F_4 into a mixture of 90% *trans*-N_2F_2, 5% NF_3 and 5% N_2. The formation of the adduct $N_2F_4.AsF_5$ inside the graphite followed by F^- abstraction by graphite is proposed to explain the results. Higher stage intercalates do not behave in the same way.

In a course of a study of the chlorination of sea water Haag[90] has demonstrated that N-bromo-N-chloroamines exist and he has prepared and characterised MeNBrCl in CCl_4 solution: in concentrated solutions equilibrium (14) is established under

$$MeNCl_2 + MeNBr_2 \rightleftharpoons 2MeNBrCl \qquad ...(14)$$

the influence of u.v. light. The magnitude of the equilibrium constant for the process is 4.01±0.045 thus indicating that the distribution of halogens is essentially statistical. The chloro- and bromo-trimethylammonium cations have been prepared by a variety of methods, equations (15)-(17).[91] Both cations are

$$Me_2NX + MeOClO_3 \longrightarrow Me_3NX^+ClO_4^- \qquad ...(15)$$

$$Me_3NX_2 + BCl_3 \longrightarrow Me_3NX^+BCl_3X^- \qquad ...(16)$$

$$Me_3NX_2 \xrightarrow[-X^-]{H_2O} Me_3NX^+;\ Me_3NX^+ + BF_4^- \longrightarrow Me_3NX^+BF_4^- \qquad ...(17)$$

quite stable in the solid phase and in the presence of a large anion, such as BF_4^- or SO_3F^-, and also at temperatures below -25°C.

The simplest fluorinated sulphur(IV) imide, $SF_4{=}NF$, has been synthesised by the sequence of reactions (18)-(20).[92] The

$$SF_5NCl_2 \xrightarrow[-ClF]{F_2} SF_5NClF \qquad ...(18)$$

$$SF_5NClF \xrightarrow{Hg/CF_3CO_2H} SF_5NHF \qquad ...(19)$$

$$SF_5NHF \xrightarrow[-HF]{KF} SF_4{=}NF \qquad ...(20)$$

compound exhibits a complex ^{19}F n.m.r. spectrum which is consistent with a structure in which the N atom lies in the equatorial plane and the F(N) atom takes up a position in an axial plane.

The vibrational spectrum of NF_4AsF_6 has been reported and the observed ^{14}N-^{15}N isotopic shifts used to compute a generalised valence force field for NF_4^+.[93] The NF stretching force constant (6.15 mdyn Å^{-1}) is significantly greater than that in NF_3 (4.31 mdyn Å^{-1}). Wilson and Christe[94] have reported a simplified synthesis of $NF_4^+SbF_6^-$. The compound is formed in high purity by the fluorination of SbF_3 and excess NF_3 under pressure at 250°C. Christe et al.[95] have investigated the metathetical reactions shown in equation (21), X = Cl, Br or I. The perchlorate was isolated

$$NF_4SbF_6 + CsXO_4 \xrightarrow[-78^oC]{HF} NF_4XO_4 + CsSbF_6 \qquad ...(21)$$

and characterised but decomposes at 25°C to NF_3 and $FOClO_3$. The perbromate and periodate analogues could not be isolated: the former decomposes already in solution to NF_3, O_2 and $FBrO_2$. Attempts to prepare NF_4^+ salts of XF_4O^- in BrF_5 were unsuccessful. However, an unstable white solid of composition $NF_4^+HF_2^-.nHF$ was obtained from CsF and NF_4SbF_6 in liquid HF at -78°C. Solutions of $NF_4^+F^-$ are stable in HF at 25°C. The analogous reaction between $2NF_2SbF_6$ and Cs_2MnF_6 was used to prepare $(NF_4)_2MnF_6$.[96] This new compound is thermally stable up to 65°C and is not shock-sensitive: a violent hydrolysis reaction yields NF_3 quantitatively. The fluorosulphate analogue, $NF_4^+SO_3F^-$, has also been prepared in HF at -78°C.[97] The white solid is stable below 0°C but decomposes at higher temperatures to NF_3 and $FOSO_2F$: solutions in HF are stable at room temperature.

The crystal structure of Cl_3VNI has been determined by X-ray methods and has been shown to be isostructural with the chloronitrene analogue, Cl_3VNCl.[98] The iodo compound is dimeric with chlorine bridges and the V-N and N-I distances in the nearly linear VNI group (angle 163°) are 1.65(2) and 1.93(2)Å.

5.1.8 Bonds to Phosphorus or Arsenic

The structure of the adduct between 1,4-pyrazine, $C_4H_4N_2$, and PCl_5 appears to be the first one of a molecular PCl_5 adduct.[99] The P-N bond distance in the 6-coordinate compound is 2.021(5)Å. Aminoarsines are known to undergo ready transamination reactions : Krannich[100] has now shown that aminoarsolanes $\overline{OCR_2CR_2OAs}NR'_2$ (R = H or Me; R' = Me, Et or n-Pr) are also highly reactive in the presence of ammonia, and primary or secondary amines at room temperature. The high lability of the As-N bond in the presence of a labile proton and the equilibrium nature of the transamination reaction permit the ready synthesis of a variety of aminoarsolanes in high yield.

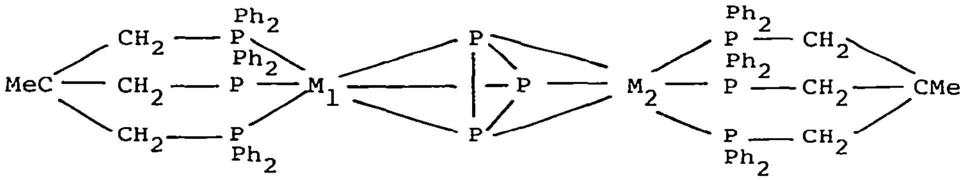
5.2 PHOSPHORUS

5.2.1 Phosphorus, Polyphosphines and Phosphides

Core binding energies from X-ray p.e. spectroscopy have been reported for a range of phosphorus(III) compounds including P_4, PX_3, where X = F, Cl, NMe_2, OMe, Me, etc., $P_4(NMe)_6$, $MePH_2$, etc. and compared with data for the corresponding lone pair ionisation potentials and proton affinities.[101] There is no single correlation between these two related processes and all the core binding energies and in the latter orbital rehybridisation plays a relatively unimportant role.

Polyatomic phosphorus cations are not produced when mixtures of P_4 in fluorosulphuric acid are electrolysed and the colouration observed results from decomposition of the acid and formation of known sulphur cations.[102]

Full details of the X-ray structure of the η-P_3 compound, (triphos)Co(P_3), and its reactions with $Cr(CO)_6$, that were mentioned in last years report are now available.[103] Further compounds containing this interesting ligand have also been reported from reactions between either $[Rh(C_2H_4)_2Cl]_2$ or $Ir(PPh_3)_2(CO)Cl$ and white phosphorus in the presence of 1,1,1-tris(diphenylphosphinomethyl)methane.[104] The products are monomeric with the formula [(triphos)M(P_3)], and they react further with cobalt(II) and nickel(II) salts to give dinuclear complexes such as $[(triphos)Rh(P_3)Co(triphos)](BPh_4)_2.2Me_2CO$ and $[(triphos)Rh(P_3)Ni(triphos)](BF_4)_2.C_4H_8O$. X-ray data for these compounds show the triple decked sandwich structure (14), in which the metal sites each have 50% Rh/50% Co(Ni) occupancy.



(14)

Evidence for the phosphinophosphite anion $OP(O)(H).PH_2^-$ has been obtained from ^{31}P n.m.r. studies on the products of hydrolysis of the polymeric suboxide P_4O and P_4 by sodium hydroxide in aqueous ethanol.[105]

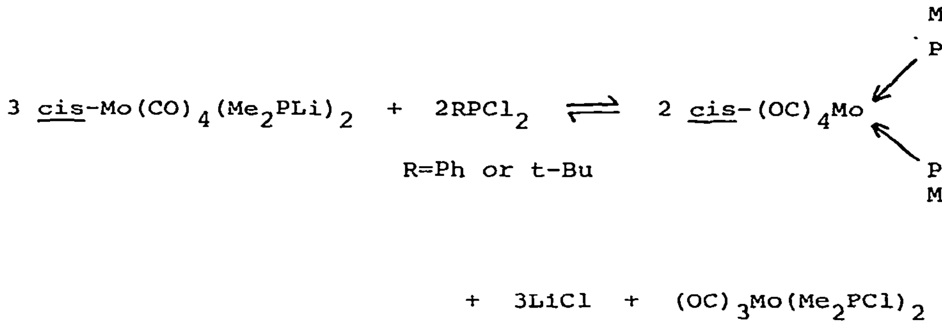
^{31}P n.m.r. data, including the signs and magnitudes of J(P-P) and J(P-H) have been obtained for a series of biphosphines $R^1R^2PPR^1R^2$, where R^1, R^2 = Me, Ph and t-Bu, and the corresponding sulphur and selenium oxidation products.[106] The data are discussed in terms of changes in hybridisation at phosphorus or in the effective nuclear charge. Other multinuclear n.m.r. data for biphosphines with bulky t-Bu or i-Pr groups are also discussed in relation to the adopted molecular conformation and the effects of inversion at the phosphorus atoms.[107]

N.m.r. spectroscopy has been used to follow the formation of a phosphine-phosphinidine complex, Me_3PPCF_3, from the reaction of trimethylphosphine and $(CF_3P)_{4\text{ or }5}$ but the data are temperature and Me_3P concentration dependent in the presence of excess Me_3P.[108] The rate determining step is an association process shown in equation (22), but the kinetics are complicated by at

$$Me_3P^* + Me_3PPCF_3 \rightleftharpoons Me_3P^*P(CF_3)PMe_3 \rightleftharpoons Me_3P^*PCF_3 + Me_3P \quad ...(22)$$

least one side reaction which leads to Me_3PF_2.

A complex with a coordinated tetraphosphine group is the product from reaction (23), while a triphosphine complex results from the related reaction, see equation (24), in which the starting material is the diphenylphosphide derivative.[109]



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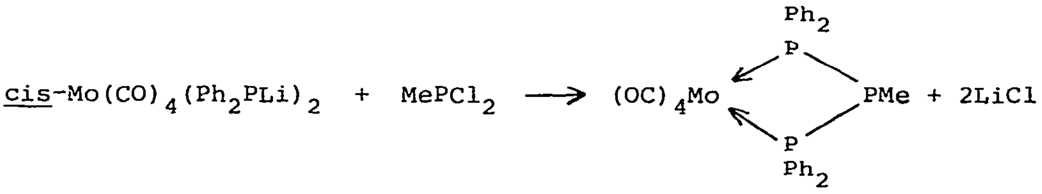
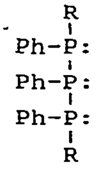
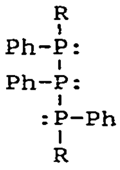


...(24)

Reaction of the 1,2,3-triphenyltriphosphide, $K_2(PPh_3)_3$ with trimethylchlorosilane gives the substituted triphosphine, $Me_3Si.PPh.PPh.PPh.SiMe_3$, which is stable to disproportionation.[110] From n.m.r. data, the compound in solution is a mixture of the three diastereoisomers (15-17, R = $SiMe_3$) in the ratio 8:3:1; due to pyramidal inversion at the phosphorus atoms, the three forms



(15)



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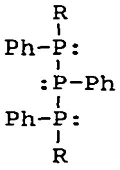
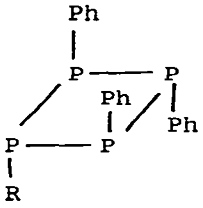


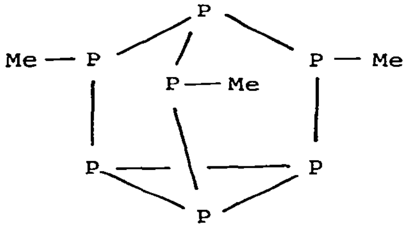
(17)

are in dynamic equilibrium. On alcoholysis, this trimethylsilyl derivative loses Me_3SiOMe with formation of $H(PPh)_3H$, which is stable in solution below -30°C.[111] Again the product is considered to be a mixture of the three isomers (15 - 17, R = H) in the ratio 1:4:3.

The potassium salt and the trimethylsilyl derivative both undergo a [3+1] condensation reaction with either phenyl- or t-butyl-dichlorophosphine to give the cyclo-tetraphosphine (18)[112]



(18, R = Ph or t-Bu)



(19)

but, while the product with R = Ph rearranges readily in solution at room temperature to the more stable cyclo-pentaphosphine, $(PPh)_5$, the t-butyl derivative is far more stable.

Reaction between Li_3P_4 and methyl bromide at -60°C in THF solution gives the heptaphosphine (19) as a mixture of two isomers which differ in the orientation of the methyl groups.[113] On thermolysis at 200°C, polycyclic phosphines in the series P_nH_{n-2m}, where n = 4 - 18 and m = 1 - 7, are the products.

Lithium heptaphosphide, Li_3P_7, can be prepared readily from white phosphorus and an excess of $LiPH_2$ in monoglyme,[114] and from ^{31}P n.m.r. measurements on the ^6Li derivative[115] the tricyclic cage structure is compressed along the three-fold axis in comparison with $(Me_3Si)_3P_7$. Predominantly ionic character is suggested.

Two new compounds with the formula Sc_3P_2 have been identified in the Sc-P system and are considered to have Cr_3C_2 and Hf_3P_2 structures respectively.[116]

The structure of α-Ti_5P_3 reveals two independent phosphorus atoms in eight- and seven-fold coordination by titanium,[117] while a new niobium phosphide, Nb_2P_5, contains infinite zig-zag phosphorus chains in a structure similar to that of $OsGe_2$.[118] During attempts to grow single crystals of MnP_3, a new triclinic modification of MnP_4 was obtained.[119] Single crystals of Re_6P_{13} have been obtained from reactions between the elements in molten tin while the elements in the presence of iodine gave only microcrystalline samples.[120] The crystals are rhombohedral $R\bar{3}$ and each rhenium is coordinated to six phosphorus atoms (Re-P, 2.290 - 2.699Å) in a distorted octahedron; further condensation leads to Re_4P_{16} units. The phosphorus atoms, which are all tetrahedrally coordinated by either P or Re, are found as P_6 rings, P_4 chains and P_2 units.

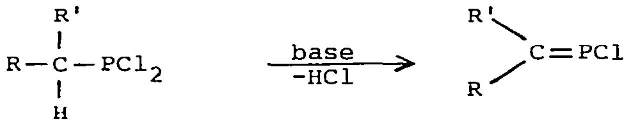
The new europium polyphosphide EuP_7, obtained from the elements in a salt melt, has a polyanionic network containing P_6, P_8 and P_{10} rings.[121] P-P distances range between 2.18 and 2.23Å; on thermal decomposition the compound gives successively EuP_3, EuP_2, Eu_3P_4 and EuP. Berkelium monopnictides, which can be prepared from the elements, have NaCl-type cubic structures.[122]

Among the new ternary phosphides reported this year are $CaCu_4P_2$,[123] $M_2Ni_{12}P_7$, where M is a lanthanoid,[124] Li_2PrP_2 (and the corresponding arsenide),[125] $Mg_{2.5}Ni_{11.5}P_7$[126] and $Ca_{2.1}Ni_{11.9}P_7$.[126] The latter two compounds and $Er_2Ni_{12}P_7$ have the $Zr_2Fe_{12}P_7$ type structure. Structures are also reported for $Cd_4P_2I_3$[127] and $Cd_7P_4Cl_6$[128]; both of which contain P_2Cd_6 units.

5.2.2 Bonds to Carbon or Silicon

The +3 Oxidation State. Phosphaethene CH_2:PH, originally obtained by pyrolysis of either $MePH_2$ or Me_2PH, can be more readily prepared by pyrolysis at 710°C of $Me_3SiCH_2PH_2$; a detailed assignment of the microwave spectrum has been presented.[129] The new compound, cyanophosphaethyne N:C·C:P, which is formed in ca. 1% yield when cyanogen azide and phosphaethyne HC:P react at 700°C, is linear with a dipole moment of 3.44D from microwave data.[130]

The necessity for the presence of bulky t-Bu or Me_3Si group to stabilise P=C double bonds is only partially true as shown by the formation of P-chloromethylenephosphoranes by the reaction in equation (25).[131] Alkyl or aryl dichlorophosphines and the lithium



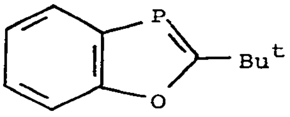
...(25)

R = R' = H or Ph
R = Ph, R' = Me_3Si

derivative $(Me_3Si)_3CLi$ give compounds in the series $RPClC(SiMe_3)_3$ but it is not possible to substitute the second chlorine atom,[132] and a similar reaction to give $Cl_2PC(SiMe_3)_3$ occurs when phosphorus trichloride is a reactant.[133] The former compounds on heating lose one mole of Me_3SiCl to give the phosphaalkene $RP{:}C(SiMe_3)_2$ but, although trimethylchlorosilane is released when $Cl_2PC(SiMe_3)_3$ is heated, the product is an oil considered to be $(Me_3SiCP)_n$.

A two-coordinate phosphorus atom which is incorporated into a five-membered ring occurs in the benzooxaphosphole (20), obtained when o-phosphinophenol reacts with pivaloyl-p-tolyl-imidoyl chloride, t-BuC(Cl):NTol.[134]

Pseudo-halogen character has been ascribed to the $P(CN)_2$ group and following this, pseudo-chalcogen behaviour might be expected



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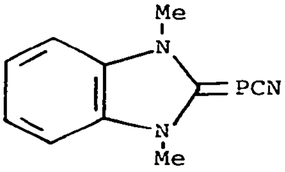

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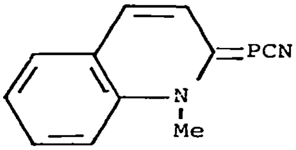
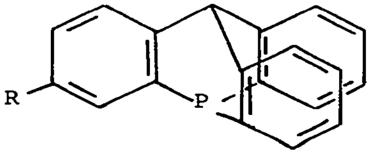


(22)

with the PCN group. This has been established by the recent synthesis of two cyanophosphinidine analogues (21) and (22) of the oxo- or thiooxo- derivatives of N-heterocycles.[135] An X-ray analysis of (21) shows there is a considerable contribution to the structure from the $C^+\text{-}P{=}C{=}N^-$ form and, in some respects, these compounds occupy an intermediate position between the phosphamethine cyanine cations and the dicyanophosphide anion.

X-ray diffraction points to there being substantial disorder in the structures of both phospha- and arsa-triptycene (23, R = H) with interchange between the P(As) atom and the bridgehead carbon



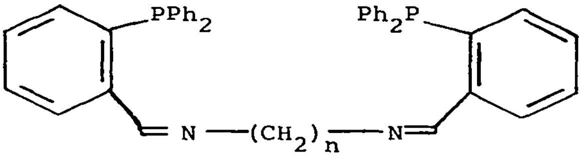
(23)

atom.[136] To obtain reliable information, the t-butyl derivative (<u>23</u>, R = t-Bu) has also been examined showing three equal P-C bond lengths (mean 1.843Å), a mean CPC angle of 94.5° and mean internal and external PCC angles of 116.3 and 123.7° respectively.[137]

Gas phase dipole moments determined by the Debye method have been obtained for the MeEtPH 1.28D, Me_2EtP 1.31D, and $MeEt_2P$ 1.58D.[138] Alkylphenylphosphide anions can be prepared when lithium and an alkyldiphenylphosphine react in THF solution, and chiral phosphines PhR^1R^2P can be obtained on further reaction with an alkyl halide.[139] ^{31}P chemical shifts for these compounds deviate markedly from those predicted on the basis of the first order additivity model but prediction is possible using a second order pairwise additivity scheme.

Tri(mesityl)-phosphine and -arsine have been used to investigate complex formation with sterically hindered donors;[140] each ligand gives a 1:2 complex, formulated as $(AgL_2)PF_6$, on reaction with $AgPF_6$.

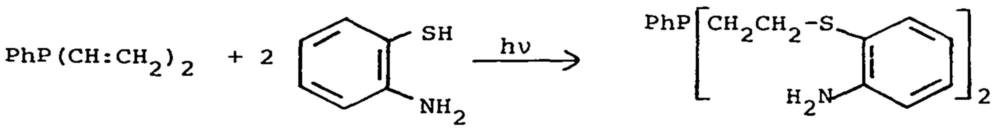
The coordination chemistry of the novel ligands (<u>24</u>) has been investigated with nickel, copper and silver ions and tetradentate behaviour shown from an X-ray structure on $(CuL)ClO_4.CH_2Cl_2$.[141] Polydentate phosphine ligands, which contain either mixed donor groups or specific types of donors at selected sites, have been synthesised by methods which involve radical chain, base catalysed or coupling reactions.[142] Some examples are given in equations (26)-(28). Palladium and platinum complexes have been



(<u>24</u>, n=2 or 3)

$$NaPHPh + ClCH_2CH_2CH_2PPh_2 \longrightarrow PhHPCH_2CH_2CH_2PPh_2 \quad ...(26)$$

$$PhPH_2 + CH_2{:}CHCH_2NH_2 \xrightarrow{h\nu} PhHPCH_2CH_2CH_2NH_2 \quad ...(27)$$



...(28)

obtained using a number of chelating amino-phosphines including $Ph_2PCH_2CH_2CH_2NH_2$ and $Ph_2PCH_2CH_2CH_2N{:}CHPh$,[143] and complexes with di- and tri-phosphines containing P-H groups have been obtained using reactions of the types shown in equations (29) and (30).[144]

$$Mo(CO)_5(PhPHLi) \ + \ Ph_2PCl \longrightarrow LiCl \ + \ (OC)_5Mo{\cdot}PHPhPPh_2 \qquad ...(29)$$

$$2Mo(CO)_5(PhPHLi) \ + \ PhPCl_2 \longrightarrow 2LiCl \ + \ (OC)_5MoPHPhPPhPHPhMo(CO)_5 \qquad ...(30)$$

Polyphosphaalkanes with α,ω-PH groups can be prepared from an alkene, such as $R^1_n(i\text{-}PrO)_{2-n}P(O)CH_2CH{:}CH_2$, and a secondary diphosphine, $R^2HP(CH_2)_3PHR^2$, in the presence of α,α^1-azabis(isobutyronitrile).[145] The general formula is $H_{2-n}R^1_nP(CH_2)_3PR^2(CH_2)_3$-$PR^2(CH_2)_3PR^1_nH_{2-n}$, where n = 0 or 1 and R^1, R^2 = Me or Ph, and complex formation occurs with Ni, Pd, or Pt dihalides (MX_2) to give compounds formulated as $(MLX)^+X^-$. For the nickel compound, the cation $NiLBr^+$ is square pyramidal. Reactions of bis(phenylphosphino)propane, $PhPH(CH_2)_3PHPh$(L), with, inter alia, $Ni(CO)_4$ and $Mo(CO)_6$ give compounds such as $Ni(CO)_2L$ and $Mo(CO)_4L$ as mixtures of the meso- and racemic forms;[146] the structure of the meso- form of the former has been determined.

Complex formation between triorganotin chlorides[147] or Os(II) and Os(III) compounds[148] and bis(diphenylphosphinoethyl)phenyl phosphine, $PhP(CH_2CH_2PPh_2)_2$, and other tertiary phosphines has been examined. Convenient syntheses are now available for the analogous phosphinopropyl compound $PhP(CH_2CH_2CH_2PPh_2)_2$ and its precursor $Ph_2P(CH_2)_3PHPh$.[149]

The 1:1 silver bromide adduct with bis(diphenylphosphino)-methane (L) contains the trinuclear cation $(Ag_3Br_2L_3)^+$ shown in Figure 4.[150] This is best described as a trigonal bipyramid with the silver and bromine atoms occupying respectively equatorial and axial positions. The ligand molecules then bridge each edge of the Ag_3 triangle. With the related ligand, bis(diphenylphosphino)-

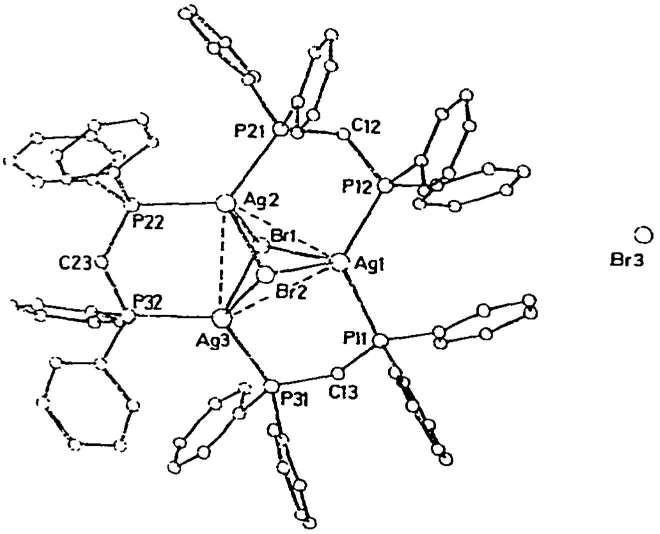
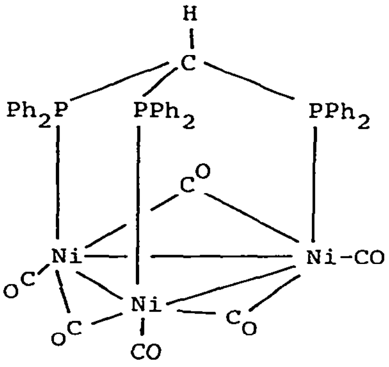


Figure 4. Structure of $\{Ag_3Br_2[CH_2(PPh_2)_2]_3\}Br$ (Reproduced by permission from Z. Anorg. Allg. Chem., 464(1980)217).

methylamine, the resulting complex is 4AgBr.2L'. Four coplanar silver atoms and two bromine atoms form a distorted octahedron in which the Ag-Ag edges are bridged alternately by bromine atoms and ligand molecules.

The geometry of the tripod ligand $HC(PPh_3)_3$ is such that it can coordinate to three metal atoms on a cluster surface; for example, three molecules of CO are displaced with formation of 1:1 complexes with $M_4(CO)_{12}$ where M = Co, Rh or Ir.[151] Further, this geometry has proved useful in the preparation of a novel Ni(O) trimer $Ni_3(CO)_6L$ (25) from the tetracarbonyl.[152] The reaction is considered to proceed via $Ni(CO)_2L$ and a dimer $Ni_2(CO)_5L$. A further tripod ligand, $MeC(CH_2PEt_2)_3$, is involved when hydrated iron(II) tetrafluoroborate reacts with carbon disulphide.[153] The product (26) arises from loss of one CH_2PEt_2 group from the second ligand molecule which coordinates as a heterocyclic diphosphoniacyclohexanedithiolate.



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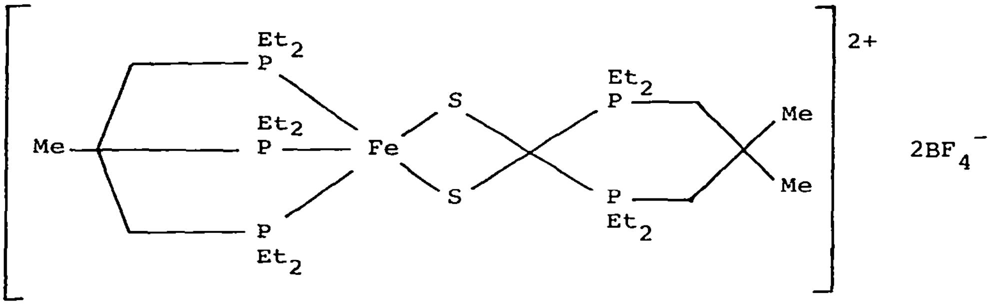
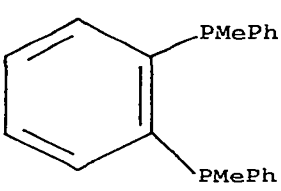


(26)

Carbonyl iridium(I) complexes with a number of ligands including 2-(diphenylphosphino)-N,N-dimethylethylamine, 3-(diphenylphosphino)-N,N-dimethylpropylamine, and o-(diphenylphosphinol)-N,N-dimethylaniline have been isolated and a full structure reported for the complex IrCl(CO)L involving the last ligand.[154]

Crystal structure determinations are also reported for the meso-form of (27) and for the complex (28).[155]



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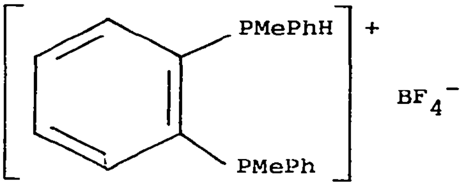
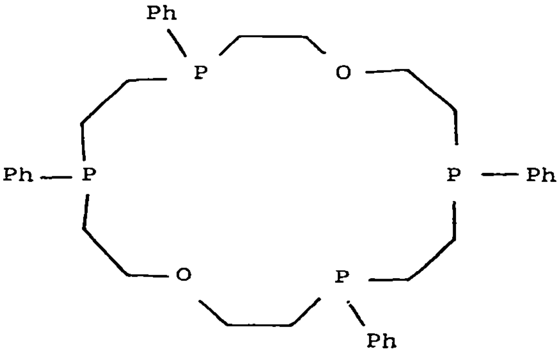


(28)

The new phosphorus containing macrocycle (29), which results when 2,2'-dichlorodiethylether is added to a mixture of 1,2-bis-(diphenylphosphino)ethane and phenyl lithium in THF, occurs in two



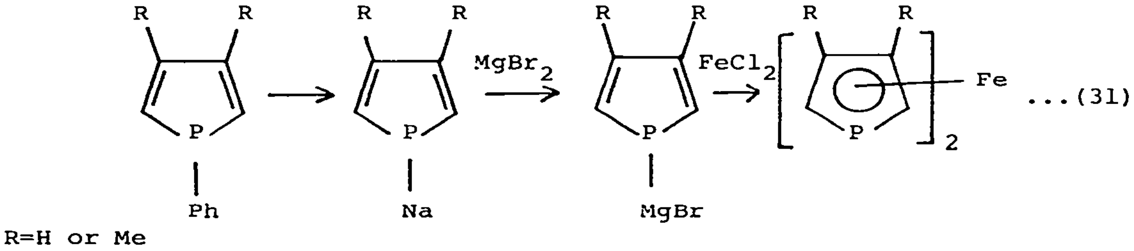
(29)

geometrical isomeric forms with distinctly different melting points.[156] Low spin cobalt complexes $CoL(BPh_4)_2$ can be obtained with each form, the lower melting isomer giving distorted square pyramidal coordination about the metal whereas in the second complex the cobalt is in distorted octahedral coordination.

Ethylene is displaced when $Ph_2PNHPPh_2$ reacts with $[Rh(C_2H_4)_2Cl]_2$ to give $[Rh(Ph_2PNHPPh_2)_2]Cl$ which has the property of incorporating small molecules such as CO, O_2 and S_2.[157] Molybdenum carbonyl complexes $Mo(CO)_5L$ have been prepared and characterised for a range of phosphine and arsine ligands including $Me_2PM(CF_3)_2$ where

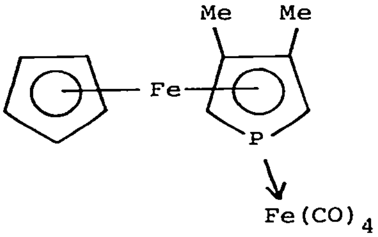
M = P or As, Me_2PXMe, and $(CF_3)_2PXMe$, where X = S, Se or Te.[158]

1,1'-Diphosphaferrocenes have been prepared by the reactions outlined in equation (31),



...(31)

and their activity assessed through formylation and acetylation reactions.[159] A crystal structure for the dimethyl compound shows the expected π-structure but the phosphorus atom of one ring is superposed above the β-carbon of the second. Aromaticity of the phospholyl ring in 3,4-dimethylphosphaferrocene remains



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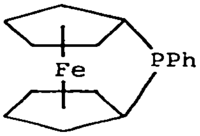

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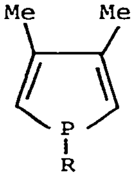


(32)

unchanged according to a crystallographic investigation when the phosphorus atom is coordinated to an iron atom as in (30).[160] Distances from iron to both rings increase on complexation and the rings take up a staggered conformation in contrast to being eclipsed in the free phosphaferrocene.

Both phospha- and diphospha-zirconocene dichlorides have been obtained as air sensitive solids by reaction between a phospholyl anion and $CpZrCl_3$ and $ZrCl_4$ respectively.[161] Structures for the (1,1'-ferrocenediyl)phenylphosphine (31) and the Ph_2Ge analogue show that the rings are eclipsed and tilted at angles of 26.7° for the phosphorus and 16.6° for the germanium compound.[162] A series of Pd(II) complexes with the general formula L_2PdX_2, where X = Cl, Br, or N_3, has been isolated for L being a 1-substituted-3,4-dimethyl-1-phosphole (32).[163]

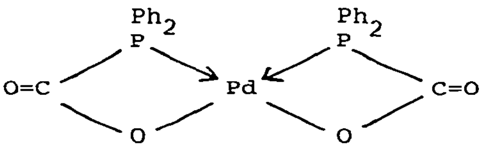
Further information is now available on the preparation and reactivity of substituted acetyl[164] and trifluoroacetyl[165] phosphines obtained via reactions such as those in equations (32) and (33).

$$CH_3COCl \ + \ Me_3SiPR^1R^2 \longrightarrow CH_3C(O)PR^1R^2 \ + \ Me_3SiCl \quad ...(32)$$

$$2(CF_3CO)_2O \ + \ 2HPR^1R^2 \longrightarrow 2CF_3C(O)PR^1R^2 \ + \ 2CF_3COOH \ ...(33)$$

Derivatives with a wide range of substituents were obtained but only those carrying mesityl groups were stable toward oxygen; in general the reactivity of these compounds depends on the electronic and steric influences of the substituents at phosphorus. Corresponding reactions between the appropriate anhydride and $HP(O)R^1R^2$ (see equation 33) yield the oxide $RC(O)P(O)R^1R^2$.

The palladium atom is at the centre of a distorted cis square planar environment in its complex with diphenylphosphinoacetate (33).[166]



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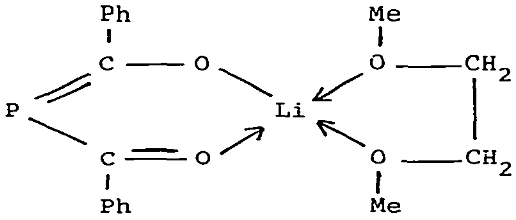

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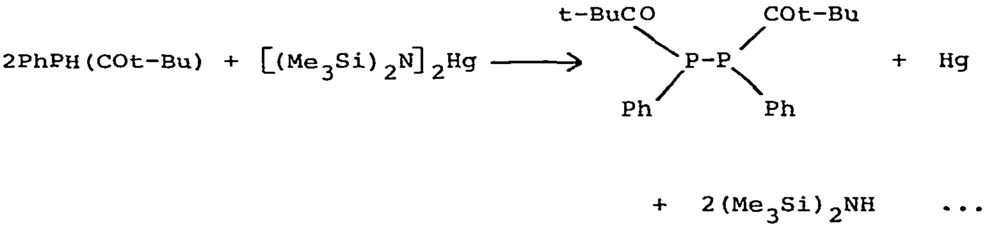
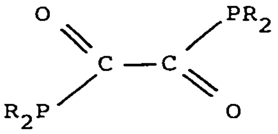
A full X-ray structure has been obtained for the acyl-diphosphine (34) prepared by the method in equation (34);[167] this shows the



...(34)

presence of both the S,S and R,R enantiomers in the asymmetric unit. Mean distances are P-C(O) 1.89, P-C(Ph) 1.84 and P-P 2.21Å, and the PPC(O) and PPC(Ph) angles are 97 and 96° respectively. In a search for the unknown dibenzoylphosphine $(PhCO)_2PH$, the reaction between benzoyl chloride and the dimethoxyethane complex of monolithium phosphide has been investigated.[168] The product which is isolated is in fact the lithium derivative (35) which X-ray studies show to be dimeric with P-C distances of 1.796 and 1.815Å and a CPC angle of 101.8°. Finally in this general area, a number of compounds related to the violet coloured P,P'-tetraphenyl oxalic acid diphosphide (36, R = Ph) have been synthesised.[169] Among these are the t-butyl derivative (36, R=t-Bu)



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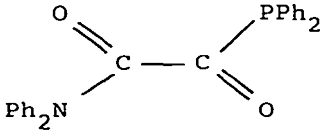


(37)

and the mixed nitrogen-phosphorus compound (37). X-ray structures for the two diphosphides show a slightly greater distortion of the framework from the coplanar trans-configuration for the t-butyl compound.

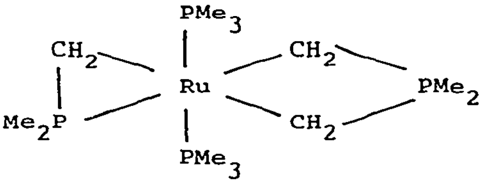
The +5 Oxidation State. A number of phosphinalkyleneboranes, considered to be zwitterionic analogues of the tetraalkylsilanes and tetraalkylphosphonium cation, have been synthesised following equation (35),[170] and a crystal structure determination for the

$$R_3\overset{+}{P}-\overset{-}{C}H_2 \quad + \quad H_3B.OC_4H_8 \longrightarrow R_3\overset{+}{P}-CH_2-\overset{-}{B}H_3 \quad + \quad OC_4H_8 \qquad \ldots(35)$$

R = Me, Et, i-Pr,
n-Bu or t-Bu

trimethyl derivative shows that the $P-CH_2$ bond length is increased to a single bond distance (1.76Å).[171] Evolution of ethylene following β-elimination is observed when reaction occurs between the ylid $Me_3P:CH_2$ and $H_3SiCH_2CH_2Cl$ in a 2:1 ratio;[172] the products $Me_3P:CHSiH_3$ and Me_4PCl arise from a transylidation step. Important parameters from an electron diffraction study of silyl ylid are: P-C 1.807, P=C 1.653, Si-C 1.85Å, and Si-C=P 123.4°; the data are consistent with a planar configuration about the methylene carbon atom. Lithiation of $Me_3P:CH_2$ followed by reaction with $(Me_3P)_4RuCl_2$

leads to the spirometallic complex (38), together with the ionic complex trans-$[(Me_3P)_4Ru(CH_2PMe_3)Cl]^+Cl^-$ as a byproduct.[173]



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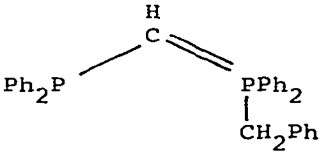

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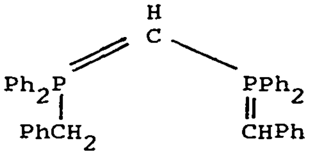
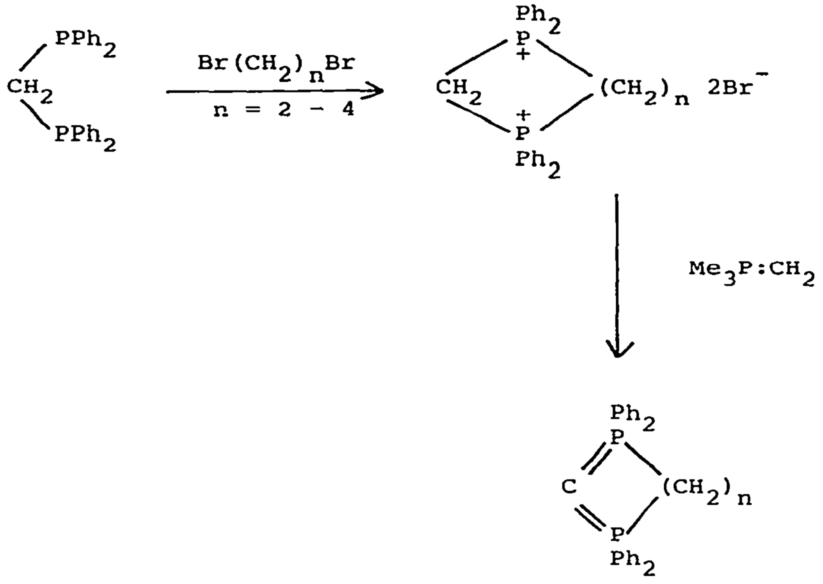


(40)

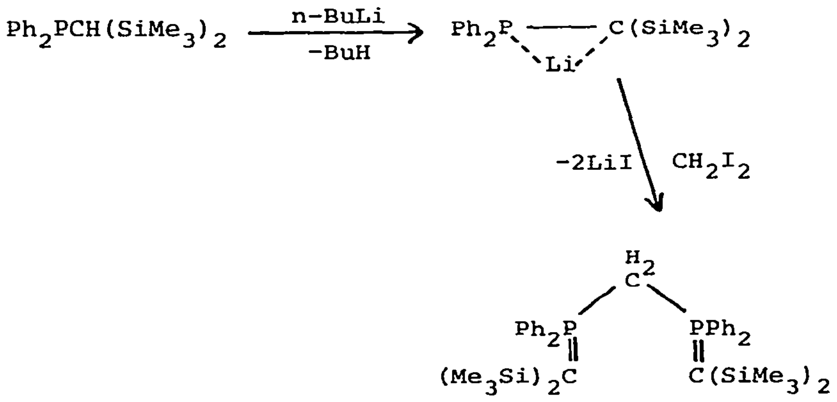
Two new ylids (39) and (40) have been synthesised from $Ph_2PCH_2PPh_2$ via the corresponding mono- and di-benzylphosphonium salts.[174] The double ylid (40) exists solely in the conjugated form shown in contrast to the more usually observed cumulative $R_3P{:}C{:}PR_3$ form. Sodium amide in THF leads to coloured complexes with both (39) and (40) which are formulated as monosodium salts resulting from proton loss from the benzyl methylene group; confirmation follows from an X-ray structure for the compound from (39) which crystallises with one mole each of ether and THF.

The bis(diphenylphosphino)methanide complexes $[(Ph_2P)_2CH]_2M$, where M = Ni, Pd or Pt, on treatment with an ylide such as $R_2MeP{:}CH_2$, where R = Me or Et, are converted to $[(Ph_2P)_2CH]M[(CH_2)_2PR_2]$ with evolution of $(Ph_2P)_2CH_2$.[175] Recent experiments have confirmed that incorporation of the P:C:P structural unit into a ring system is possible.[176] The method involves quaternisation of methylene bis(diphenylphosphine) with an α,ω-dibromoalkane followed by dehydrohalogenation as outlined in (36). An X-ray structure for the product where n = 3 shows disorder but the PCP angle at 117° is the smallest yet found in this type of compound.



...(36)

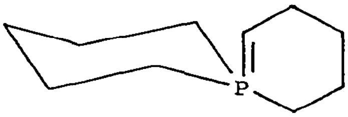
Although deprotonation of methylene bridged bis(phosphonium) salts generally occurs at the central carbon atom to give either a carbodiphosphorane, $R_3P{:}C{:}PR_3$, or a double conjugated ylid, $R_2HC.PR_2{:}CH.PR_2{:}CR_2$, an example has now been observed where the product is an isomer based on a methylene phosphorane carrying two terminal ylidic groups.[177] The preparative method is outlined in equation (37). Amino-substituted carbodiphosphoranes,



...(37)

$Ph_3P{:}C{:}PPh_2NR_2$, can be synthesised from the P-chloro derivative and secondary amines by dehydrohalogenation of the intermediate phosphonium salt $[Ph_3P\cdots CH\cdots PPh_2NR_2]^+Cl^-$ with sodium hydride.[178] The formulation is supported by n.m.r. data and the compound reacts with water and methyl iodide to give $Ph_3P{:}CH\cdot P(O)Ph_2$ and $[Ph_3PC(Me)PPh_2(NR_2)]^+I^-$ respectively.

An ylid (41) in which the phosphorus atom is part of a bicyclic system has been prepared via the phosphonium salt (42), and characterised spectroscopically.[179] The previously unknown



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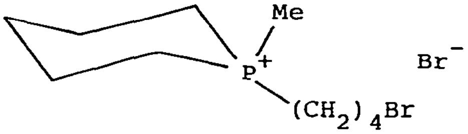


(42)

$(t\text{-}Bu)_4P^+$ cation has now been prepared by the series of quaternisation and ylidation steps outlined in Scheme 1.[180]

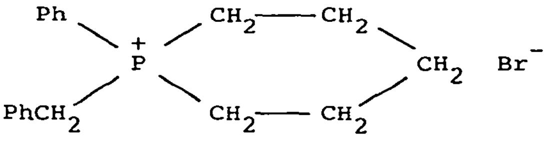
$$\begin{tikzcd}
(t\text{-}Bu)_3P \arrow[r, "MeBr"] & (t\text{-}Bu)_3PMe^+ \arrow[r, "base"] & (t\text{-}Bu)_3P{:}CH_2 \arrow[d, "MeBr"] \\
(t\text{-}Bu)_3PCHMe_2^+ \arrow[d, "base"] & (t\text{-}Bu)_3P{:}CHMe \arrow[l, "MeBr"'] & (t\text{-}Bu)_3PC_2H_5^+ \arrow[l, "base"'] \\
(t\text{-}Bu)_3P{:}CMe_2 \arrow[r, "MeI"] & (t\text{-}Bu)_4P^+ &
\end{tikzcd}$$

Scheme 1

As expected there is extremely high steric hindrance in the cation which has T-symmetry leading to long P-C bonds (1.924Å) and reduced C-C-C angles (106.5°).

Full X-ray structures have been obtained for the pseudo-chalcogen derivative $Ph_3P{:}C(CN)_2$[181] and the corresponding cyanamide $Ph_3P{:}NCN$.[182]

As a preliminary to an investigation into the steric course of the base hydrolysis of cyclic phosphonium salts, X-ray structures have been determined for two compounds (43) and (44)[183] with six-membered and one compound (45)[184] containing a five-membered ring. In (43) and (44) the rings are in the chair conformation while in (45) the methyl and benzyl groups are *trans* and the ring has a envelope conformation. Molecular mechanics calculations simulating the base hydrolysis of the *cis* and *trans* isomers of (43) support, in agreement with experimental data, less inversion of configuration for the *trans* compound.



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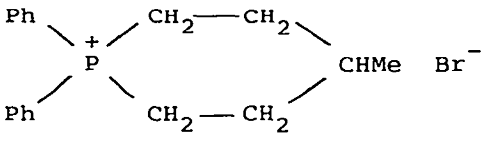

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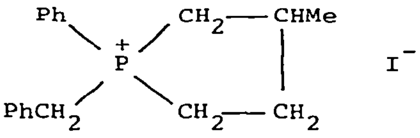
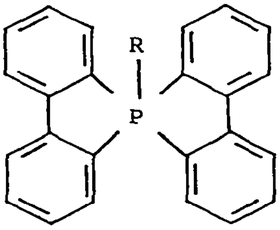


(45)

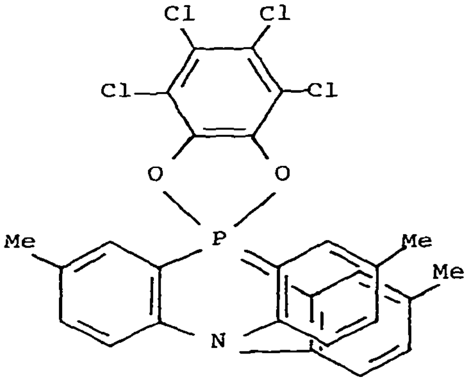
Further information on the distortion of the trigonal bipyramidal geometry in constrained five coordinate phosphorus compounds has become available from X-ray structures on four biphenylyl derivatives (46). Although there is only 25% distortion



(46)

along the Berry coordinate for R = 1-naphthyl, increased steric crowding when R = 8-Me_2N-naphthyl raises this to 64% toward the square pyramidal alternative in which the substituted naphthyl group occupies a basal position.[185] Approximately trigonal bipyramidal structures are found when R = Me or Ph where the biphenylyl groups each span axial and equatorial positions, but consideration of the dihedral angles shows that these structures are distorted away from both alternatives as a consequence of a slight tilt of the axial ligands away from the unique ligand.[186]

Novel geometry might have been expected from the rigidity of the tridentate group in the five coordinate species (47), but the structure is basically trigonal bipyramidal with an oxygen (1.816Å) and a carbon atom (1.869Å) in axial positions and two carbon (1.815Å) and the second oxygen (1.670Å) in the equatorial sites.[187]



(47)

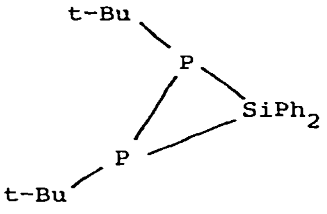
The preparation and n.m.r. spectra for all the oxidised products, $Ph_2P(X)CH_2P(Y)Ph_2$, where X = Y or X ≠ Y and X, Y = O, S, Se, CH_3^+ or a lone pair, based on $Ph_2PCH_2PPh_2$ have been obtained.[188] The data are interpreted in terms of an increase in the effective positive charge on phosphorus in the order $Ph_2P < Ph_2P(O) < Ph_2P(S) < Ph_2P(Se) < Ph_2PMe^+$; several coordination compounds have been isolated. Two t-butyl analogues, i.e. $Ph_2P(S)CH_2P(t\text{-}Bu)_2$ and $Ph_2PCH_2P(S)(t\text{-}Bu)_2$, have also been prepared.[189] The lithium derivative, $Ph_2P(S)CH_2Li$, serves as a useful intermediate in the formation of polydentate ligands such as $[Ph_2P(X)][R_2P(X)]_2CH$, where R = Me or Ph and X = O, S or a lone pair;[190] related processes have yielded $[Ph_2P(S)CH_2]_2PPh$ and $[Ph_2P(S)CH_2]_3P$.

Silylation of the secondary phosphine oxides, $[Ph(H)P(O)]_2(CH_2)_n$

where n = 2-4, with trimethylchlorosilane leads to $Me_3SiOP(Ph)(CH_2)_nP(Ph)OSiMe_3$, which can be converted to the corresponding bis(phosphonium)iodides $[Me_3SiOPMePh(CH_2)_nPMePhOSiMe_3]I_2$ by methyl iodide.[191]

Diethylacetyl phosphonate and its benzoyl analogue, $(EtO)_2RC(O)P{:}O$, form complexes with a range of metals including Al, Ti, V, Cr and Fe in the +3 oxidation state and Th and U in the +4 state, behaving as a bidentate ligand through the P:O and C:O groups.[192]

Silicon Compounds. An X-ray structure for the phosphadilirane (48) shows ring angles of 60° and a *trans* arrangement of the two t-butyl groups;[193] P-P and P-Si distances are 2.226 and 2.225Å respectively. $LiP(SiMe_3)_2$ has been shown to react with $CpFe(CO)_2X$, where X = Cl or Br, to give $CpFe(CO)_2P(SiMe_3)_2$, which with $Ni(CO)_4$ and $Fe_2(CO)_9$ gave respectively the bridged complexes $CpFe(CO)_2[\mu\text{-}P(SiMe_3)_2]Ni(CO)_3$ and $CpFe(CO)_2[\mu\text{-}P(SiMe_3)_2]Fe(CO)_4$.[194] One mole of CO was lost on u.v. irradiation of the latter to give the cyclic species (49) while treatment with methanol cleaved the Si-P bonds to give the PH_2 bridged compound $Cp(CO)_2Fe(\mu\text{-}PH_2)Fe(CO)_4$. Similar reactions between $Ni(CO)_4$ and the trisilyldiphosphine $Me_2Si[P(SiMe_3)t\text{-}Bu]_2$ also yield cyclic products, for example (50), which is obtained as a mixture of *cis* and *trans* isomeric forms.[195]



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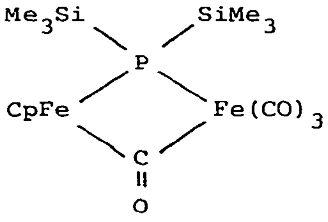

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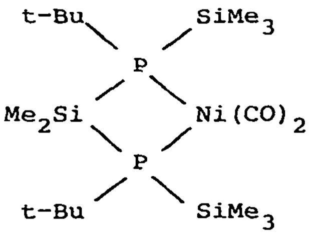

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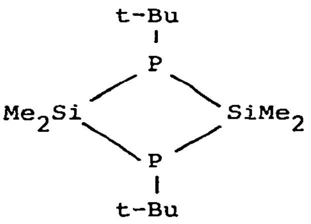
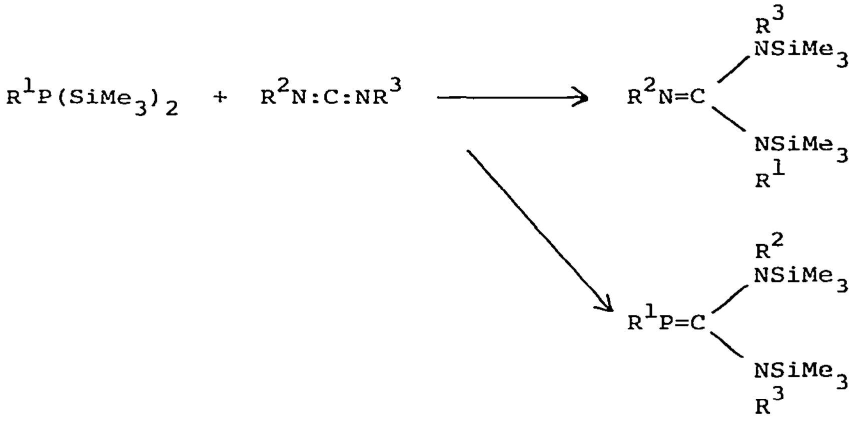


(51)

When the cyclic silylphosphine (51) reacts with either $Ni(CO)_4$ or $Cr(CO)_6$, one carbon monoxide molecule is displaced and the metal carbonyl residue is coordinated to one of the phosphorus atoms.

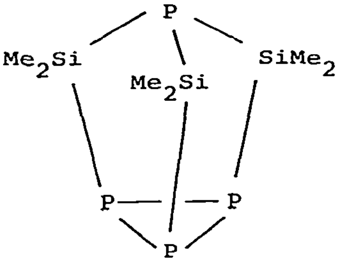
Small molecules such as carbon disulphide,[196] carbodiimides[197] and carbonyl compounds[198] can be inserted into the P-Si bonds of bis(trimethylsilyl)phosphines. The initial product with carbon disulphide is an unstable, red 1:1 adduct, $Ph(Me_3Si)_2\overset{+}{P}-C(:S)S^-$, which rearranges to the sulphanomethylidene phosphine $PhP:C(SSiMe_3)_2$.[196] With carbodiimides the products are phosphaguanidines, and depending on the substituents either the N, P- or the N,N'-bis(silyl)isomer (see equation (38)) can be isolated.[197] Formaldehyde insertion leads to $PhP(CH_2OSiMe_3)_2$,



...(38)

rather than the alternative isomeric $PhP(OCH_2SiMe_3)_2$ form, which was excluded on the basis of the i.r. and n.m.r. data. Reaction with DMF led to elimination of $(Me_3Si)_2O$ with formation of the methylidenephosphine $PhP:CHNMe_2$ and its cyclic dimer as a byproduct.[198]

The tricyclic silicon phosphorus compound (52) reacts with $Mo(CO)_6$ and $Cr(CO)_5THF$ to give complexes in which the metal carbonyl residue is attached to one of the phosphorus atoms of the P_3 ring.[199] X-ray structures have been determined for the $Cr(CO)_5$ derivative and for the dimeric complex (53) obtained with $Cr(CO)_4$.norbornadiene.[200] Coordination appears to have only a small effect on the parameters of the $Me_6Si_3P_4$ unit but the angles about the donor atom become more closely tetrahedral, though the PPP angle necessarily remains at ca. 60°.



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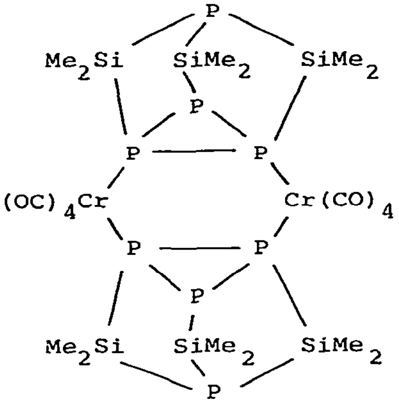


(53)

A new cyclotetraphosphine $(Me_3SiP)_4$ with an all trans arrangement of substituents is produced by way of the diphosphine $[H(Me_3Si)P]_2$ from reactions between trimethylsilyl phosphine and di-t-butyl mercury.[201] The compound, which disproportionates at ca. 80°C, reacts with ethanol to give P_5H_5.

5.2.3 Bonds to Halogens

The +3 Oxidation State. Two conformers of bis(difluorophosphino)-amine $HN(PF_2)_2$ are present in the gas phase at room temperature; that in 72% abundance has symmetry close to C_{2v}.[202] Principal parameters from an electron diffraction study are P-F 1.584, P-N 1.684Å, P-N-P 122.1 and F-P-N 98.3°. Reactions have been described between $PBrF_2$ and trigermyl phosphine to give the new biphosphine $F_2P.P(GeH_3)_2$.[203] An excess of $PBrF_2$ with bis(trimethylsilyl)acetamide at -80°C gives initially $MeC(OPF_2):NPF_2$ which rearranges in part at -40°C to produce a mixture with $MeCON(PF_2)_2$.[204] If the reactants are in a 1:1 ratio, the product is the $MeC(OSiMe_3):NPF_2$. All these compounds were characterised spectroscopically but they are all unstable and decompose to MeCN and either $(PF_2)_2O$ or PF_2OSiMe_3. The germylbiphosphine mentioned above is a colourless liquid, for which a trans conformation about the P-P bond is suggested from electron diffraction measurements.[203] The P-P distance (2.18Å) is among the shortest known.

The bis(difluorophosphino)sulphide, $S(PF_2)_2$, is also a useful starting material for novel PF_2-containing derivatives; with germyl chloride it yields the thiophosphine $PF_2(SGeH_3)$,[205] while the reaction with organic and inorganic hydroxy compounds represented by the general equation (39) is a method for the production of multidentate fluorophosphine ligands.[206] Two

$$S(PF_2)_2 + ROH \longrightarrow SPF_2H + ROPF_2 \qquad \ldots(39)$$

examples of this use are the production of $OP(OPF_2)_3$ and $S(CH_2CH_2OPF_2)_2$ from H_3PO_4 and $S(CH_2CH_2OH)_2$ respectively.

Reactions between allyldifluorophosphite, $CH_2{:}CHCH_2OPF_2$, and the palladium or platinum complexes $(PhCN)_2MCl_2$ gives either mono- or di-substitution products depending on reaction time which can be isolated by addition of a phosphorus(III) ligand such as Ph_3P.[207] The products are trans-$(Ph_3P)_2MCl(POF_2)$ and trans-$(Ph_3P)_2M(POF_2)_2$ respectively. Similar reactions with n-$BuOPF_2$ give mixtures of trans-$(Ph_3P)_2PtCl(POF_2)$ and trans-$(Ph_3P)_2PtCl(n\text{-}BuO)POF$, the latter resulting from ligand scrambling in $BuOPF_2$.

Compounds in the series $CF_nCl_{3-n}SP(O)Cl_2$, where n = 0-3, are obtained when an alkoxydichlorophosphine reacts with the appropriate chlorofluoromethyl sulphenyl chloride $CF_nCl_{3-n}SCl$, while with white phosphorus the sulphenyl chlorides give the corresponding chlorophosphines $CF_nCl_{3-n}PCl_2$ as products.[208]

^{31}P n.m.r. spectroscopy has been used to follow the reaction between an alkali metal azide and various phosphorus compounds.[209] Both substitution and decomposition occurs with PCl_3 and PBr_3 and the products are cyclic or linear azidophosphazenes, $[NP(N_3)_2]_n$; the series of six coordinate anions $[PCl_{6-n}(N_3)_n]^-$ has been identified and problems of geometrical isomerism discussed.

Unsuccessful attempts have been made via PCl_3-$P(CN)_3$ scrambling reactions, the $P(CN)_3$-HCl displacement reaction, etc. to isolate the mixed compound $P(CN)_2Cl$.[210] There is interest in this species from the possible π-back coordination from a CN group to an empty phosphorus orbital and concomitant stabilisation of a di-coordinate phosphorus cation. The compound however is thought to be much less stable than $P(CN)F_2$ and disproportionates at temperatures as low as -80°C.

^{35}Cl chemical shift data have been collected for, inter alia, compounds in the series Me_nPCl_{3-n}, $(MeO)_nPCl_{3-n}$ and Me_nAsCl_{3-n}, where n = 0-2, together with Cl_3PO and Cl_3PS.[211]

Reaction between phosphorus tribromide and the triazidocarbenium salt, $[C(N_3)_3]SbCl_6$, leads to bromination of the anion while the cation is converted into a halogenophosphazene species, $[C(N{:}PBr_{2.34}C^{-}_{0.66})_3]^+$;[212] X-ray diffraction points to the carbon, nitrogen and phosphorus atoms being coplanar with a statistical distribution of the bromine and chlorine atoms.

Phosphorus triiodide exerts a powerful deoxygenating effect with, for example, conversion of sulphoxides, selenoxides, aldehyde oximes and nitroalkanes to respectively sulphides, selenides and nitriles at temperatures as low as -78°C.[213]

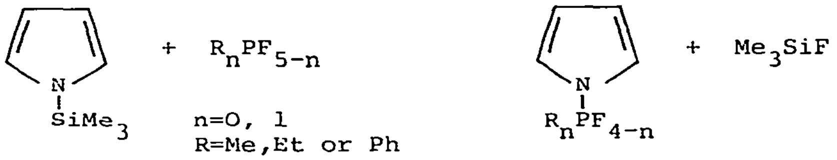
The +5 Oxidation State. The formation of complexes between simple anions, such as acetate, thiocyanate, formate and azide, and PF_5, PF_3, AsF_5 and AsF_3 has been followed by n.m.r. spectroscopy.[214] Species such as PF_5A^- and $PF_4A_2^-$ are observed with PF_5 and with the azide ion both the *mer*- and *fac*- isomeric forms of $PF_3(N_3)_3^-$ were detected. Complex formation does not take place with PF_3 under the same conditions, but in the presence of Bu_4NCN in dichloromethane solution, evidence was obtained for PF_5H^-, $PF_4H(CN)^-$. The AsF_6^- ion is the only product from reactions between AsF_5 and Cl^-, Br^- or acetate but with NO_3^-, NCS^- and N_3^- there are weak lines from unidentified species in addition to AsF_6^-. There is no complex formation between AsF_3 and Cl^- but 1:1 adducts can be identified with a range of other anions including Br^-, I^-, ClO_4^-, NO_3^-, CN^-, FSO_3^-. Sulphur and selenium trioxides reactions with PF_5 follow the course shown in equation (40).[215]

$$PF_5 + nXO_3 \longrightarrow POF_3 + X_nO_{3n-1}F_2 \qquad \ldots(40)$$

$$X = S \text{ or } Se$$

An octahedral structure in which the chlorine and trimethylamine groups occupy *trans* positions has been proved for the 1:1 complex $Me_3N.PClF_4$ by X-ray diffraction,[216] while in the anion of Me_4NPF_6 two *trans* bonds are slightly longer (1.585, 1.591Å) than the remainder (1.568Å) giving overall 4mm symmetry.[217] Dynamic n.m.r. spectroscopy to investigate the fluorine exchange processes in $PhPHF_3$ gives the following parameters for the unimolecular axial-equatorial exchange $\Delta G^{\ddagger}_{298}$ 13.3±0.5 kcal mol^{-1}, $\Delta H^{\ddagger}$ 12.6±0.4 kcal mol^{-1}, and $\Delta S^{\ddagger} = -2.1 \pm 1.3$ e.u.[218] Rate studies also showed that intermolecular fluorine exchange occurred when either triethylamine or pyridine was added to the phosphorane by a mechanism involving the slow production of $PhPF_4H^-$. There is then a rapid fluorine transfer between the five- and six-coordinate species.

A comprehensive investigation with the preparation and properties of the series of pyrrole substituted fluorophosphoranes has been reported.[219] The basic preparative method is given in equation (41), and although there is evidence, in solution, for the product



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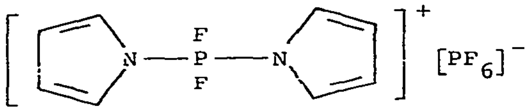
with n = 0, rearrangement occurs on isolation to give the phosphonium salt (54). In reactions using the 2-methyl



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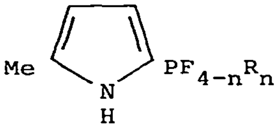


(55)

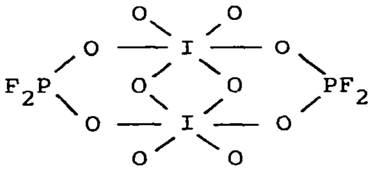
substituted silyl-1-pyrrole, substitution took place at the 2-position giving C-fluorophosphoranyl products (55). Diphenyl trifluorophosphorane reactions were also carried out with lithium derivatives of pyrrole and 2-methylpyrrole and again the former gave N- and the latter C-substitution products.

It has now been shown possible to produce the Phase III form of phosphorus pentachloride, i.e. $2PCl_4^+PCl_6^-Cl^-$, previously isolated from high pressure experiments, by recrystallisation of the pentachloride from dichloromethane solutions containing either bromine or sulphur dichloride.[220] The product has a Raman spectrum identical to that previously reported, but the phase is metastable with respect to $PCl_4^+PCl_6^-$ (Phase II) to which it reverts on standing. Estimated lattice energies for Phases II and III are 232 and 370.4 kJ mol^{-1} respectively. Similar isomerism in other phosphorus(V) species, in particular $PCl_nBr_{4-n}^+$ for $0 \leqslant n \leqslant 3$, is considered likely from the observation of new Raman shifts.

Raman spectral data are reported for solid and molten mixtures of PCl_5 with $TeCl_4$[221] and $ZrCl_4$;[222] solid 1:1 mixtures with the former show evidence for the compound $n(PCl_4^+)(TeCl_5^-)_n$ while both $ZrCl_6^{2-}$ and $ZrCl_5^-$ anions have been identified in the latter systems. A six-fold non-ionic formulation is found for the 1:1 adduct between PCl_5 and pyrazine ($C_4H_4N_2$);[223] the P-N distance is very long (2.021Å) and P-Cl distances fall in the range 2.088 - 2.127Å.

Weak electrolyte behaviour is shown by solutions of the methylfluorophosphoranes, Me_nPF_{5-n} where n = 1-3, in acetonitrile, the maximum conductance occurring with Me_3PF_2, the compound in this series with the weakest P-F bond.[224] New adducts of both PPh_3Cl_2 and $AsPh_3Cl_2$ with halogens and interhalogens have been identified from conductometric measurements in acetonitrile and assigned the formulae $MPh_3Cl_2X_2$, for M = P or As and X_2 = Br_2, I_2, ICl or IBr, and MPh_3Cl_5I for M = P or As.[225] From the high molar conductances, formulation as $MPh_3X^+\ ClX_2^-$ and $MPh_3Cl^+\ ICl_4^-$ is suggested. Highly conducting solutions are also obtained when MPh_3 is treated with ICl or ICl_3 but these systems are complicated although crystalline compounds such as MPh_3Cl_3I and $AsPh_3Cl_5I$ can be isolated.

Oxygen exchange takes place when POF_3 reacts with VF_5 according to an n.m.r. study to give PF_5 and VOF_3.[226] Vibrational spectra have been reported and discussed for fluorinated species $P_2O_3F_4$ and $K_2P_2O_5F_2$,[227] and the reaction of the former with HIO_3 and H_5IO_6 investigated.[228] Difluorophosphoric acid is liberated and the hygroscopic products are respectively $IO_2PO_2F_2$ and $IO_3PO_2F_2$; a dimeric structure (56) is proposed for the latter from vibrational



(56)

data.

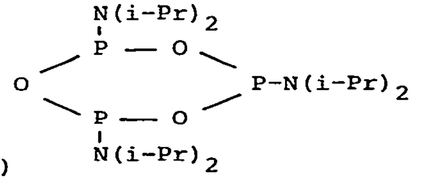
According to a recent X-ray study, an unusual boat conformation is forced on the two benzene rings in the highly substituted bis(2,4,6-tri-t-butylphenyl)phosphinic dichloride;[219] the compound is the product when $POCl_3$ reacts with 2,4,6-tri-t-butylphenyl lithium. On reaction with bis(trimethylsilyl)sulphide, $(Me_3Si)_2S$, phosphoryl halides give the dihalogenothiophosphate, $Me_3SiOP(S)X_2$ where X = Cl or Br, while with the corresponding acetate, Me_3SiOAc, and $POBr_3$ the products are $Me_3SiOP(O)Br_2$ or $(Me_3SiO)_3PO$ depending on the ratio of the reactants.[230] Phosphoryl chloride is the solvent for reactions between cyanogen and WCl_6 or between cyanogen, chlorine and MCl_5, where M = Mo, W or Re, to give products such as $Cl_3PO{\rightarrow}Cl_4M{\equiv}N{-}C_2Cl_4{-}N{\equiv}MCl_4{\leftarrow}OPCl_3$;[231] with $ReNCl_4$ the product on treatment with an excess of $POCl_3$ is $(ReNCl_3.POCl_3)_4.2POCl_3$, a compound which contains an eight membered Re_4N_4 ring.[232]

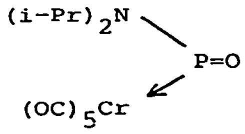
The products that result from reaction of $SbCl_5$ or $TiCl_4$ with trimethylsilyl dichlorophosphate are the adduct $Cl_2PO_2SiMe_3.SbCl_5$ and $Cl_2Ti(O_2PCl_2)_2$ respectively;[233] the latter can also be prepared from the titanium chloride and $P_2O_3Cl_4$. Similar products, i.e. $Cl_2Ti(O_2PMe_2)_2$ and $Cl_2Ti(O_2PF_2)_2$, can be obtained using $Me_3SiOPOR_2$ where R = Me or F.[234] Direct reactions between difluorophosphoric acid and aluminium, gallium and zinc chlorides lead to $Al(O_2PF_2)_3$, $Ga(O_2PF_2)_3$ and $Zn(O_2PF_2)_2.2HOPOF_2$ respectively, which from i.r. data and their high melting points are formulated as polymers with bridging difluorophosphate groups.[235]

Chlorosulphuric acid, PCl_5 and $(HO)_2P(O)CH_2COOH$ react in phosphoryl chloride solution to give the phosphinyl-methanesulphonyl chloride, $Cl_2P(O)CH_2SO_2Cl$,[236] which has been fluorinated with AsF_3 and NaF and shown to give the C-chloro compounds, $Cl_2P(O)CH_nCl_{2-n}SO_2C$ where n = 0 or 1, on treatment with PCl_5. Fluorophosphate anions of the type $(F_5PCH_2SO_2X)^-$ and $(OFP(O)CH_2SO_2X)^-$ have also been investigated.

5.2.4 Bonds to Nitrogen

The +3 Oxidation State. The previously unknown trioxaphosphorin system has been found in (57), the product formed together with t-butyliminosulphur oxide t-BuN:S:O from a pseudo-Wittig reaction between the iminophosphorane $i\text{-}Pr_2NP{:}N\text{-}t\text{-}Bu$ and sulphur dioxide.[237]


(57)


(58)

In the solid, the P_3O_3 ring has a boat conformation with close to C_s symmetry; the P-N distances 1.64 and 1.66Å are short suggesting a measure of π-bonding. The monomeric aminooxophosphine, $i\text{-}Pr_2N{\cdot}P{:}O$, which is probably formed during the reaction cannot be isolated, but it has been trapped as the chromium carbonyl adduct (58) from a reaction in which the initial iminophosphorane is treated with $Cr(CO)_6$ before reaction occurs with sulphur dioxide.[238] Both P-N and P-O distances at the planar phosphorus atom are short (1.624 and 1.475Å respectively) and are consistent with a pseudo-allylic $R_2\overset{+}{N}\cdots P\cdots\overset{-}{O}$ interaction.

Iminomethylenephosphoranes are obtained from the reactions of the iminophosphine $(Me_3Si)_2N{\cdot}P{:}NSiMe_3$ summarised in equations (42) and (43),[239] while with diazomethane itself the product is

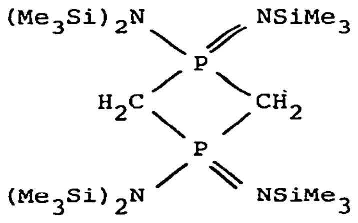
$$(Me_3Si)_2N{\cdot}P{:}NSiMe_3 \;+\; MeCRN_2 \longrightarrow (Me_3Si)_2NP({:}NSiMe_3)({:}CRMe) \;+\; N_2$$

R = Me, Et, i-Pr and t-Bu ...(42)

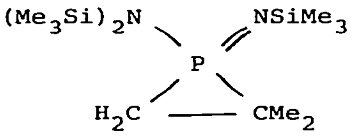
$$(Me_3Si)_2N{\cdot}P{:}NSiMe_3 \;+\; HCRN_2 \longrightarrow (Me_3Si)_2NP({:}NSiMe_3)({:}CRH) \;+\; N_2$$

R = Me or t-Bu ...(43)

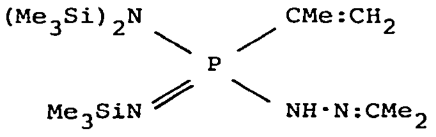
the diphosphetan (59). Further reactions with diazoalkanes are



(59)



(60)



(61)

reported which show specific effects, e.g. with diazomethane the product from reaction (42) gives the phosphirane (60) while with Me_2CN_2 the product is (61).

Stable phosphorus, arsenic, and antimony(III) radicals with half-lives in the range 1 day to 1 year have been produced and studied by e.s.r.[240] Their precursors are compounds containing bulky substituents such as $M[CH(SiMe_3)_2]Cl_2$ or $M[CH(SiMe_3)_2]_2Cl$ for M = P, As or Sb and $M[N(SiMe_3)_2]Cl_2$ or $M[N(SiMe_3)_2]_2Cl$ for M = As or Sb, prepared from the appropriate trichloride and either $LiCH(SiMe_3)_2$ or $LiN(SiMe_3)_2$. In addition, further phosphorus compounds including $P(N\,i\text{-}Pr_2)[N(SiMe_3)_2]Cl$ and $P(NMe_2)[CH(SiMe_3)]_2Cl$ were prepared and investigated.

Primary aminophosphines, $(RNH)_3P$, have not previously been unambiguously characterised because of their general instability but recently the trans-amination reaction (44) has been followed by ^{31}P n.m.r. spectroscopy.[241] At temperatures above 25°C, the

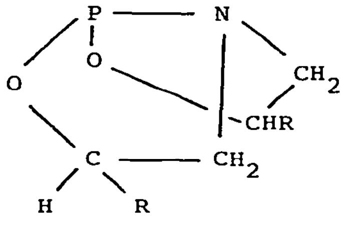
$$(Et_2N)_3P \;+\; 3PhNH_2 \longrightarrow (PhNH)_3P \;+\; 3Et_2NH \qquad \ldots(44)$$

$$2(PhNH)_3P \longrightarrow [(PhNH)_2P]_2NPh \;+\; PhNH_2 \qquad \ldots(45)$$

data indicate that the condensation process (45) occurs at a rate comparable to that of (44), and the product is a 1:1 mixture of these two compounds. Slow crystallisation from ether gave the pure aminophosphine for which an X-ray determination showed a C_3 structure with P-N and N-P-N values of 1.697Å and 99.5°. The related tris(diphenylamino)phosphine $(Ph_2N)_3P$, can be obtained among other methods in almost quantitative yield from a reaction between $(Ph_2N)_2PCl$ and Ph_2NSiMe_3.[242]

The ligand properties of $(Ph_2P)_2NH$ toward Ir(I) and Pt(II) have been investigated,[243] and detailed vibrational data obtained for the deuterated derivative $(Ph_2P)_2ND$.[244] N.m.r. data for some 50 aminophosphines have been analysed to show topological, electronic and steric effects;[245] changes in screening, coupling constants, barriers to P-N rotation, etc. are discussed in terms of the substituents at phosphorus and nitrogen, the hybridisation at these atoms and (p-d)π bonding.

In phosphorus(III)-nitrogen compounds the lone pair on the nitrogen atom is considered to be involved in (p-d)π bonding to phosphorus and donor properties are manifest only at the phosphorus atom. It has now been shown that the bicyclic amino-phosphines (62, R = H or Me) in which both the phosphorus and nitrogen atoms are constrained to remain pyramidal will, in fact, form both mono-



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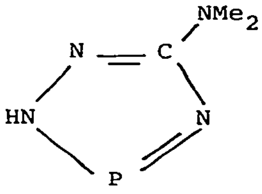

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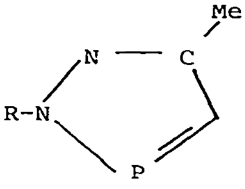


(64)

and di-adducts with BH_3.[246] An X-ray structure for the di-borine adduct with (62, R = Me) indicates a normal length (1.655Å) for the B-N bond while the absence of a π-component in the P-N bond follows from its length (1.757Å).

Condition for the formation of a 1,2,4,3-triazaphosphole (63)[247] unsubstituted at the heteroatoms from tris(dimethylamino)phosphine and N,N-dimethyl-N'-aminoguanidinium iodide, and the diazaphospholes (64)[248] from phosphorus trichloride and acetone hydrazones have been established. The latter can be methylated at the nitrogen atom, but with reagents such as organochlorophosphines or thiophosphoryl chloride substitution occurs at carbon atom adjacent to phosphorus.

Insertion reactions between the aminophosphines $(Me_2N)_3P$, $(Me_2N)_2PX$ or Me_2NPX_2 where X = F or Cl and CO_2, COS or CS_2 have been investigated and the products identified by i.r., n.m.r., and mass spectrometry.[249] Not all are stable but an X-ray structure confirms a tris(dithiocarbamate) structure for $(Me_2N)_3P.3CS_2$. The coordination polyhedron about phosphorus is best described as a capped trigonal prism which includes the lone pair; there are three short (2.162 - 2.202Å) and three long (2.873 - 3.016Å) P-S bonds.

A neutral complex, which contains a coordinated phosphenium ion, has been prepared from $NaCpMo(CO)_3$ and the cyclic aminophosphine $\overline{Me\text{-}NCH_2CH_2N(Me)P}$ and shown to have the structure illustrated in Figure 5.[250] Interesting features of the structure are the short (2.21Å) Mo-P bond suggesting a degree of multiple bonding, planarity about the phosphorus and nitrogen atoms and the observation that the plane containing the molybdenum and the non-hydrogen atoms of the phosphenium group lies almost perpendicular to the $Mo(CO)_2$ plane.

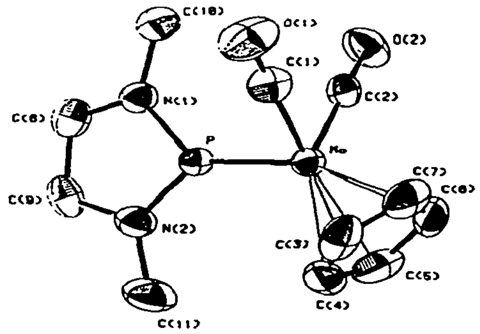
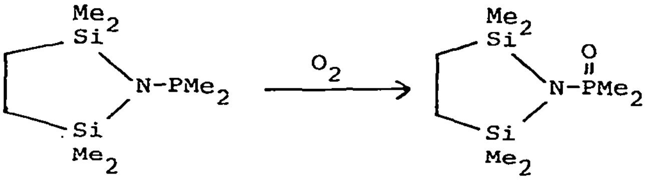


Figure 5. Molecular structure of Me$\overline{\mathrm{NCH_2CH_2N(Me)P}}$CpMo(CO)$_2$ (reproduced by permission from J. Am. Chem. Soc., 102(1980)4521).

Oxidation of silylaminophosphines using either oxygen or t-butyl-trimethylsilyl peroxide can give either a phosphine oxide, equations (46) and (47) or a silyloxyphosphinimine as a result of silyl migration, equations (48) and (49).[251] The course of the



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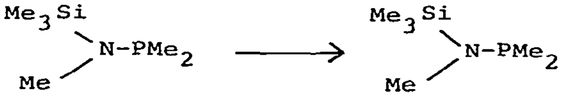

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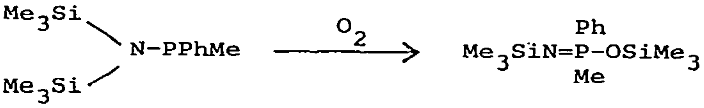

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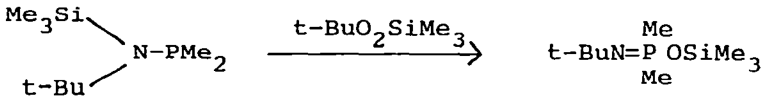


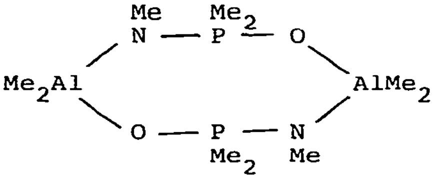
$$(Me_3Si)(t\text{-}Bu)N\text{-}PMe_2 \xrightarrow{t\text{-}BuO_2SiMe_3} t\text{-}BuN{=}P(Me)_2OSiMe_3 \qquad \ldots(49)$$

reaction depends on the substituent at nitrogen with bulky groups favouring the silyl migration process.

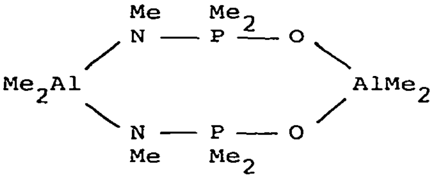
Titanium and zirconium tetrachlorides react with both phosphorus tri-isocyanate and the tricyanide to give respectively $MCl_3P(NCO)_2$ and $MCl_3P(CN)_2$;[252] the i.r. spectra are discussed on the basis of trigonal pyramidal structures with C_{3v} symmetry.

The +5 Oxidation State. The structure of potassium phosphoramidate $K[O_3PNH_3]$ has been determined to obtain a more accurate value for the single P-N bond length.[253] The anion contains an sp^3 hybridised nitrogen atom which cannot participate in P-N π-bonding and yields a value of 1.800(4) compared with the previously accepted value 1.769(19)Å obtained from the corresponding sodium salt.

The trimethyl derivatives of Al, Ga or In react with phosphoric or phosphinic amides, $POCl_2(NHMe)$ or $POMe_2(NHMe)$, in equimolar ratios to give products with the stoichiometry $Me_2MOPN(Me)Cl_2$ or $Me_2MOPN(Me)Me_2$ respectively.[254] Dimeric structures are indicated for a number of the products and from ^1H n.m.r. data two structural isomers (65a and b) are present for $Me_2AlOPN(Me)_2$ $_2$.



(65a)



(65b)

The corresponding thiophosphoryl derivatives are also known.

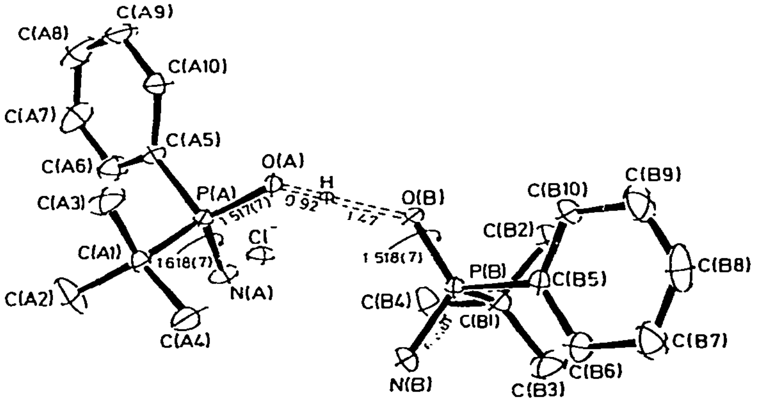
Reactions are reported between PCl_3 and either $OP(NMeH)_3$ or $P(NMe_2)_3$ to give $OP(NMePCl_2)_3$ and $Me_2NP[OP(:O)(NMe_2)_2]$ respectively.[255] The phosphorylamides $X_{3-n}P(O)(NH_2)_n$, where n = 1 or 2 and X = OEt, NMe_2 or NEt_2, can be silylated to give $X_{3-n}P(O)(NHSiMe_3)_n$,[256] and such compounds on reaction with phosphorus pentachloride give linear and branched phosphazenes, equations (50) and (51).[257] With monoamides, e.g. $X_2P(O)NHSiMe_3$,

$$XP(O)(NHSiMe_3)_2 \ + \ 2PCl_5 \longrightarrow XP(O)(N{:}PCl_3)_2 \ + \ 2HCl \ + \ 2Me_3SiCl \qquad ...(50)$$

$$OP(NHSiMe_3)_3 \ + \ 4PCl_5 \longrightarrow [ClP(N{:}PCl_3)_3]Cl \ + \ POCl_3 \ + \ 3HCl \ + \ 3Me_3SiCl \qquad ...(51)$$

on the other hand the products are the isomeric N-dichlorophosphoryl phosphazenes $Cl_2P(O){\cdot}N{:}PClX_2$ rather than the expected trichlorophosphazenes $X_2P(O){\cdot}N{:}PCl_3$. Complex formation between hexamethylphosphoramide (L) and titanium, vanadium or chromium(III) chlorides gives non-ionic, octahedral, $MCl_3.3L$ products and with MCl_4 for M = Ti, Zr, Hf and Sn the products are again octahedral with the stoichiometry $MCl_4.2L$.[258] In addition it has been possible to isolate $2TiCl_4.L$ and $SnCl_4.L$ for which a confacial bioctahedral structure and a dimeric halogen bridged structure respectively are proposed.

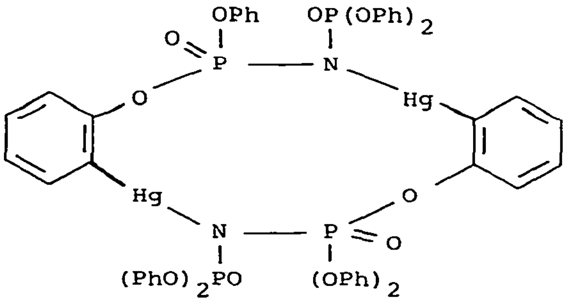
A crystal structure determination for the hydrochloride of phenyl(t-butyl)phosphoric amide, see Figure 6, shows that protonation occurs at oxygen rather than nitrogen with formation of a very asymmetric hydrogen bond between two phosphoryl oxygen atoms.[259] There are four N···Cl distances between 2.26 and 2.75Å indicating further hydrogen bonding from the amino groups.



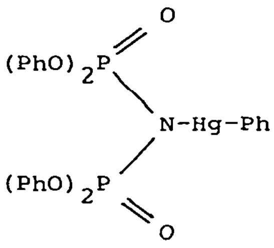
<u>Figure 6</u>. Molecular structure of $[Ph(t\text{-}Bu)P(O)NH_2]_2.HCl$ (reproduced by permission from J. C. S. Chem. Commun., (1980)195).

An X-ray structure for the diimidotriphosphoramide, $Me_2NP(O)[NMe\cdot P(O)(NMe_2)_2]_2.H_2O$ (L), shows the presence of a hydrogen bonded dimeric unit in the solid state,[260] and the compound gives complexes of the type $M(NO_3)_3L_3$.acetone, $M(NO_3)_3L$, $M(NO_3)_3L_2$.nitromethane, and $M(NO_3)_3L_2$.acetone with a range of lanthanide nitrates.[261]

A new 12-membered ring system (<u>66</u>), for which an X-ray structure is available, is the product when mercuric oxide reacts with the



(<u>66</u>)



(<u>67</u>)

tetraphenyl ester of imidodiphosphoric acid;[262] use of PhHgOH in place of the oxide yields (<u>67</u>). Direct hydrolysis of $(PhO)_2P(O)NCl_2$ in petrol solution yields the monochloride $(PhO)_2P(O)NHCl$, the first example of a new type of N-halogeno compounds.[263]

Reaction between thiophosphoryl chloride and 1,2-bis(trimethylsilyl)hydrazine gives a mixture of isomers and a crystal structure determination of one of these, $SP(NHNHSiMe_3)[N(NH_2)SiMe_3]_2$, shows that for two of the substituents a Me_3Si group has migrated from the β to the α nitrogen atom.[264] N-Silylated diphosphazenes $R^1_3P{:}N.P(OR^2)_2{:}NSiMe_3$ are the products when trimethylsilyl azide reacts with $R^1_3P{:}N.P(OR^2)_2$ where R^1=Me or NMe_2 and R^2=CH_2CF_3.[265]

When potassium amide in liquid ammonia reacts with N-methyltriorganyliminophosphoranes, the product may result from either nucleophilic displacement of an organic group or alkene elimination as shown in equations (52) and (53) respectively.[266] The unstable

$$(PhCH_2)_3P{:}NMe + KNH_2 \longrightarrow [N{:}P(NMe)(NH)]K_4 + 3PhCH_3 + NH_3 \quad \ldots(52)$$

$$(Me_2CH)_3P{:}NMe + KNH_2 \longrightarrow [(Me_2CH)_2P{-}NH]K + MeCH{:}CH_2 + MeNH_2 \qquad \ldots(53)$$

isodiazomethane, $CNNH_2$ can now be "stored" in the form of N-isocyanoiminotriphenylphosphorane which is synthesised as shown in equation (54); thermal decomposition at ca. 160°C yields the

$$HCO{\cdot}NHNH_2 + 2PPh_3 + 2CCl_4 + 2NEt_3 \longrightarrow CNNPPh_3 + 2HCCl_3 + 2Et_3NHCl + OPPh_3 \qquad \ldots(54)$$

the isodiazomethane.

Full vibrational data and a crystal structure are now available for $[C(N{:}PCl_3)_3]SbCl_6$, in which the cation has close to C_{3h} symmetry.[268] The P-N distances are 1.539, 1.556 and 1.571Å, and the carbon, nitrogen and phosphorus atoms together with one chlorine atom of each PCl_3 group lie in a plane. Reactions between PCl_3 and ClN_3 lead to the nitrogen bridged species $(Cl_3PNPCl_3)Cl$, while with the diazidoiodate phosphorus trichloride gives the azidochlorocyclotriphosphazene, $N_3P_3Cl_3(N_3)_3$, as a mixture of cis and trans isomers.[269]

The nitrogen bridged compound $(Cl_3PNPCl_3)(PCl_6)$, one of the products from a reaction between phosphorus pentachloride and S_7NH, has a solid state structure containing two independent molecules, each with a cisoid configuration.[270] There is essentially tetrahedral coordination about phosphorus and the very short P-N bonds (mean 1.54Å) point to substantial π character. The P-N-P angle is 137.5°. Complex formation between copper[271] and bismuth[272] and the imidodiphosphinate ligands $(Ph_2P(X){\cdot}N{\cdot}P(X)Ph_2)^-$ where X = O or S has been studied.

The first compound containing a bond between two phosphorus(V) atoms with the structure shown in Figure 7 has been isolated from a reaction between two phosphorus(V) derivatives of the ligand 1,4,7,10-tetraazacyclododecane.[273] The P-P distance, 2.264Å, is slightly longer than twice the covalent radius and crowding in the molecule is mitigated by a rotation of 70.6° about the P-P axis from the eclipsed position. Trigonal bipyramidal geometry, distorted by ca. 33% along the Berry coordinate toward the square pyramid, is found for the phosphorus atoms.

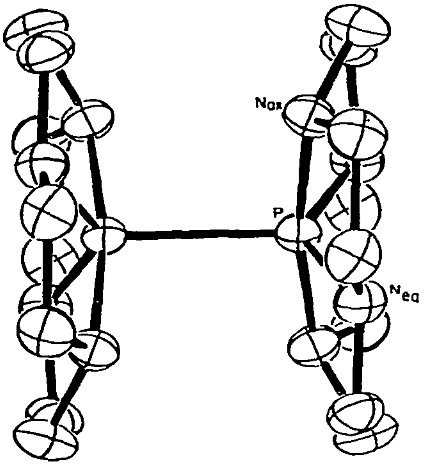
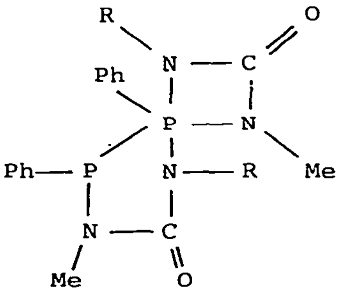
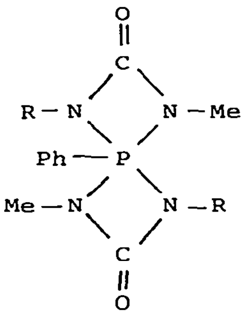


Figure 7. Structure of the dicyclen diphosphorane $(C_8H_{16}N_4)_2P_2$ (reproduced by permission from J. Am. Chem. Soc., 102(1980)3955).

Phosphoranes incorporating a direct link between three- and five-coordinate phosphorus atoms such as (68) are obtained when phenyl dichlorophosphine reacts with trimethylsilylureas.[274]



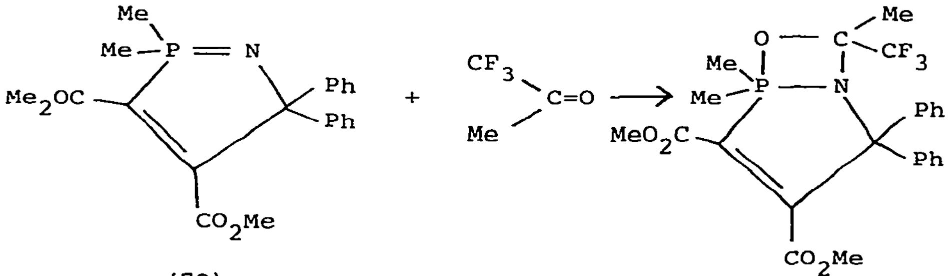
(68, R = Me or Ph)



(69, R = Me or Ph)

These compounds on treatment with PCl_5 and chlorine eliminate phenyldichlorophosphine giving the strained bicyclic phosphorane (69). Similar reactions in which $C_2F_5PCl_2$ and PCl_3 were used as starting materials are also described.

A stable [2+2] cycloaddition compound (71) can be obtained as shown in equation (55) by treating the azaphosphole (70) with a ketone;[275] full structure determinations for (70) and (71) point



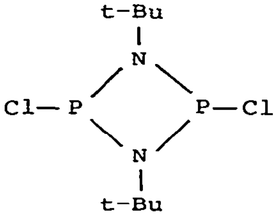
(70)

(71) ...(55)

to there being little change in the angles at phosphorus on conversion to (71).

X-ray structures have been determined for 4-nitrobenzyltri(morpholino)phosphonium perchlorate and for the piperidine analogue,[276] and for tri(morpholino)phosphine telluride.[277]

P-N Ring Compounds. Chlorine replacement by a variety of primary and secondary amines occurs with the cyclodiphosphazene (72) to give in some cases a pair of geometrical isomers.[278] In



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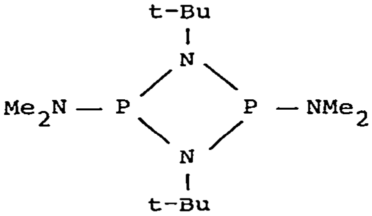
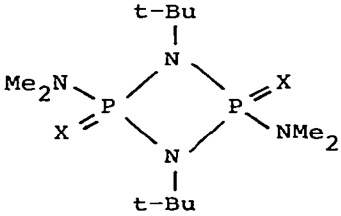


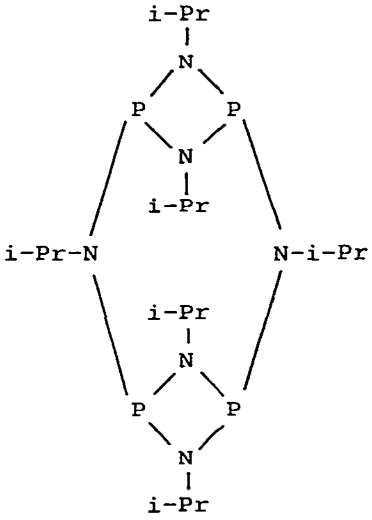
(73)



(74, X=O, S, Se, Te)

conjugation with X-ray crystallographic results it has been shown that the isomer with the high field ^{31}P chemical shift (90-110p.p.m.) has a cis arrangement of substituents; the lower field shift (170-200 p.p.m.) is associated with the corresponding trans structure. Isomerisation reactions show that the cis form is thermodynamically stable although steric interactions are higher. One of these amino-derivatives (73) has been oxidised with elemental S, Se or Te, t-butyl hydroperoxide and methyl iodide to give, with the exception of the tellurium reaction, *cis* and *trans* isomeric forms of the mono- and di-oxidation (74) products.[279] *Cis* and *trans*-forms of (72) have different reactivities, but with sulphur or selenium reaction takes place with retention of configuration. Detailed n.m.r. spectroscopy has been used to investigate the slow rotation about the phosphorus(V)-nitrogen bonds in (74, X=O, S or Se),[280] and also the bonding between halogeno-cyclodiphosphazenes related to (72) and transition metals.[281]

The interesting, non-adamantane, structure (75) has been found for $P_4(N\text{-}i\text{-}Pr)_6$ which is obtained by thermolysis of the diazadiphosphetidine (76).[282] The molecule lies on a crystallographic centre and the two $P_2(N\,i\text{-}Pr)_2$ systems are almost planar. Quantitative conversion to the more stable adamantane-



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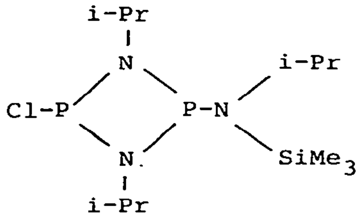
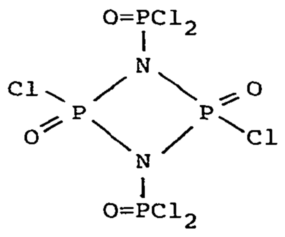


(76)

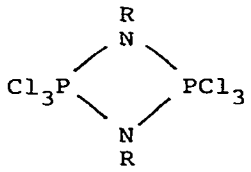
like isomer occurs on heating to ca. 156°C.

A crystalline dimer $[Me(CF_3)_2PNMe]_2$, containing a P_2N_2 ring with trigonal bipyramidal geometry about phosphorus, is the product when methylamine reacts with $Me(CF_3)_3PCl$.[283] Axial positions are occupied by a ring nitrogen (1.806Å) and one of the CF_3 groups (1.963Å) and, as expected, the equatorial distances to the second nitrogen (1.633Å) and the CF_3 groups (1.916Å) are shorter.

Optimum conditions have been determined for the preparation of the novel cyclodiphosphazane (77) from a reaction between $POCl_3$ and ammonium chloride;[284] among other compounds formed are $P_2O_3Cl_4$,



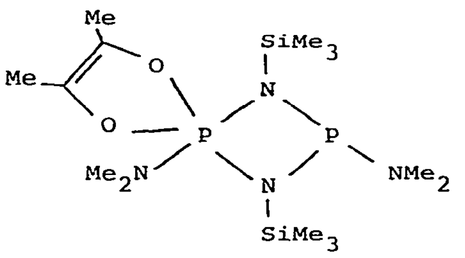
(77)



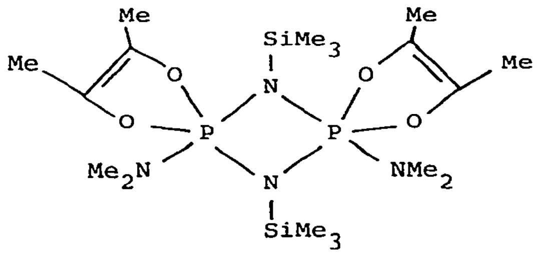
(78, R = C_6H_4F, $C_6H_4CF_3$, $C_6H_3F_2$, etc.)

$N_3P_3Cl_6$ and $Cl_3P{:}N{\cdot}P(O)Cl_2$. Aniline derivatives and PCl_5 react to give the ring compounds (78) which dissociate in solution to monomeric substituted phenylimidotrichlorophosphoranes.[285]

Structures are now available for two diazadiphosphetidines (79) and (80) obtained previously from biacetyl reactions.[286] In each case the dimethylamine groups occupy *cis* positions and the ring nitrogen and one oxygen atom occupy the axial positions of the trigonal bipyramidal arrangement about the phosphorus(V) atoms.

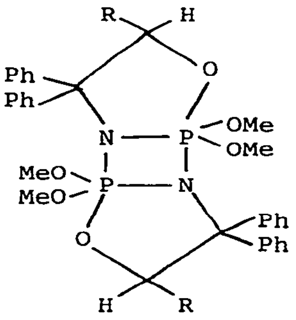


(79)

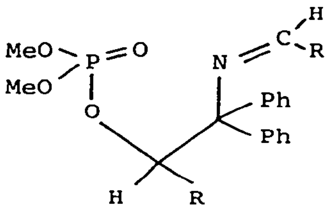


(80)

A tricyclic diphosphorane (81) and the linear compound (82) are obtained from a cycloaddition reaction between p-nitrobenzaldehyde and dimethoxy(diphenylmethyleneamino)-phosphane, $(MeO)_2P.N{:}CPh_2$.[287] The brige-head phosphorus atoms in (81) have trigonal bipyramidal geometry and the P_2N_2 ring is planar with mean distances of 1.60 and 1.77Å.



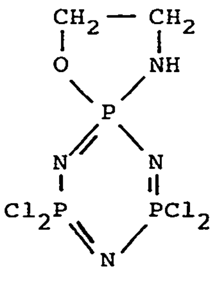
(81, R = p-$NO_2C_6H_4$)



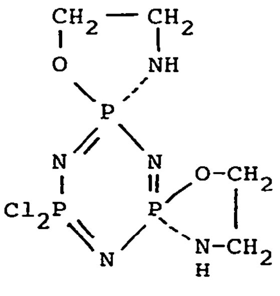
(82, R = p-$NO_2C_6H_4$)

Difficulties in the isolation and identification of the trans-tetrasubstituted chlorotriphosphazene $N_3P_3Cl_2(NMe_2)_4$ have been discussed,[288] and the effect of solvent on the course of the $N_3P_3Cl_6$-Et_2NH reaction investigated.[289] At the bis and tetrakis stages of substitution, change of solvent affects the cis-trans ratio of the non-geminal isomers, but at the tris stage, benzene and similar solvents give the geminal tris isomer while in acetonitrile the corresponding cis and trans non-geminally isomers are the exclusive products. The electrical conductivity of a number of crystalline cyclotriphosphazenes has been determined.[290]

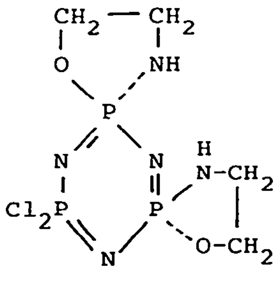
Spirocyclic products are produced when $N_3P_3Cl_6$ reacts with either ethylenediamine or ethanolamine,[291] the latter giving in addition to the monosubstitution product (83) the disubstituted species as a mixture of the cis-(84) and trans-(85) isomers.



(83)



(84)

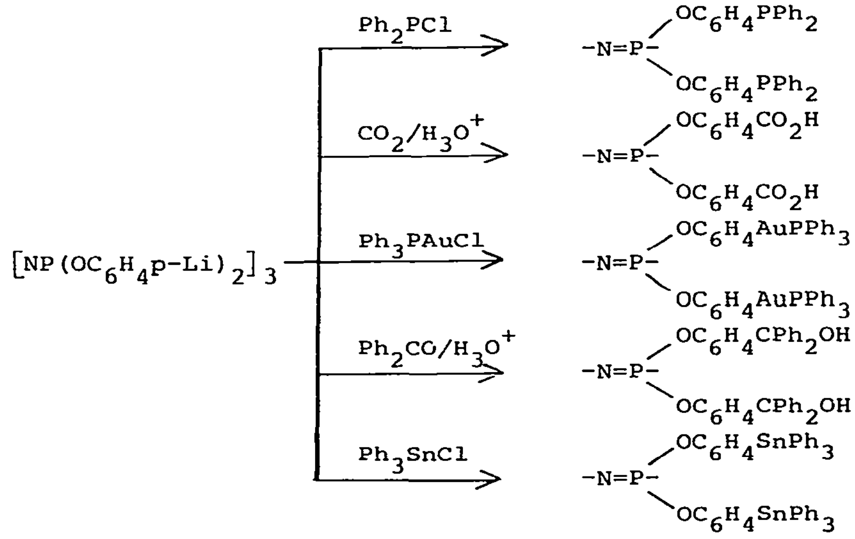


(85)

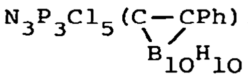
Among trimeric phosphazene structures determined during 1980 are the cis and trans non-geminal isomers of $N_3P_4Cl_4(NMe_2)_2$,[292] and the fully substituted imidazoyl[293] and aziridinyl[294,295] derivatives. The imidazoyl compound is readily hydrolysed, an observation associated with the fact that the lone pair on the nitrogen attached to phosphorus is involved in π-bonding to the imidazole group rather than to the phosphorus atom. The aziridine compound has been examined as a benzene solvate in which both phosphazene and benzene lie on a three fold axis[294] and as a solvate with three molecules of carbon tetrachloride.[295] In the latter the structure can be described in terms of an 'anticlathrate' structure in which a phosphazene guest molecule is inserted into a monocapped icosahedron formed by 13 carbon tetrachloride molecules.

A number of new phosphazenyl-triphosphazenes, $N_3P_3X_5(N{:}PY_3)$ with X = F or Cl and Y = Me, Ph, OEt, etc., have been isolated,[296] and aminolysis of the compound with X = Cl and Y = Ph investigated.[297]

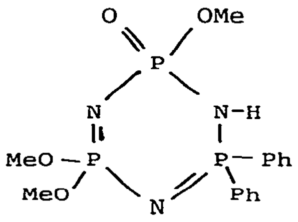
As a model for the introduction of functionality with a preformed organopolyphosphazene, reactions have been carried out in the trimeric system with hexakis(p-bromophenoxy)triphosphazene.[298] A low temperature reaction with butyl lithium replaces the bromine atoms and the products, unobtainable by other methods, produced in subsequent reactions are summarised in Scheme 2. Carbaborane



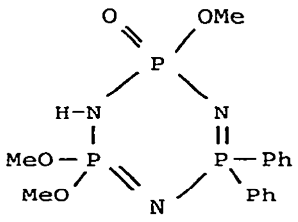
Scheme 2

substituted derivatives have been isolated from reactions between either $N_3P_3Cl_6$ or $(NPCl_2)_n$ and the lithium derivative of either methyl or phenyl o-carbaborane to give prototypes of materials with high temperature stability or unusual electrical behaviour.[299] A crystal structure is available for  $N_3P_3Cl_5(\underset{B_{10}H_{10}}{C{-}CPh})$.

N.m.r. spectra for $N_3P_3Ph_2(OMe)_3(OH)$ indicate the presence of the two tautomers (<u>86</u>) and (<u>87</u>), with the former predominant; in



(<u>86</u>)

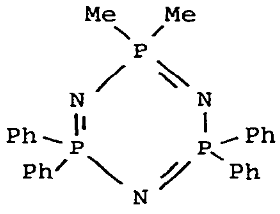


(<u>87</u>)

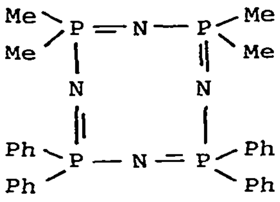
the solid state the structure is a centrosymmetric dimer with hydrogen bonds between NH group as in (<u>86</u>) and the oxygen of the second molecule.[300]

Moderate yields of the monosubstituted derivative $N_3P_3F_5(C_6H_4X)$, where X is an electron donating group in the para position, have been obtained from the hexafluoride and the appropriate aryl lithium reagent;[301] these products react further via Friedel-Crafts reactions to give geminally substituted compounds. He(I) p.e.s. for $N_3P_3F_5(C_6H_4NMe_2)$ and compounds in the series $N_3P_3F_{6-n}Ph_n$ for n = 1, 2 and 4 confirm the strong electron withdrawing effect of the $N_3P_3F_5$ group which is dramatically reduced when fluorine atoms are substituted by phenyl groups.[302]

The reaction between Me_2PCl_3 and bis(aminodiphenylphosphine)-iminium chloride $(H_2NPPh_2{:}N{\cdot}PPh_2NH_2)Cl$ on reinvestigation has been shown to give in addition to the trimer (<u>88</u>), three tetrameric compounds, i.e. $N_4P_4Me_8$, $N_4P_4Ph_8$ and the mixed compound (<u>89</u>).[303] The structure of the trimer (<u>88</u>) contains a non-planar ring with no variation in P-N bond lengths (mean 1.60Å) in accord with the similar electronegativities of the methyl and phenyl groups.

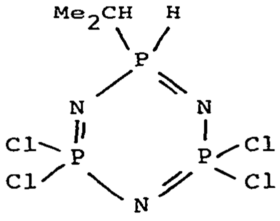


(88)

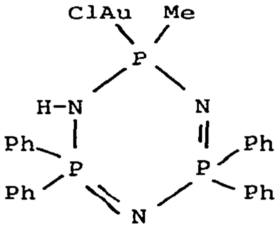


(89)

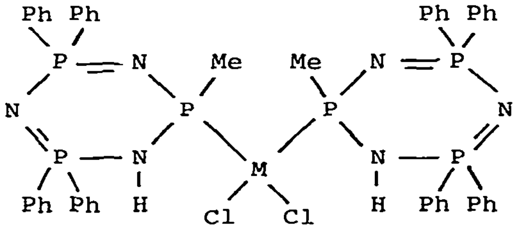
A full structure of the hydrido-triphosphazene (90) indicates the presence of a planar ring system with a curious alternation of



(90)



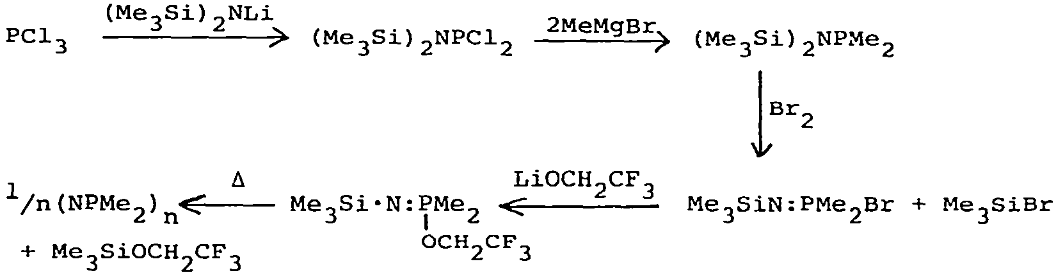
(91)



(92, M = Pd or Pt)

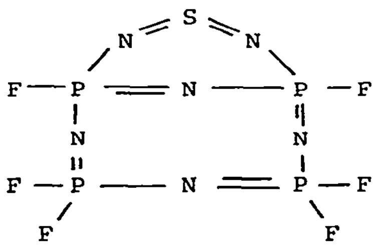
bond lengths.[305] Those associated with the hydride substituted phosphorus are longest (1.606, 1.614Å), the intermediate lengths (1.575, 1.581Å) are to the nitrogen trans to the PH group while the shortest (1.548, 1.553Å) are associated with the adjacent nitrogen atoms. A related hydride has been converted into gold (91)[306] and platinum or palladium compounds (92).[307] In these cases the hydrogen atom is transferred to an adjacent nitrogen atom and from a crystal structure determination on (92, M = Pd) there is a cis arrangement of ligands. The Pd-P distance is 2.242Å. The N_3P_3 rings have a distinct boat conformation and while the endocyclic NPN angle at the coordinated phosphorus atom is small (106.7°) showing a degree of P(III) character, the angle at the protonated nitrogen is increased to 126.2°.

A new direct route to poly(dimethylphosphazene), a compound which cannot be obtained from $(NPCl_2)_n$, involves the thermal decomposition of an N-silylphosphinime as shown in Scheme 3. The product consists of ca. 650 repeating units and is soluble in dichloromethane, chloroform and ethanol. Rather surprisingly cyclic phosphazenes in good yields are the products when the closely related P-bromoderivatives, i.e. $Me_3SiN{:}PR_2Br$ where R = Me, Ph or OCH_2CF_3, are heated.[309] A new series of non-elastomeric, film forming polymers with the composition $[NPPh_x(OCH_2CF_3)_{2-x}]_n$ for x = 0.38, 0.64 and 1.24 have been prepared by further treatment with sodium trifluoroethoxide of the product from reactions between $(NPF_2)_n$ and phenyl lithium.[310]

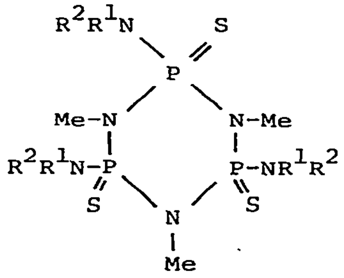


Scheme 3

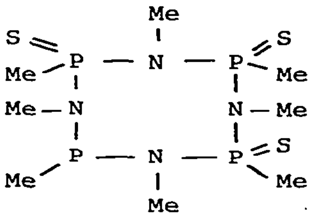
A full crystal structure for the SN_2 bridged tetraphosphazene (93) shows the ring in a flattened crown-saddle conformation with P-N(S) bonds longer (1.666Å) than those in the N_4P_4 ring (1.517 - 1.565Å).[311]



(93)



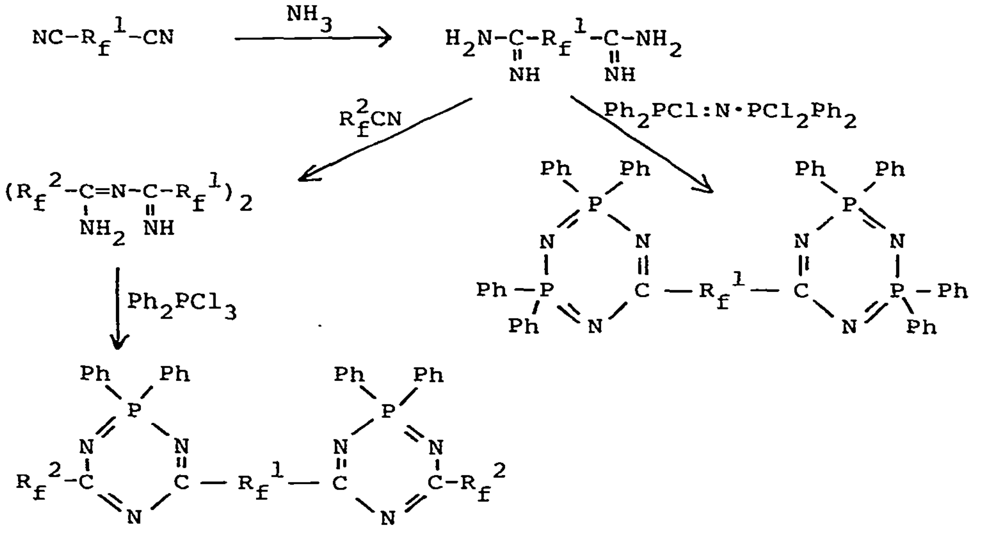
(94, $R^1=R^2$=Me or Et, R^1=Me, R^2=Ph)



(95)

Sulphur can be added under mild conditions to both cyclotri-[312] and tetra-phosph(III)azanes[313] to give compounds (94) and (95) respectively. For the trimeric compounds the amine groups are thought to occupy two equatorial and one axial position; in the unsymmetrical trisulphide (95) ring bonds to the phosphorus(III) atom are 1.748 and 1.731Å while to phosphorus(V) the distances range from 1.667 to 1.702Å.

Bridged mono- and di-phospha-s-triazine derivatives can be synthesised following the reactions in Scheme 4,[314] while reactions

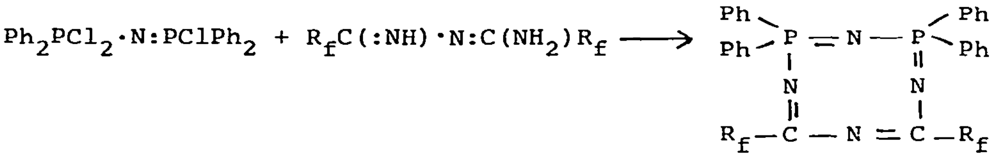


$R_f^1 = (CH_2)_8$

$R_f^2 = C_3F_7OCF(CF_3)OCF(CF_3)-$

Scheme 4

leading to two new isomeric $C_2P_2N_4$ heterocycles are summarised in equations (56) and (57).[315] The latter reaction also produces a monophospha derivative. These compounds with eight membered rings are markedly less stable thermally than the six membered analogues, and at temperatures >300°C the 1,3-compound gives a monophospha-s-triazine and $(NPPh_2)_n$ while the 1,5-compound yields a diphospha-s-triazine.[316]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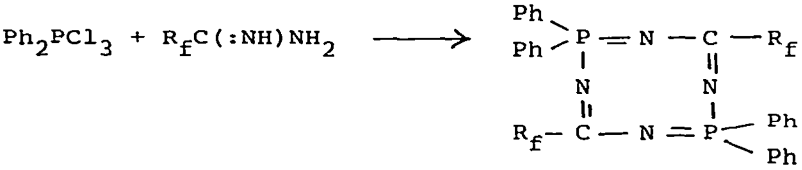
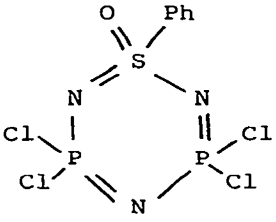
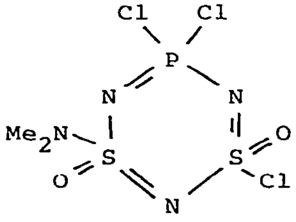
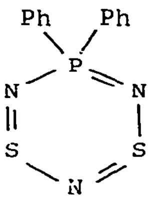

...(57)

Aminolysis reactions of (96) with methyl- and ethyl-amines in ether follow a basically non-geminal route while in acetonitrile as solvent both geminal and non-geminal substitution products can be isolated.[317] A structure for (97), the most abundant isomer from dimethylaminolysis of the corresponding tetrachloride in acetonitrile, shows the oxygen atoms <u>trans</u> to each other with the ring system in a highly asymmetric conformation.[318]


(96)


(97)

A new six membered PS_2N_3 ring system (98) is found by X-ray crystallography to be the product when tetraphenyldiphosphine reacts with N_4S_4.[319] The S_2N_3 section of the ring is planar with



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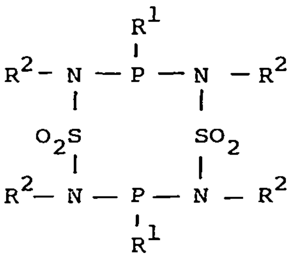
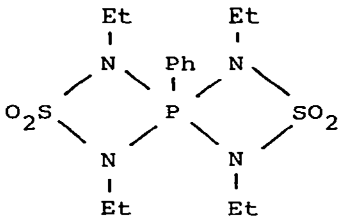


(99, R^1=Me or Ph
R^2=Me or Et)



(100)

the phosphorus atom 0.28Å out of this plane, mean P-N and S-N distances are 1.62 and 1.58Å respectively. The compound, which contains eight π-electrons, occupies a position intermediate between the ten electron compound $S_3N_3^-$ and the six electron $(NPPh_2)_3$ and provides support for the conclusion that in electron rich systems the presence of (4n+2) π-electrons is not associated with any special stabilization. New eight membered $P_2S_2N_4$ compounds (99) are produced when organodichlorophosphines react with substituted sulphamides;[320] the structure of one of these products (99, R^1=Me, R^2=Et) has been determined. Further reaction to give a spirocyclic compound (100) takes place when phosphorus pentachloride reacts with (99, R^1=Ph, R^2=Et).

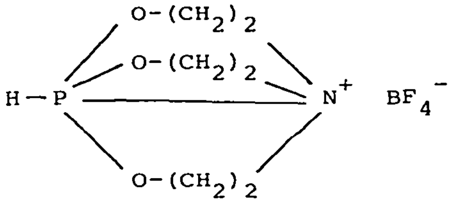
5.2.5 Bonds to Oxygen

Gas phase p.e.s. for P_4O_6, As_4O_6, Sb_4O_6, and P_4O_{10} have been assigned by reference to ab initio m.o. calculations for P_4, P_4O_6, and P_4O_{10}.[321] The results for P_4O_6 can be carried over to the heavier oxides but down the series P, As, Sb all the levels are progressively destabilised implying that for levels with predominantly oxygen 2p character there is an increasing partial negative charge on oxygen as the electronegativity difference increases. Variations for the "metal" based levels appear to reflect variations in atomic ionisation.

Pure crystalline samples of copper(II) hypophosphite have been obtained by treating a copper salt and a hypophosphite in the presence of a complexing agent such as glycerin;[322] new X-ray powder data and a definitive i.r. spectrum are reported. Thermal decomposition to give metallic copper begins at ca. 50°C and the major volatile products are H_2O, PH_3 and H_3PO_2; at higher temperatures P_4O_6 and P_4 can be observed. A crystalline vanadium hydrogen phosphite, $V(H_2PO_3)_3$, is the product from a redox reaction between V_2O_5 and molten phosphorous acid.[323] The compound, isostructural with the iron(III) species, contains the metal in octahedral coordination by bridging hydrogen phosphite groups; on heating to 400°C it is converted to the diphosphite, $V_2[O_2(H)POP(H)O_2]_3$.

Further details of the chemistry of monomeric methyl metaphosphate have been announced.[324] Previously it was identified by its electrophilic attack on the aromatic rings of substituted anilines and it has now been shown to react with acetophenone, ethyl benzoate and aniline.

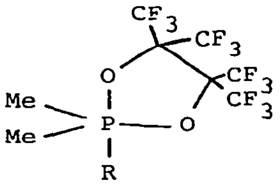
Trigonal bipyramidal structures with an unpaired electron in an equatorial position are usually assigned to phosphoranyl radicals in solution, but recent work on the radical produced by X-ray irradiation of (<u>101</u>) points to the unpaired electron occupying an axial position *trans* to the nitrogen which remains in the other axial position.[325]



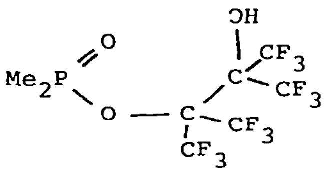
(<u>101</u>)

Both substitution and redox reactions take place when catechyl phosphorus tribromide reacts with phosphorus(III) species, such as $(EtO)_3P$, Ph_2PO-i-Pr, and $(PhO)_3P$.[326] Reactions with the triethyl phosphite are summarised in Scheme 5.

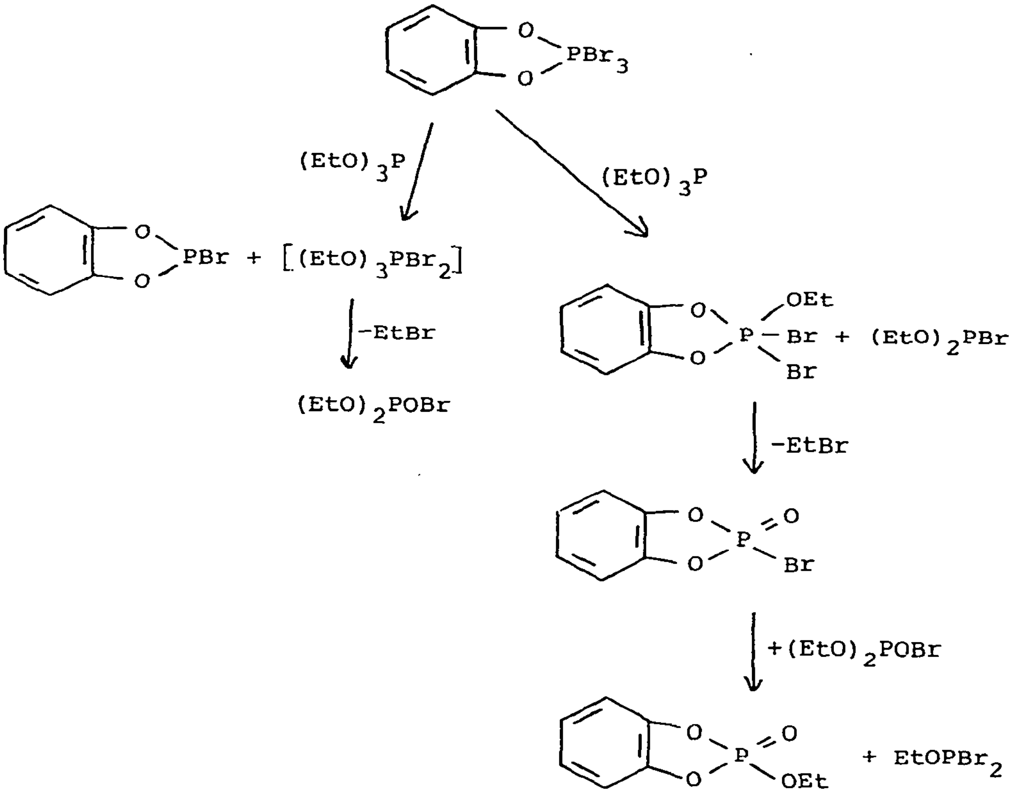
When the dioxaphospholane (<u>102</u>, R=$OSiMe_3$) is treated with either



(<u>102</u>)



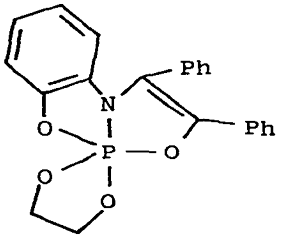
(<u>103</u>)



Scheme 5

water or hydrogen chloride, the product is not the hydroxyphospholane (102, R=OH) but the phosphinate (103),[327] which is a hydrogen bonded dimer (O···O 2.559Å) in the solid state. Reaction of (103) with trimethylchlorosilane regenerates the starting material while with thionyl chloride the product is (102, R=Cl).

Structures have been determined for two new tricyclic phosphoranes (104) and (105).[328] For the former coordination about the central atom is distorted by 34.9% from trigonal bipyramidal geometry along the Berry coordinate towards square pyramidal geometry. In the second compound there are two independent molecules, distorted by respectively 12.7 and 22.5% along the Berry coordinate. The structure of (106), a product obtained during an unsuccessful attempt to prepare a five coordinate spiro bicyclic compound has also been determined.[329]



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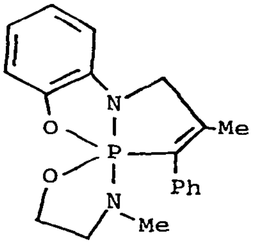

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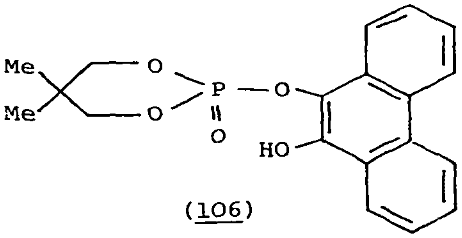
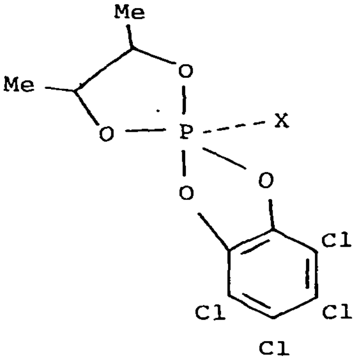


(106)

N.m.r. data have been presented to show that when six coordinate anions are formed from spirocyclic phosphoranes such as (107), the attacking nucleophile initially occupies a position trans to the



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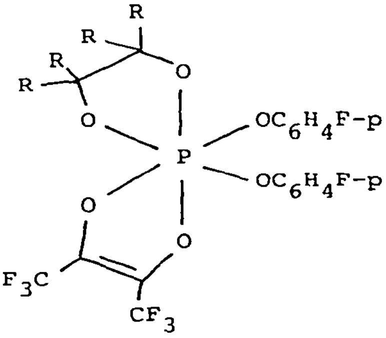


(108, R=Me or H)

group X but on warming to room temperature isomerisation to the more stable cis form takes place.[330a] Variable temperature data on the related species (108) is most readily interpreted in terms of isomerisation via a trigonal prismatic intermediate.[330b]

p-Nitrophenol reacts with methyldichlorophosphine to give as product $MeP(OC_6H_4NO_2)_3Cl.HOC_6H_4NO_2$, in which the nitrophenol molecule persists even after repeated recrystallisations.[331] A recent structure determination shows that this is probably a result of the formation of a strong hydrogen bond between the chloride ion and the phenol group (O···Cl 3.02, O-H 0.82, H···Cl 2.19Å); in addition there are short non-bonded interactions involving the methyl group ($C-H\cdots Cl^-$ 3.440, 3.490, C-H···O 3.312Å) suggesting its behaviour as a proton donor.

Acyl phosphates have now been isolated as the products from reactions between stannyl phosphates and acyl chlorides in carbon tetrachloride.[332] The reaction, outlined in equation (58), proceeds rapidly at room temperature and as the products generally

$$RCOCl + Bu_3SnOP(O)(OEt)_2 \longrightarrow RC(O)OP(O)(OEt)_2 + Bu_3SnCl \qquad \ldots(58)$$

R = Me, Et, t-Bu, Ph, etc.

decompose on distillation they can be purified by column chromatography.

Coordination between polymeric tri(allyl)phosphate and a number of metal salts has been investigated, and among some 45 compounds isolated are $CuL_2(NO_3)_2$, $CuL_4(BF_4)_2$, CoL_2Cl_2 and CoL_2Br_2.[333] Spectroscopic data are interpreted to show that coordination is very similar to that with monomeric phosphoryl ligands. The formation of metal complexes between di-isopropyl methylphosphonate, $MePO(O\text{-}i\text{-}Pr)_2(L)$ and a wide range of salts and complexes has been reported,[334] and the strong complexing ability of the diorganophosphinate group $R_2(O)P{:}^-$ in particular to gold is shown by the ready conversion of $t\text{-}Bu_3PAuMe$ to $t\text{-}Bu_3PAuP(O)R_2$.[335]

Hydrogen bonds (O···O 2.76, P-O 1.48Å, P-O···O 134.7°) link together the units in the hydrogen peroxide addition compound $(Ph_3PO)_2{\cdot}H_2O_2$.[336] Hydrogen bonds also play an important role in the solid state structure of the zwitterionic 3-aminopropylphosphonic acid $H_3\overset{+}{N}\text{-}(CH_2)_3\text{-}PO_3H^-$;[337] there are three of the type N-H···O (2.81 - 2.83Å) and one O-H···O bond with length 2.52Å. Aminomethane phosphonic acid esters $R^1NHCH_2P(O)(OR^2)_2$ can be isolated from reactions between N-substituted hexahydro-s-triazines and $HP(O)(OR^2)_2$.[338]

A variety of solid state reactions leading to Na_3PO_4 has been investigated by d.t.a. and X-ray powder methods to show the existence of two modifications of the compound with a reversible first order phase transition at 325°C.[339] The high temperature form has a Li_3Bi type structure with orientationally disordered PO_4^{3-} anions. The recently determined structure of $Ca_2(NH_4)H_7(PO_4)_3.2H_2O$ contains chains of $CaH_2PO_4^+$ cations linked by Ca···O bonds to form corrugated sheets similar to those in $Ca(H_2PO_4)_2.H_2O$ and other calcium phosphates and NH_4^+, H_2O and $[H_3(PO_4)_2]^{3-}$ groups between the sheets.[340] A noteworthy feature in the structure of the last unit is the formation of hydrogen bonds (O···O 2.50 - 2.56Å) from three of the oxygen atoms of one PO_4 group to form infinite $[H_3(PO_4)_2]_n^{3-}$ sheets.

A crystalline compound with the formula $H_3O[Al_3(H_2PO_4)_6(HPO_4)_2].4H_2O$ has been isolated during an investigation into the $AlPO_4$-H_3PO_4-H_2O system.[341] The structure, shown in Figure 8, is based on layers of AlO_6 octahedra which share vertices with $O_2P(OH)_2$ and $O_3P(OH)$ tetrahedra; vacancies within these layers are occupied by the H_3O^+ ions. The crystal structure of $SnHPO_4$ has been reinvestigated and that for the corresponding phosphite, $SnHPO_3$, reported for the first time.[342] Both contain infinite sheets of fused SnO_3 and PO_4 groups for the phosphate and SnO_3 and HPO_3 units for the phosphite. The sheets differ in relative orientations in the two compounds; the determining factor in the phosphite is the closest approach between non-bonded oxygens while formation of the

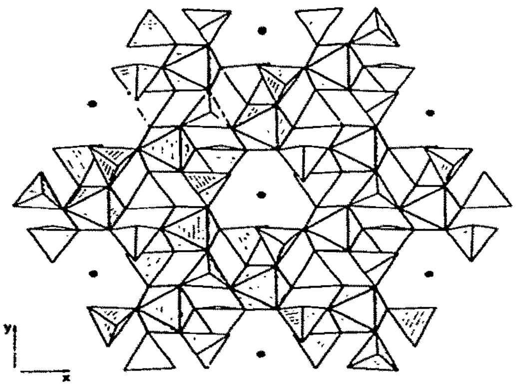


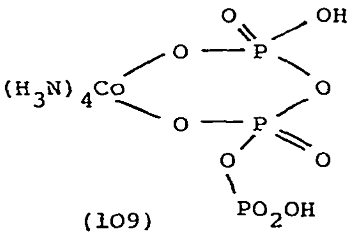
Figure 8. Structure of $H_3O[Al_3(H_2PO_4)_6(HPO_4)_2].4H_2O$ (reproduced by permission from Z. Naturforsch., 35b(1980)403).

maximum number of hydrogen bonds is most important for the phosphate. Two new lead antimony phosphates, $Pb_3Sb(III)(PO_4)_3$ and $Pb_{11}Sb(V)(PO_4)_9$, have been identified;[343] the former is obtained by heating a stoichiometric mixture of $Pb_3(PO_4)_2$ and $SbPO_4$ to 750°C and the latter by the action of oxygen on a 3:1:1 mixture of $Pb_3(PO_4)_2$, $Pb_2P_2O_7$ and $SbPO_4$ at 700°C.

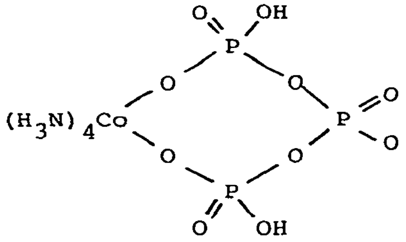
Three different crystallographic modifications of hydrated chromium(III) phosphate have been identified.[344] The most stable form is monoclinic, space group Cc, containing octahedral $Cr(H_2O)_6^{3+}$ and tetrahedral PO_4^{3-} ions while a cubic form, isostructural with hydrated chromium(III) arsenate, is the least stable.

The structures of two diphosphates, $CsH_3P_2O_7.H_2O$[345] and α-$CaNa_2P_2O_7.4H_2O$,[346] and a pentaphosphate, ErP_5O_{14}[347] have been published.

Further details are becoming available on the structure and reactivity of polyphosphate-metal complexes which are important as model compounds for biological systems. Unidentate and bi-dentate diphosphate groups respectively are present in $[Co(HP_2O_7)(NH_3)_5].H_2O$ and $[Co(HP_2O_7)(NH_3)_4].2H_2O$; in the latter the CoO_3P_2 ring has a distorted boat conformation with two axial diphosphate oxygens forming hydrogen bonds with two of the ammonia ligands. Co-O-P and P-O-P angles are respectively 139.3 and 131.3° in the unidentate compound and 126.1/127.0 and 127.1° in the bidentate analogue. Compounds formed between diphosphate groups and aquated $N_4Co(III)$ complex ions, where $N_4 = (en)_2$, $(H_2NCH_2CH_2CH_2NH_2)_2$ or $N(CH_2CH_2NH_2)_3$, have been investigated by n.m.r. methods showing the formation of a 3:1 N_4Co-diphosphate species.[349] In this system there is a ca. 10^5 enhancement in the rate of diphosphate hydrolysis over that in the absence of complexation to cobalt. In contrast, hydrolysis of the β,γ-coordinated triphosphate group in the complex (<u>109</u>) occurs at only two thirds the rate for that of the free ligand and the rate is linearly dependent on $[H^+]$ over the range 0.1 - 1.0M.[350]



(<u>109</u>)



(<u>110</u>)

Evidence suggests further that hydrolysis at the phosphate linkage which is part of the chelate ring and at that between the uncoordinated phosphate and the chelate takes place at comparable rates. A linkage isomer of (109) in which the triphosphate group is αγ-coordinated (110) has now been identified,[351] in which the eight membered chelate ring has a boat conformation.

A number of methods are available for the preparation of the molybdenum(V) triphosphate complex $[Mo_2O_4(HP_3O_{10})_2]^{6-}$, which has a structure based on tridentate behaviour of the triphosphate group.[352] The terminal phosphate groups are equivalent and the central group is coordinated trans to the molybdenyl oxygen of the Mo_2O_4 core.

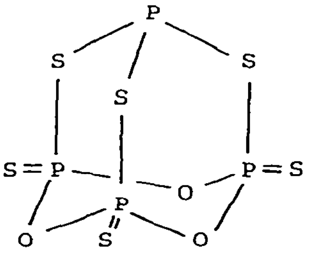
Hydroxyapatites with Ca:P ratios between 1.66 and 1.70 on heating to 800-1250°C can be represented by the formula $Ca_{10}(PO_4)_6(OH)_{2-2x}O_x\square_x$;[353] the samples are stable in air at room temperature and the data tend to disprove the theory that the reduction of dental caries by fluoride is due to inhibition of diffusion in hydroxyapatite. Homogeneous solid solutions of calcium and magnesium hydroxyapatite over the complete concentration range have been obtained by coprecipitation reactions in aqueous solution.[354] High-resolution ^{31}P n.m.r. spectra for a range of solid calcium phosphates, including $Ca_{10}(OH)_2(PO_4)_6$, $Ca_{10}F_2(PO_4)_6$, $Ca_8H_2(PO_4)_6.5H_2O$, $CaHPO_4.2H_2O$, $Ca(H_2PO_4)_2.H_2O$, $CaHPO_4$ and $Ca(H_2PO_4)_2$ have been obtained by a combination of magic angle spinning and proton enhancement to show that isotropic shifts move upfield upon protonation of the phosphate.[355] Non-stoichiometric hydroxyapatites with Ca:P ratios as low as 1.33 closely resemble the stoichiometric compounds and it is considered that a scheme based on Ca^{2+} vacancies in the lattice, which leads to concomitant loss of OH^- and addition of protons, is a more appropriate explanation than one postulating the presence of an additional calcium phosphate species with a lower ratio. The recent chemistry of phosphate minerals constituting bone, dentin and tooth enamel has been reviewed.[356]

Among papers concerned with inorganic phosphate ion exchanges are the H^+-NH_4^+ exchange on γ-$Ti(HPO_4)_2.H_2O$,[357] the exchange of Ag^+ in acetate and nitrate solutions on α-zirconium phosphate,[358] and an investigation of the unusual, initial shape of titration curves of α-zirconium phosphate with various hydroxides. The direct precipit ation method has been modified to give large crystals of α-$Zr(HPO_4)_2.H_2O$ but the major part is formed by geminates.[360] Salt formation can be carried out without appreciable breakage but if the interlayer spacing is greatly increased, there is cleavage parallel to the layers giving thin sheets. Cobaltocene can be intercalated from toluene at 100-120°C into α-$Zr(HPO_4)_2.H_2O$ giving the cobaltocenium ion, $Zr(CoCp_2)_{0.5}H_{1.5}(PO_4)_2$.[361] Phase changes and dehydration have been investigated for the fully exchanged Cu(II) species, $ZrCu(PO_4)_2.4H_2O$.[362]

5.2.6 Bonds to Sulphur, Selenium or Tellurium

Vibrational spectra for the cage compounds, P_4S_3, P_4Se_3, and As_4Se_3, in both the solid and melt have been measured.[363] A new method for the preparation of β-$P_4S_3I_2$ involves reaction between P_4S_3 and PI_3 in carbon disulphide but attempts to prepare the arsenic analogue by the corresponding method were not successful.[364] The specific heats and enthalpies and entropies of melting for $P_4Se_3I_2$ and both α- and β-$P_4S_3I_2$ have been determined.

At temperatures greater than 500°C, mixtures of P_4S_{10} and P_4O_{10} react to give reorganisation products in the series $P_4O_{10-n}S_n$, where n = 1 - 9, which can be distilled out when n<6.[365] This reaction also gives rise to a new compound $P_4O_3S_6$ with the adamantane structure (111), in which one quarter of the phosphorus is in the +3 oxidation state. The compound is stable in the absence of moisture but hydrolysis at <10°C with sodium bicarbonate leads to a P(III)-P(V) anion $(P_3O_3S_6)^{3-}$ (112),[366] and reaction with an excess of alcohol follows equation (59).



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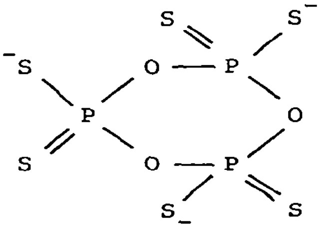


(112)

$$P_4O_3S_6 + 6ROH \longrightarrow (RO)_2P(O)H + 2ROP(S)(SH)(OH) + (RO)_2P(S)SH \quad (59)$$

Evidence for two congruently melting compounds Na_3PS_4 and $(NaPS_3)_n$ has been obtained during an investigation of the Na_2S-P_4S_{10} section of the Na_2S-GeS_2-P_4S_{10} system.[367]

The structure of TiP_2S_6 confirms its formulation as a hexathiohypodiphosphate, each phosphorus is surrounded tetrahedrally by three sulphur atoms (mean P-S 2.039Å).[368] The layer compound $MnPS_3$ intercalates compounds such as Cp_2CoI, Cp_2CrI, NH_4Cl, CsCl, KCl etc. by a route which does not involve electron transfer. Products such as $Mn_{1-x}PS_3M_{2x}.(H_2O)_y$ are formed with release of x mols of Mn^{2+}.[369] X-ray data point to an increase in the interlayer spacing from 6.50Å in the pure compound to 9.37 (for KCl) and 12.26Å (for Cp_2CrI). Data have also been presented for a pyridine intercalate $MPSe_3.py_{0.33}$ with the corresponding manganese and iron selenophosphates.[370] From X-ray powder diffraction the compounds $M(II)PS_3$ and $M(II)PSe_3$, where M = Cr, Mn, Fe, Ni, Zn or Cd, belong to the same structure type.[371]

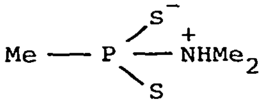
Two new anionic thiophosphorus fluorides, identified as $(Et_4N)_2P_2S_2F_8$ and $Et_4NPS_2F_2$, have been isolated from reactions between $PF_5.MeCN$ and Et_4NSH,[372] and the little known trithiofluorophosphate is formed as the major product from the reaction in equation (60).[373] A trithiophosphite, $(Me_2NH_2)_2HPS_3$,

$$4Et_4NF \ + \ 4Et_4NSH \ + \ P_4S_{10} \longrightarrow 4(Et_4N)_2PS_3F \ + \ 2H_2O \qquad ...(60)$$

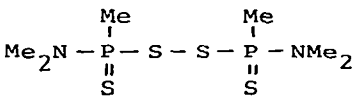
has also been prepared, in this case by reaction of $P(NMe_2)_3$ with hydrogen sulphide in hexane solution.[374]

Monomeric structures are suggested for the tin dithiophosphate complexes $Ph_3SnS_2P(OR)_2$, where R = Et or i-Pr, on the basis of variable temperature Mössbauer and Raman data.[375]

The preparation of (dimethylamino)dithiomethylphosphonic acid, which exists in the zwitterionic form (<u>113</u>), results via the salt $Me_2NH_2{}^+MePS_2NMe_2{}^-$ from reactions between the thioanhydride, $Me_2P_2S_3$ and dimethylamine.[376] The compound gives complexes with



(<u>113</u>)



$$Me_2N-\underset{\underset{S}{\|}}{\overset{\overset{Me}{|}}{P}}-S-S-\underset{\underset{S}{\|}}{\overset{\overset{Me}{|}}{P}}-NMe_2$$

(<u>114</u>)

transition metal salts and a structure has been obtained for the nickel derivative $Ni(S_2PMeNMe_2)_2$; oxidation of the anion with iodine gives the disulphane (<u>114</u>) and with H_2S, H_2Se and MeSH the products are respectively salts of the anions $MePS_3^-$, $MePS_2Se^-$ and $MePS_2SMe^-$.

Square planar Pd(II) and Pt(II) complexes have been isolated from the unsymmetrically substituted dithiophosphinic acids, $R^1R^2PS_2H$ where R^1=$MeC\equiv C$, $Me_3SiC\equiv C$ or Me and R^2=Me or $MeOC_6H_4$,[377] and a tetranuclear complex $Mo_4O_8(Me_2POS)_4$ is obtained when sodium dimethylthiophosphinate $Na(Me_2POS)$ and molybdenum pentachloride react.[378]

An X-ray structure of $Et_2N(C_6H_{11})P(S)P(S)(C_6H_{11})(NEt_2)$ shows it to be the <u>meso</u> form with short P-N distances (1.665Å) suggesting that coordination to metal atoms would be via the sulphur atoms.[379]

The rapid bimolecular selenium exchange which occurs in solutions containing R_3PSe and R_3P for R_3=$MePh_2$ or $Ph_2(CH_2Ph)$ can be put to preparative use;[380] for example, mixtures of $Ph_2P(Se)CH_2(Se)PPh_2$ and $Ph_2PCH_2PPh_2$ rapidly give exclusive formation of $Ph_2P(Se)CH_2PPh_2$. A similar rapid exchange is known to occur with tellurium in R_3^1PTe $-R_3^2P$ systems, but tellurium transfer is followed by insertion into a P-Si bond in the $n\text{-}Bu_3PTe\text{-}(t\text{-}Bu)_2(Me_3Si)P$ system;[381] the product is $(t\text{-}Bu)_2P{\cdot}Te{\cdot}SiMe_3$.

Complex formation in liquid sulphur dioxide solution between $Cd(SbF_6)_2$ and a wide range of phosphorus ligands, including Ph_3PX, $Ph_2P(X)(CH_2)_nP(X)Ph_2$, $t\text{-}Bu_3PX$ and $(C_6H_{11})_3PX$, where X=S or Se and n=1 or 2, has been examined by ^{31}P n.m.r. spectroscopy.[382,383] Among the new species identified were ligand complexes in a number of series including $\{Cd[SeP(C_6H_{11})_3]_n[SP(C_6H_{11})_3]_{4-n}\}^{2+}$.

5.3 ARSENIC

5.3.1 <u>Arsenic and Arsenides</u>

A deep red salt containing the As_{11}^{3-} anion has been prepared from a reaction between KAs_2 and 2,2,2-crypt in ethylenediamine.[384] The structure, shown in Figure 9, has close to D_3 symmetry with eight of the arsenic atoms occupying the corners of a bicapped twisted trigonal antiprism. Three bridging atoms in two fold coordination complete the structure. As-As distances vary between 2.36 and 2.48Å with those between two three coordinate atoms being somewhat longer. The synthesis is also reported of

$Sr_3Si_2As_4$ and the corresponding germanium compound both of which contain infinite $(Si_2As_4{}^{6-})_n$ and $(Ge_2As_4{}^{6-})_n$ anions.[385] In the

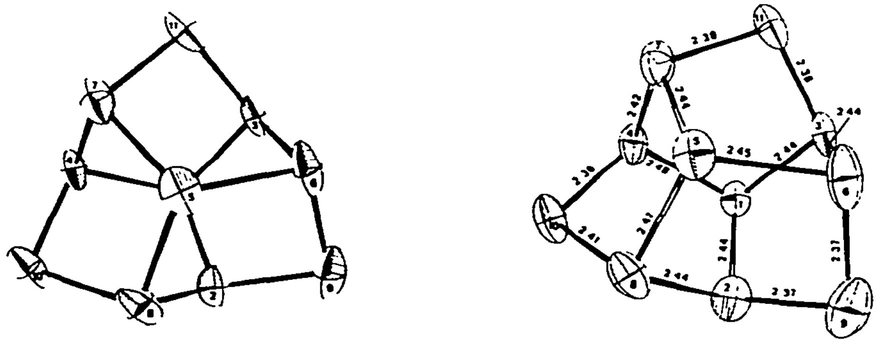

(a) (b)

Figure 9. Structure of the $As_{11}{}^{3-}$ ion, (a) viewed down the three fold axis with As(1) eclipsed by As(5), (b) slightly tilted, (reproduced by permission from J. Am. Chem. Soc., 102(1980)6036).

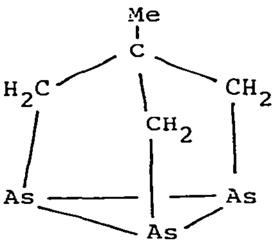
former the Si_2 units are linked by edges to form one dimensional infinite chains while in the germanium compound interconnection involves three arsenic atoms of one $GeAs_3$ group but only one arsenic of the other group is involved in the bridging.

Crystal structures have been determined for both Cd_3AsCl_3[386] and Cd_2AsCl_2;[387] the latter contains As_2Cd_6 groups (As-As 2.404, As-Cd 2.53 - 2.56Å) which share a Cd-Cd edge to form layers along the b axis. Anti- Th_3P_4 structures are reported for Eu_4As_3 and La_4Sb_3 with mean Eu-As and La-Sb distances of 3.20 and 3.34Å respectively.[388] Direct interaction of the elements at 500°C for arsenic and 700°C for antimony leads to CfAs and CfSb which have NaCl-type structures.[389]

New ternary arsenides ABAs, where A=Ca, Sr or Ba and B=Cr, Fe, Co, Ni or Cu, have been prepared and from powder diffraction data have the $ThCr_2Si_2$ structure.[390] Two new phases, $CaNi_2As_2$, again with the $ThCr_2Si_2$ structure, and a hexagonal compound $Ca_{2.3}Ni_{11.7}As_7$ for which a $Zr_2Fe_{12}P_7$ type structure is proposed have been identified in the Ca-Ni-As ternary system.[391] A strontium compound $SrNi_2As_2$, isotypic with the calcium compound above has also been isolated. Preparative and structural information have also been reported for KHgAs, KHgSb, KZnAs,[392] Na_2AuAs, Na_2AuSb and K_2AuSb.[393] A feature of the structure of the gold compounds is the presence of zig-zag Au-As(Sb) chains containing linear As-Au-As bonds and angles of ca. 70° at the Au-As-Au bonds.

5.3.2 Bonds to Carbon or Silicon

Tris(arsinomethyl)ethane, $MeC(CH_2AsI_2)_3$ reacts with three moles of $NaAsPh_2$ to give the tricyclic triarsaheptane (115), which can



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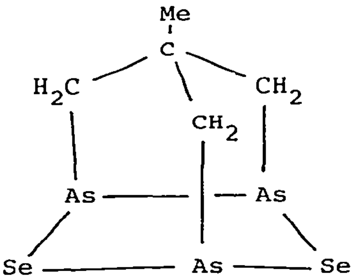

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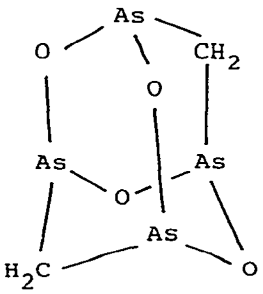
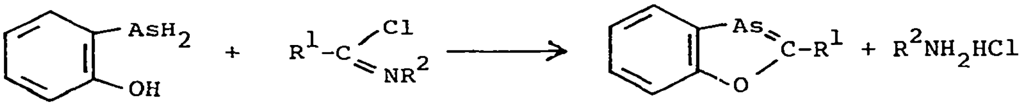


(117)

also be obtained by desulphuration of the arsenic(V) species, $MeC(CH_2AsS)_3$, previously obtained.[394] A related cage compound, $MeC(CH_2As)_3Se_2$ (116), results when sodium hydroselenide in THF is used in place of $NaAsPh_2$. A crystal structure determination on the soluble form of the oxide $[CH_2(AsO)_2]_n$, obtained by hydrolysis of methylene bis(dichloroarsine), shows the presence of discrete tetrameric $As_4O_4(CH_2)_2$ molecules with the adamantane structure (117).[395] Mean values for important parameters are As-O 1.80, As-C 1.96Å, O-As-O 101.8 and C-As-O 99.3°.

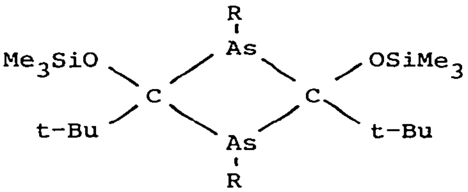
Acyl and imidoyl chlorides react with o-arsinophenols, the latter according to equation (61).[396]



R^1=Me, t-Bu, Ph or mesityl. ...(61)

(For similar reactions with o-phosphino-phenols, see reference 134).

On u.v. irradiation, enols such as RAs:C(OSiMe$_3$)t-Bu, where R=Me or Et, dimerise to 1,3-diarsetanes (118), and an X-ray structure of the methyl derivative shows ca. C_2 symmetry and a *cis* arrangement of the substituents at carbon.[397] As-C distances in the ring are 2.05Å and to methyl 1.96Å; the C-As-C and As-C-As ring angles are 85.9 and 92.5° respectively. Partially oxidised elemental arsenic on treatment with 1,2-diiodotetrafluorobenzene gives $(C_6F_4)_2As_2O$ with the "butterfly" structure (119); this is closely related to the structure of $(C_6F_4)_3As_2$.[398]



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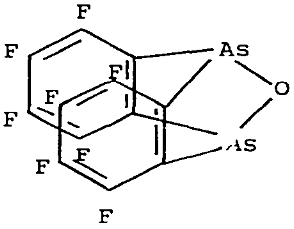
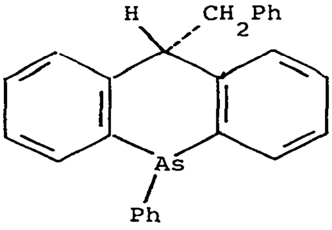


(119)

The crystalline isomer of 9-arsa-anthracene, melting at 304K, has structure (120) in which the benzyl and phenyl groups are *trans* to each other.[399] Reference has already been made (page 289) to the problems arising from disorder in the structures of both arsa- and phospha-triptycene; for the arsenic compound a solution has been achieved by substitution of the hydrogen atom *trans* to arsenic by a phenyl group.[400] The As-C distances are unequal (1.938, 1.952 and 1.955Å) and ring flexibility is shown by three different values (90.2, 91.0 and 93.3°) for the C-As-C angles. A related quaternary arsenic



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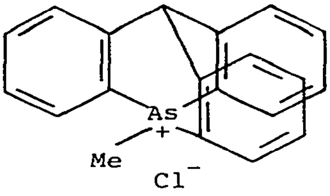
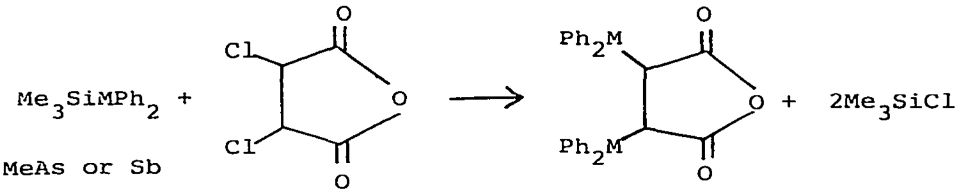


(121)

compound (<u>121</u>) has also been investigated crystallographically,[401] showing that the aryl C-As-C angles are increased to ca. 97.7°.

Maleic anhydride derivatives containing either diphenylarsino or diphenylantimony groups can be produced as shown in equation (62);[402] i.r. and u.v.-visible spectra are reported together with

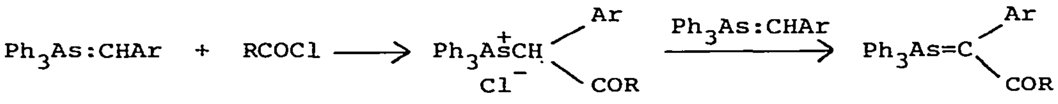


...(62)

an X-ray structure for the antimony compound. α-Hydroxylalkylarsines, $Ph_2AsCHR(OH)$ for R=Et, i-Pr or Ph, have been obtained from reactions between aldehydes and either diphenylarsine or its lithium derivative, but because of thermal instability they cannot be isolated in the pure form.[403] Oxidation to the corresponding sulphide and selenide occurs when the di- and tri-tertiary arsines $N(CH_2CH_2AsMe_2)_3$, $MeC(CH_2Cl)(CH_2AsMe_2)_2$ and $(ClCH_2)_2C(CH_2AsMe_2)_2$ are treated with the appropriate element in ethanol.[404]

Pentavalent compounds $(CF_3)_{3-n}Me_nM[ON(CF_3)_2]_2$, where M=As or Sb, are obtained from reactions at room temperature between $Me_n(CF_3)_{3-n}As$ for n=1-3 or Me_3Sb and bis(trifluoromethyl)nitroxyl.[405]

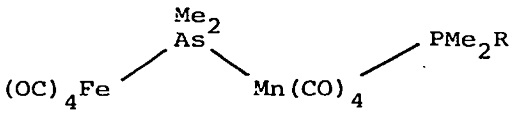
Triphenylarsine and substituted benzyl bromides give the corresponding arsonium bromide, $(Ph_3AsCH_2Ar)Br$, at reflux temperatures, but in the presence of either sodium hydride or sodium methoxide there is loss of hydrogen bromide and formation of the arsonium ylid $Ph_3As{:}CHAr$.[406] Although such species cannot be isolated, treatment with an acid chloride or an anhydride points to transylidation via a C-acylated arsonium salt as shown in equation (63).[407]



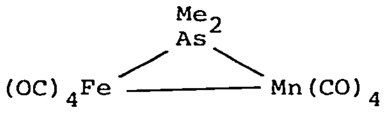
$$Ph_3As{:}CHAr + RCOCl \longrightarrow \underset{Cl^-}{Ph_3\overset{+}{As}}CH(Ar)(COR) \xrightarrow{Ph_3As{:}CHAr} Ph_3As{=}C(Ar)(COR)$$

...(63)

Dinuclear complexes (122) containing functional groups are the products when the arsenic bridged species (123) reacts with either Me_2PCl or Me_2PPMe_2.[408] Further chain lengthening can be achieved

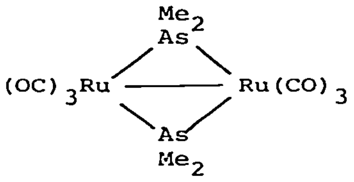


(122, R=Cl or PMe_2)



(123)

by hydrolysis of (122, R=Cl) giving an Fe-As-Mn-P-O-P-Mn-As-Fe chain which can subsequently be reacted with metal carbonyls. The cluster structure of $Ru_3(CO)_{12}$ is not maintained on reaction with Me_2AsH, Me_2AsCl or Me_2AsNMe_2 but compounds such as (124) and (125) are produced.[409] Further polynuclear complexes (126) and



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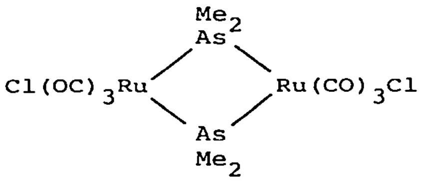

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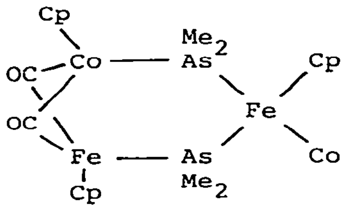

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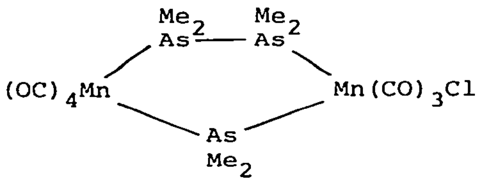
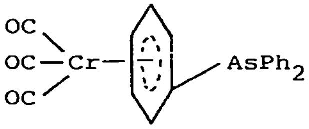


(127)

(127) have been isolated from respectively the $CpCo(CO)_2$-$Cp(CO)_2FeAsMe_2$ and $KMn(CO)_5$-Me_2AsCl reactions.[410]

One of the phenyl groups of triphenylarsine behaves as an $(\eta^6\text{-}C_6H_5)$ group in the complex (128) recently isolated from a reaction with $Cr(CO)_6$ in refluxing decane for 8 hours;[411] the Cr···As distance (3.730Å) is clearly non-bonding and the Cr-arene bond lengths vary from 2.193 to 2.220Å.



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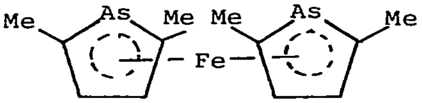


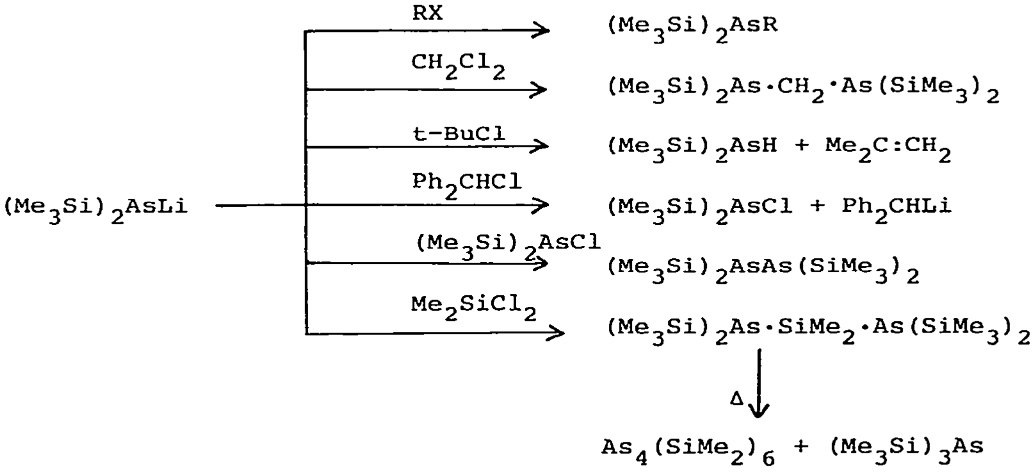
(129)

In the methylated-1,1'-diarsaferrocene structure (129) recently determined, the π-arsolyl rings are eclipsed but are neither strictly planar nor parallel.[412]

An adamantane structure has been confirmed by X-ray crystallography for $As_4(SiMe_2)_6$ obtained previously by thermolysis of $[(Me_3Si)_2As]_2SiMe_2$.[413] The As-Si distance is 2.351Å and the angles Si-As-Si and As-Si-As 103.2 and 121.0° respectively.

Replacement of one of the trimethylsilyl groups occurs when a bis(trimethylsilyl)arsine reacts with 2,2-dimethylpropionyl chloride.[414] Although the resulting acyl arsine $RAs(SiMe_3)(COCMe_3)$, where R=Me, Et, i-Pr, t-Bu, Ph etc., are more stable than the corresponding phosphorus analogues rearrangement to the isomeric alkylidene arsine $RAs{:}C(OSiMe_3)CMe_3$ occurs at higher temperatures.

The mixture of Na_3As-K_3As, which results when arsenic powder reacts with the Na-K alloy, can be treated with trimethylchlorosilane to give high yields of $(Me_3Si)_3As$.[415] This compound on reaction with methyl lithium loses one mole of tetramethylsilane to give $(Me_3Si)_2AsLi.2THF$, which as shown in Scheme 6 is a highly reactive intermediate.



Scheme 6

5.3.3 Bonds to Halogens

The trifluoroarsonium ion, $HAsF_3^+$, and $As_2F_5^+$ have both been identified in a recent investigation of the gas phase ion chemistry of arsenic trifluoride.[416]

On reaction with peroxydisulphuryl fluoride arsenic trifluoride gives $AsF_3(SO_3F)_2$ as a clear viscous liquid which could not be crystallised.[417] Attempts to form anionic species were also unsuccessful; the product from vibrational spectroscopy is considered to be polymeric with bridging fluorosulphate groups. Heptafluorodiarsenates, MAs_2F_7 where M=K, Rb or Cs, are the products when alkali metal fluorides are crystallised at room temperature from arsenic trifluoride.[418] A full structure for the potassium salt shows the presence of pseudo-trigonal bipyramidal AsF_4^- ions (As-F 1.73, 1.91Å) and AsF_3 molecules which interact to give the complex chain arrangement shown in Figure 10.

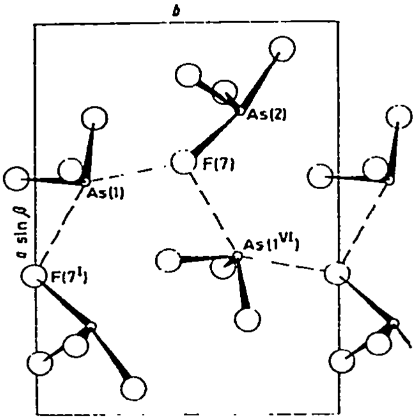


Figure 10. The structure of the anionic chain in KAs_2F_7 (reproduced by permission from J. Chem. Soc. Dalton Trans., (1980)1630).

The structure of arsenic triiodide has been refined and can be described in terms of a hexagonal close packed array of iodines with the arsenic atoms and the lone pair of electrons occupying two-thirds of the octahedral sites in every second layer.[419] This leads to an A(AsE)BA(AsE)B repeating structure. An alternative description is in terms of discrete molecules in which As-I and I-As-I are 2.59Å and 99.7° respectively. Arsenic triiodide adds to nickel dithiocarbamates in CS_2 solution to give dark purple crystals of $Ni(S_2CNR_2)_2(AsI_3)_2$ where R=Et or Bu.[420] A crystal structure shows octahedral coordination about nickel with four sulphur atoms in a plane (Ni-S 2.216, 2.226Å) and AsI_3 molecules in trans positions (Ni-As 2.736Å). The compound is unusual as from magnetic susceptibility measurements, the Ni(II) has a spin singlet ground state.

The equilibrium in equation (64) has been established as occurring for AsF_5 intercalation in graphite from the interconversion

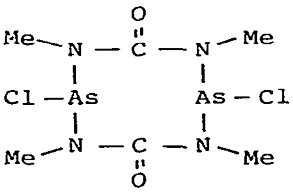
$$3AsF_5 + 2e^- \rightleftharpoons 2AsF_6^- + AsF_3 \qquad \ldots(64)$$

of such intercalates and $C_{12n}^{+}\,AsF_6^{-}$ salts.[421]

A structure determination on $S_4N_4.AsF_5$ shows opening of the cage to give a boat shaped ring with the arsenic atom coordinated to one of the ring nitrogen atoms.[422]

5.3.4 Bonds to Nitrogen

A new eight-membered diarsine (130) is the product when arsenic trichloride reacts with the substituted urea $OC[NMe(SiMe_3)]_2$.[423]



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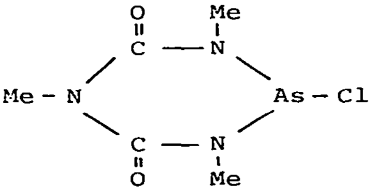
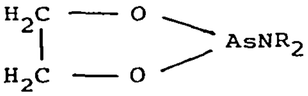


(131)

X-ray crystallography indicates a boat shaped ring with transannular As···N interactions (2.31, 2.47Å); on heating to 110°C the compound decomposes with sublimation of (131). High yields of the trans-amination products from (132) or (133) and ammonia, primary and secondary amines can be obtained at room temperature;[424]



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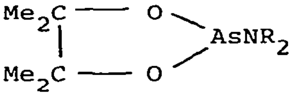

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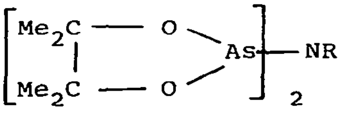


(134, R=H or Me)

among the compounds isolated were the novel diarsolanylamines (134). Products with the formula $Me_2As(OCH_2CH_2)_nOH$, where n=3 or 4, have been obtained from reactions between Me_2AsNMe_2 and either tri- or tetra-ethyleneglycol in a 1:1 ratio.[425]

The structure of tris(morpholino)arsine is closely similar to that of the phosphorus analogue with two short As-N distances (1.853Å) and two small N-As-N angles (94.1°).[426] The longer bond is to a nitrogen atom in essentially sp^3 hybridisation with its lone pair anti with respect to the arsenic lone pair.

5.3.5 Bonds to Oxygen

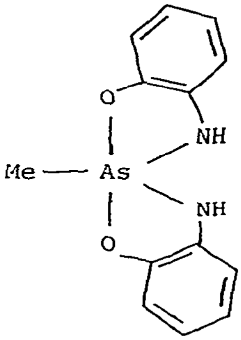
A very hygroscopic compound with the empirical formula AsO_2 results when As_4O_6 is heated at 533-633K for 14 days under an oxygen pressure of 5-50MPa.[427] The formula has been confirmed by a structure determination which shows the presence of infinite arsenic-oxygen layers containing both As(III) and As(V). For the former, coordination is to three oxygen atoms with O-As-O angles of 90°, while the latter is in distorted tetrahedral coordination with angles varying between 89.7 and 119.4°. As(V)-O distances are 1.72Å to a bridging oxygen and 1.61Å to a terminal atom, the latter probably including a degree of π-character.

^{13}C n.m.r. spectra have been obtained for aqueous solutions of the sodium salts of arsenic and antimony(III) with the (±)tartrate anion, the threo-monomethyl and the (±) dimethyl derivatives.[428] The data point to the presence of M_2L_2 dimers with the dd- and ℓℓ-forms more stable than the dℓ-form; mixed arsenic-antimony complexes were observed.

It has now been possible to stabilise the dimethylarsinous acid molecule, Me_2AsOH, in complexes such as $CpMoCl(CO)_2AsMe_2OH$ and $BrMn(CO)_4AsMe_2OH$, by alkaline hydrolysis of the respective complexes containing coordinated $AsMe_2Cl$.[429]

Infinite $(HAsO_4)_n^{n-}$ chains are present in the solid state structure of the diarsenite, $K\ HAs_2O_4 \cdot \frac{1}{2}H_2O$.[430] Each arsenic atom is in three fold coordination to oxygen with non-bridging As-O distances of 1.684 and 1.719Å; bridging distances are 1.815 and 1.770Å. The As-O-As angle is 125.0°. There is no evidence for the presence of H-As bonds and it is thought probable that the hydrogen atom is statistically associated with both non-bridging oxygens.

A crystal structure for the spiro-benzoxazarsoline (135) shows a basically trigonal bipyramidal arrangement about arsenic with



(135)

distances to the axial oxygen atoms of 1.860 and 1.893Å.[431] The O-As-O angle is 169.6° and the equatorial N-As-N and the two C-As-N angles are respectively 125.9, 118.9 and 115.2°.

Low enthalpies and highly negative entropies of activation have been observed for exchange reactions between arsenic(V) triesters and alcohols by ^1H n.m.r. line broadening and deuterium labelling techniques.[432] These data are rationalised on the basis of an associative mechanism involving at least one mole of each reactant with a five coordinate arsenic atom in the transition state.

A mixed species, $AsSbO_4$, is the product when a 1:1 mixture of $As_2O_5.^5/3H_2O$ and Sb_2O_3 is heated.[433] The compound contains an infinite layer structure with tetrahedral coordination about arsenic (As-O ca. 1.68Å) and irregular coordination by four oxygens about antimony (Sb-O 1.98-2.17Å) consistent with stereochemical activity of the antimony lone pair. A new compound containing the previously unknown cyclotetraarsenate ion has been isolated from a high temperature, high pressure reaction between chromium hydroxide and As_2O_5.[434] Single crystal X-ray data give its formula as $Cr_2H_2(As_2O_7)(As_4O_{12})$; some important parameters are bridging As-O distances of 1.74 and 1.73Å respectively for the di- and tetraarsenate and terminal distances of 1.637 and 1.665Å respectively. The diarsenate anion has an eclipsed conformation with the bridge As-O-As angle of 137.4°; bridging As-O-As angles in the tetraarsenate are ca. 129°.

A new cadmium orthoarsenate $CdH_{10}(AsO_4)_4$ has a structure based on chains of CdO_6 octahedra and AsO_4 tetrahedra linked by hydrogen bonds.[435] A thortveitite structure has been found for $Ca_2As_2O_7$.[436] Three corner sharing AsO_4 tetrahedra are present in the structure of $K_5As_3O_{10}$ with mean terminal and bridging As-O distances of 1.65 and 1.78Å respectively.[437] The bridge As-O-As angles are 131.4 and 134.9° but a major feature of the structure is the strong folding of the anion so that the As-As-As angle is 105°. This should be compared with a value of 173° for the P-P-P angle in the corresponding triphosphate.

I.r. spectra have been reported for the halogeno-arsenic apatites, $M_5(AsO_4)_3X$ where M=Ca, Sr, Ba or Pb and X=F, Cl or Br.[438] Metal ion exchange on stannic arsenate has been investigated.[439]

5.3.6 Bonds to Sulphur or Selenium

The As-S and As-Se phase systems have been investigated by differential scanning calorimetry as have the transitions between different modifications of As_4S_4, As_4S_3 and As_4Se_3;[440] thermodynamic data are reported.

Arsenic(III) complexes, i.e. $As(S_2C{\cdot}C_6H_4X)_3$ where X=Cl, Me or COPh, have been isolated from reactions between arsenic triiodide and the tetraalkylammonium salt of the appropriate thiocarboxylic acid.[441]

5.4 ANTIMONY

5.4.1 Antimonides and Bonds to Carbon

The compound previously described as Ca_2Sb has been shown by X-ray and neutron diffraction to be, in fact, Ca_4Sb_2O which has a K_2NiF_4 type structure.[442]

Reactions of R_2SbBr, where R=i-Pr or Bu, with magnesium lead to distibines R_2SbSbR_2, while black solids analysing as $(RSb)_n$ are the products from similar reactions with the dibromides $RSbBr_2$.[443] Related reactions of dialkyliodostibines with the metal, but in the presence of Me_3SiCl and THF, give products which result from cleavage of solvent molecules as shown in equation (65).[444] Polymeric products are obtained, equation (66), when nickel

$$R_2SbI + Me_3SiCl + C_4H_8O + Mg \longrightarrow Me_3SiO(CH_2)_4SbR_2 + MgClI \quad ...(65)$$

$$Ni(CO)_4 + (Ph_2Sb)_2MMe_2 \longrightarrow {}^1/_n[Ph_2SbMMe_2SbPh_2Ni(CO)_2]_n + 2CO$$

M=C, Ge or Sn ...(66)

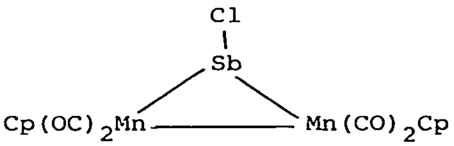
carbonyl reacts with the potentially bidentate antimony ligands

$(Ph_2Sb)_2MMe_2$,[445] but the corresponding reaction between $Cr(CO)_5.THF$ and the tin ligand gives a dinuclear complex, $Me_2Sn[SbPh_2Cr(CO)_5]_2$.

5.4.2 Bonds to Halogens

The structures of two mixed anionic antimony(III) fluorides have been determined. In the 1:1 compound obtained by crystallisation of sodium sulphate and antimony trifluoride from aqueous solution, the antimony shows mono-capped octahedral coordination with bonds to two oxygens of a sulphate group (2.484Å) and a longer Sb···F interaction at 2.972Å.[446] A compound formulated as $Na_3H(C_2O_4)_2SbOF.-H_2O$ has been isolated from a 2:3 mixture of the trifluoride and sodium oxalate in water.[447] X-ray diffraction reveals the presence of $SbOF(C_2O_4)_2^{4-}$ anions in which the antimony is surrounded by a distorted pentagon of oxygen atoms from two chelating oxalate groups (Sb-O 2.33, 2.44 and 2.22, 2.40Å) and a fifth oxygen at 2.06Å. The fluorine atom occupies an axial position (Sb-F 1.93Å) with pentagonal bipyramidal coordination being completed by the antimony lone pair in the *trans* axial site.

Treatment of antimony trichloride with $Cp(CO)_2Mn.THF$ in THF solution leads to partial dehalogenation and, depending on reaction conditions, compounds (136) and (137) can be isolated.[448]



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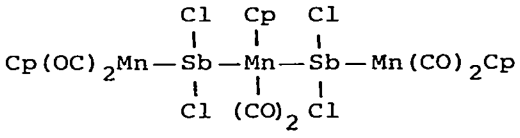


$$Cp(OC)_2Mn-\overset{Cl}{\underset{Cl}{Sb}}-\overset{Cp}{\underset{(CO)_2}{Mn}}-\overset{Cl}{\underset{Cl}{Sb}}-Mn(CO)_2Cp$$

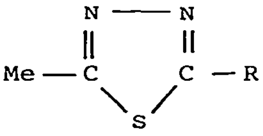
(137)

X-ray structures have been obtained for both compounds.

The 1:1 adducts between antimony trichloride and diphenylamine[449] and 2,2'-bipyridyl[450] have been investigated by X-ray methods. Both contain discrete molecules and in the former the antimony atom is directed toward one of the phenyl groups of the amine (Sb···Ph 3.13Å). Although the $SbCl_3$ unit is pyramidal there is a weak intermolecular Sb···Cl interaction (3.53Å). The chlorine environment about antimony in the second compound is very similar (three Sb-Cl distances between 2.505 and 2.588 and one at 3.34Å) and distorted octahedral coordination is completed by the two nitrogen atoms of the ligand at 2.245 and 2.317Å.

Structures are also reported for $(PhNH_3)SbCl_4$ and $(PhNH_3)_2SbCl_5$, two congruently melting compounds from the $SbCl_3$-aniline hydrochloride phase system.[451] In both cases there is octahedral coordination about antimony through chlorine bridging. The tetrachloroantimonate contains three antimony atoms in the asymmetric unit, each forming four short and two longer Sb-Cl bonds. In the $SbCl_5^{2-}$ species, there are in contrast five short (2.394 - 2.845Å) and one long (3.192Å) Sb-Cl distances. There is again a chlorine bridged structure in the 4,4'-bipyridinium salt of the $SbCl_5^{2-}$ anion, but here a doubly bridged dimer is formed. As in the anilinium compound there are again five short (2.42 - 2.75Å) bonds and one longer (3.19Å) one.[452]

Antimony and bismuth halide complexes have been reported with the thiadiazole ligands (138, R=Me or NH_2).[453] From ^{121}Sb Mössbauer data on a series of heterocyclic base salts of either the



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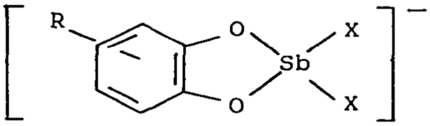
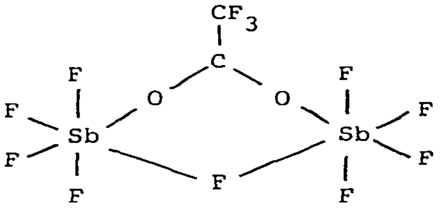


(139, R=H, Cl or Br
X=Cl or Br).

$SbBr_4^-$ or the benzene-1,2-diolate anions (139), the chemical isomer shift is found to be a function of the number and length of the short bonds to antimony rather than a function of the total number of bonding interactions.[454] In the diolate complexes, the shift is dominated by the presence of two short Sb-O bonds.

A new investigation into the i.r. spectra of HF-SbF_5 solutions points to $H_3F_2^+$ being the dominant cation in solutions up to 40 mol% SbF_5.[455] At low concentrations the anion is $SbCl_6^-$ while between 20 and 40 mol% the spectra show strong similarities to that of $CsSb_2F_{11}$; at higher concentrations there is evidence for the formation of more highly polymerised $Sb_nF_{5n+1}^-$ ions.

Two compounds, both containing bridging trifluoroacetate groups, have been isolated during an investigation of the SbF_5-trifluoroacetic anhydride reaction.[456] The initial product (140) can be converted into (141) by thermal decomposition but the change can also be achieved in a step-wise fashion by treatment of (140) with trifluoroacetic anhydride. Full crystal structures have been determined for both compounds showing that the antimony atoms are



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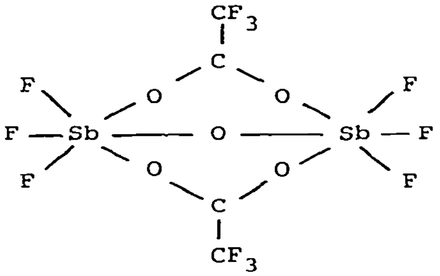


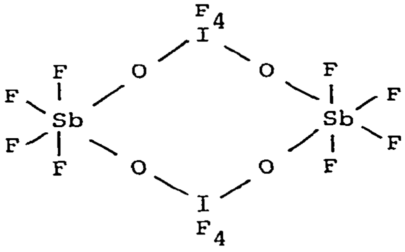
(141)

in distorted octahedral coordination.

A reexamination of the reaction between SbF_5 and AsF_3 in the presence of a small amount of bromine shows the reaction products are the adduct, $SbF_3.SbF_5$, and AsF_5.[457] Although water has been previously suggested as a catalytic agent, these recent experiments can be interpreted as proceeding via formation of small amounts of BrF according to equation (67).

$$2SbF_5 + Br_2 \rightleftharpoons 2BrF + SbF_3.SbF_5 \qquad \ldots(67)$$

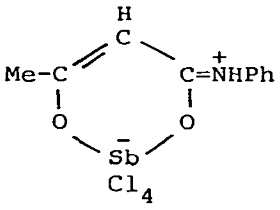
An oxygen bridged dimeric structure (142) in which both antimony and iodine atoms are in distorted octahedral coordination has been revealed by X-ray crystallography for the 1:1 addition compound between SbF_5 and IO_2F_3.[458] The oxygen bridges are asymmetrical, Sb-O 2.05, I-O 1.80Å, I-O-Sb 134.4°, and these data are interpreted in terms of a contribution from an ionic $SbF_4^+IO_2F_4^-$ structure. 1:2 addition compounds are formed by both α- and β-UF_5 and antimony



(142)

pentafluoride from which the 1:1 adducts can be isolated by thermal decomposition.[459] The former contain rings of alternating UF_8 and SbF_6 polyhedra interconnected further by other SbF_6 groups to give a structure similar in some respects to that of $UOF_5.2SbF_5$.

Adduct formation between $SbCl_5$ and acetoacetanilide occurs at the C:O groups to give both 1:1 and 2:1 complexes.[460] Loss of HCl occurs on heating in 1,2-dichloro-ethane to give the heterocycles (143) and (144).[460] With p-benzoquinone in 1,2-dichloroethane, the final product on treatment with $SbCl_5$ is the 2,3,5,6-tetrachloride but both the 2,5- and 2,6-dichlorides were identified as intermediates.[461] The methyl esters of both methyl- and trifluoromethylsulphonic acids react with $SbCl_5$ to eliminate methyl chloride and form the dimers $(RSO_3SbCl_4)_2$ where R=Me or CF_3.[462] On the other hand, if dimethyl sulphate is a reactant the products are either $(MeOSO_3SbCl_4)_2$ or the polymer $[(Cl_4Sb)_2SO_4]_n$ depending on the relative amounts of the reactants.[462] An orange-yellow addition compound $OsO_4.2SbCl_5$ can be prepared and a structure containing Os-O-Sb bridges is proposed on the basis of vibrational data.[463]



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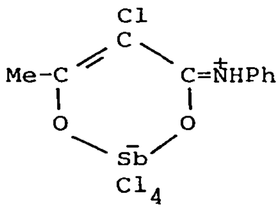


(144)

A major structural feature in $HSbCl_6.3H_2O$ is the centrosymmetric $H_{14}O_6^{2+}$ cation formed by head to tail linking of two $H_5O_2^+$ units by two further water molecules.[464] The $SbCl_6^-$ anion is close to octahedral (Sb-Cl 2.363 - 2.375Å, Cl-Sb-Cl 89.3 - 90.7°).

5.4.3 Bonds to Oxygen

Structural studies have been reported on three antimony(III) tricarboxylates.[465,466] The tris(monothioacetate), which can be obtained as a water stable species from antimony(III) oxide and thioacetic acid, has a structure which is very similar to that of the triacetate, an extremely water sensitive compound.[465] In both cases the antimony forms three strong primary bonds-to oxygen (Sb-O 2.06Å) in the acetate and sulphur (Sb-S 2.47Å) in the thioacetate. There are further weak, intramolecular interactions in each case (Sb-O 2.596-2.775 for the acetate and 2.745-2.918Å for the thioacetate) and finally one ligand in each compound also serves as a bridging group, linking the molecules into polymeric chains. Coordination about antimony in both cases is best described in terms of a distorted dodecahedron. In the tris(trifluoroacetate) $Sb(O_2CCF_3)_3$, which has crystallographic C_3 symmetry, there is again strong Sb-O primary bonding (Sb-O 2.043Å, O-Sb-O 84.9°) and weaker intramolecular Sb···O=C interactions, 2.869Å.[466] Intermolecular Sb···O interactions at 3.039Å complete the oxygen polyhedron about antimony.

In the structure of diphenylantimony(III) acetate, on the other hand, the acetate group serves as an asymmetric bridge between antimony atoms giving polymeric chains.[467] The asymmetric unit contains two independent antimony atoms with Sb-O distances of 2.137 and 2.592 to Sb(1) and 2.137 and 2.513Å to Sb(2). Coordination about the heavy atom is best described as pseudo-trigonal bipyramidal with oxygen atoms in the axial positions (O-Sb-O ca. 168°) and two phenyl groups (C-Sb-C ca. 95°) and the antimony lone pair in equatorial positions.

Mass spectrometric data have been obtained for compounds in the series $Sb(OEt)_{3-n}Cl_n$, where n=0-3, and full X-ray structures have been published for the two mixed ligand species $Sb(OEt)_2Cl$ and $Sb(OEt)Cl_2$.[468] In both cases the antimony is in distorted octahedral coordination with, for $Sb(OEt)_2Cl$, the following distances to antimony Sb-Cl 2.494, Sb-O 1.966 2.026, Sb···Cl 3.538 and Sb···O 2.400 2.956Å.

Mono thio-β-diketone complexes of antimony(III) can be isolated as hydrolytically unstable compounds by treating $Sb(i\text{-propoxide})_3$ with the ligand or by reactions between $SbCl_3$ and the sodium salt of the ligand.[469]

The structure is reported for a further member in the Sb(III)-sulphate series of compounds.[470] Although formulated as $Sb_2O_3.2SO_3.2H_2O$, the structure points to $Sb_4O_2(OH)(SO_4)_4(H_5O_2).H_2O$ as being the correct representation. Antimony is present in two different coordination polyhedra - a distorted SbO_4E pseudo trigonal bipyramid ($Sb\text{-}O_{eq}$ 1.97, 2.10; $Sb\text{-}O_{ax}$ 2.18, 2.35Å) and in a unit consisting of two octahedral SbO_5E units sharing an axial-equatorial edge.

Single crystals of Na_3SbO_3 and Na_3BiO_3 have been obtained for the first time and are isostructural.[471] The compounds, which crystallise in the cubic space group $F\bar{4}3m$, have a structure based on that of NaCl with systematic vacancies in the anion sub-lattice. There are three Sb-O and Bi-O distances of 1.890 and 2.054Å respectively, leading to isolated MO_3^{3-} units with C_{3v} symmetry. A new tungstoantimonate $[M(Sb_3O_7)_2(SbW_7O_{24})_3]^{(19-n)-}$ has been prepared by treating the 9-tungstoantimonate $(SbW_9O_{33}H)^{8-}$ with Sb^{3+}.[472]

^{121}Sb Mössbauer data for compounds in the two series $R_2Sb(OMe)_3$ and $R_2Sb(O_2CMe)_3$ have been interpreted as showing octahedrally coordinated antimony; in the first compounds this is achieved by dimer formation by methoxy bridging while in the latter, one acetate group is bidentate.[473] Data were also obtained for dialkylstibinic acids $R_2SbO(OH)$ which are considered to indicate tetrahedral coordination. This is in contrast to the distorted trigonal bipyramidal arrangement suggested from Mössbauer measurements on the corresponding diarylstibinic acids.

Ph_3SbBr_2 and $Ph_3Sb(OMe)_2$ on reaction with the sodium salts of β-diketones and the free diketones respectively give compounds of the type $Ph_3SbBr(R^1COCHCOR^2)$ and $Ph_3Sb(OMe)(R^1COCHCOR^2)$.[474] Molecular weight, i.r. and n.m.r. data suggest that the ligands behave as bidentate group and the possibility of isomerism is discussed.

The reaction between Ph_3SbCl_2 and catechol in the presence of ammonia yields a catecholate which is formulated as $Ph_3Sb(O_2C_6H_4).H_2O.Ph_3Sb(O_2C_6H_4)$ according to an X-ray structure determination.[475] The structure shown in Figure 11 contains Sb(1) in distorted octahedral coordination by three phenyl groups, two

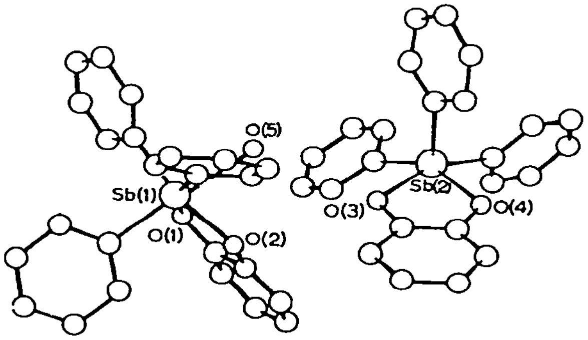


Figure 11. Structure of $(Ph_3SbO_2C_6H_4)_2.H_2O$ (reproduced by permission from J. Am. Chem. Soc., 102(1980)628).

oxygen atoms from the chelating catechol group and a third oxygen atom from an adventitious water molecule. Coordination about the second antimony atom is square pyramidal with the apical Sb-C distance (2.099Å) being, as expected for this arrangement, slightly shorter than the bsal Sb-C bonds (2.125 and 2.143Å). This is only the second antimony(V) compound for which there is X-ray confirmation of square pyramidal geometry; distortion from the more usual trigonal bipyramidal geometry is thought to be a consequence of the presence of a dioxo chelating group.

Three new compounds, $K_4Sb_2O_7$, $Rb_4Sb_2O_7$ and $CsSbO_3$, have been isolated as products from solid state reactions between Sb_2O_5 and the appropriate M_3SbO_4.[476] The structure of KTi_3SbO_9 has been determined.[477]

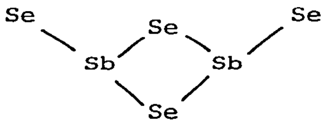
Exchange systems on crystalline antimonate(V) acid recently investigated include those between H^+ and NH_4^+ or $MeNH_3^+$ [478] and a series involving transition metal ions.[479]

5.4.4 Bonds to Sulphur, Selenium or Tellurium

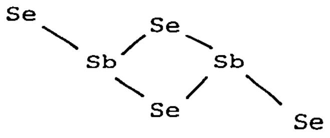
Coordination about the antimony atom in the tris(diphenyldithio phosphinate $Sb(S_2PPh_2)_3$ is distorted pentagonal pyramidal,[480] and similar to that observed previously for the anionic oxalate $Sb(OX)_3^{3-}$. The antimony-sulphur distance to the apical atom (2.456Å) is substantially shorter than the other two, primary Sb-S bonds (2.591 and 2.598Å) and the three remaining distances are 2.923, 2.978 and 3.187Å. This unusual coordination polyhedron suggests that the vacant axial position might accommodate the antimony lone pairs. In contrast is the distorted octahedral structure with three short (2.58 - 2.63Å) and three long (2.78 - 2.86Å) Sb-S bonds recently reported for the related dithiophosphate $Sb[S_2P(OEt)_2]_3$, where the lone pair occupies a capping position.[481] Asymmetrically bidentate ligands are also present in the structure of tris(1-pyrrolodinecarbodithioato)antimony(III).[482] The Sb-S distances range between 2.484 and 2.848Å and, as in the case above, there is a place in the coordination sphere for the antimony lone pair.

Reactions between the antimony mercaptides, $Ph_4SbSC_6H_4X$, and electrophiles such as chloromethylmethyl sulphide, allyl halides, sulphenyl halides, halogens, acyl halides, etc. are rapid and complete halogen-mercaptide exchange takes place.[483] The thermal decomposition of these mercaptides has also been investigated showing that a major part of the reaction occurs via free radical processes.[484] Among the products are Ph_3Sb, Ph_2, PhH and XC_6H_4SPh.

Structural data have been obtained recently for a new selenoantimonate $Ba_4Sb_4Se_{11}$ obtained from a reaction at 600°C between barium acetate, antimony and selenium in a 1:1:10 ratio.[485] The solid contains in addition to the Se_2^{2-} unit, a pseudo-tetrahedral $SbSe_3$ group with a mean Sb-S distance of 2.59Å and S-Sb-S angles ca. 102°, and both the <u>cis</u> and <u>trans</u> forms (<u>145</u>) and (<u>146</u>) which would arise if two $SbSe_3$ pyramids shared a common Se···Se edge.



(<u>145</u>)



(<u>146</u>)

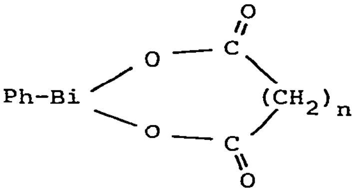
The new phase $Sn_4Sb_6S_{13}$ isolated from the $SnS-Sb_2S_3$ system contains ribbon-like $[(Sn/Sb)_5S_7]_n$ sheets,[486] while in the compounds $BaSbTe_3$ and $BaBiSe_3$, recently prepared by direct synthesis from the elements, the structural units are $SbTe_6$ or $BiSe_6$ octahedra which are connected by edge sharing into four unit strings.[487]

A stoichiometric mixture of SnS and SbI_3 on heating to 650°C for 5 days yields the new sulphoiodide $Sn_2SbS_2I_3$,[488] which has a structure in which antimony atoms link together parallel ribbon-like $(Sn_2S_2I_2)_n$ units to give bicapped trigonal prismatic coordination about antimony.

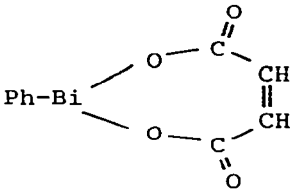
5.5 BISMUTH

A new ternary bismuthide, $CaMnBi_2$ can be obtained from the elements at 1620K which contains square pyramidal $BiMn_4$ units inter-connected to give two dimensional sheets (Bi-Mn 2.874Å).[489] The sheets are separated by double layers of calcium atoms between which there are further bismuth atoms in the form of a square net (Bi-Bi 3.182Å). The structure is related to that of $SrZnSb_2$.

Two molecules of benzene are lost per mole of triphenyl bismuth in reactions with aliphatic dicarboxylic acids in acetone solution to give compounds represented by the formulae (<u>147</u>) and (<u>148</u>).[490] Alkyldiphenylbismuthines, Ph_2BiR where R=Me, n-Bu or



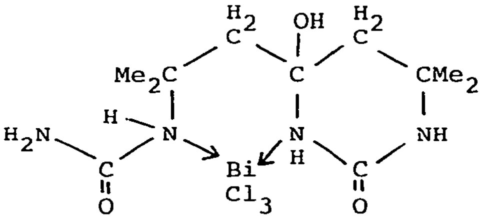
(147, n=0-2)



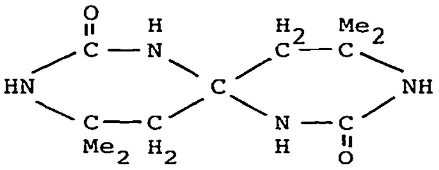
(148)

n-C_6H_{13}, have been synthesised from Ph_2BiCl and the appropriate alkyl lithium as thermally stable but oxygen sensitive compounds.[491] The authors also showed that it was possible to introduce the Ph_2Bi group into organic compounds by use of Ph_2BiNa or Ph_2BiCH_2Li and that it behaved as a 'mobile functional group'.

Bismuth trichloride reacts with N,N'-bis(trimethylsilyl)urea to give (149), which on further treatment with acetone and DMF is



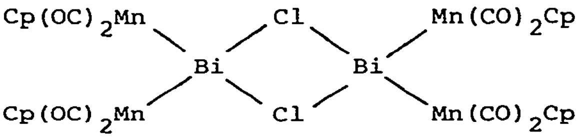
(149)



(150)

converted into (150) with expulsion of $BiCl_3$.[492] Bismuth trichloride is partially dehalogenated in reactions with $Cp(CO)_2Mn(THF)$ to produce a compound with the stoichiometry $[Cp(CO)_2Mn]_2BiCl$.[493] An X-ray structure showed the presence of dimeric molecules (151) with an asymmetric double chloride bridging system (Bi-Cl 2.798, 2.895Å).

$Cs_3Bi_2Cl_9$ has been shown to exist in two forms with a transition



(151)

temperature of 373°C.[494] The low temperature form which has the β-$Cs_3Sb_2Cl_9$ structure differs from the high temperature modification in the sequence of the Cs-Cl sheets and in the occupation by Bi^{3+} of the octahedral sites. Structures are also reported for two bismuth bromide species $[Sr(H_2O)_8]_2Bi_2Br_{10}$[495] and $Na_7(BiBr_6)(Bi_2Br_{10}).18H_2O$,[496] both obtained by reactions between bismuth hydroxide, the appropriate metal carbonate and dilute hydrobromic acid. The anion in the former is formed from edge sharing by two $BiBr_6$ octahedra to give terminal Bi-Br distances of 2.72 and 2.84 and bridging Bi-Br distances of 3.05Å. The second compound contains, in addition to the same Bi_2Br_{10} unit, octahedral $BiBr_6$ units with Bi-Br distances falling between 2.824 and 2.884Å.

Chloro- and bromo-bismuthates BiX_4^-, $Bi_2X_9^{3-}$ and BiX_6^{3-} have been investigated by Bi, and Br or Cl n.q.r. spectroscopy.[497] The data for diethylammonium salts of BiX_6^{3-} show a single set of halogen resonances in agreement with the presence of only terminal halogen atoms, but for $(EtNH_3)_3BiCl_6$, for example, the data indicate the presence of either bridging or at least highly associated halogen atoms. Changes in the far i.r. and Raman spectra of similar bromo- and iodo-bismuthates are also sometimes observed but differentiation between the different stoichiometries is possible on the basis of the spectra.[498] The ranges observed for the Bi-Br and Bi-I frequencies are summarised in Table 1.

Table 1 Bi-X Stretching Frequencies (cm^{-1})

X	type	BiX_6^{3-}	BiX_5^{2-}	BiX_4^-	$Bi_2X_9^{3-}$
Br	terminal	123-158	142-180	173-189	145-180
	bridge		108-131	110-134	99-123
I	terminal	105-139		130-143	110-138
	bridge			95-118	80-99

An investigation of the fluoride ion acceptor properties of bismuth pentafluoride has led to the isolation of the new noble gas fluoride adducts $XeF_4(BiF_5)_n$ and $XeF_2(BiF_5)_n$, where n=1 or 2, $2XeF_2.BiF_5$ and $KrF_2.BiF_5$.[499] Although the Raman data can be interpreted to a first approximation in terms of ionic structures, there is evidence for double fluorine bridges between 'cations' and 'anions' implying substantial covalent character. BiF_5 is therefore considered to be a much weaker Lewis acid than SbF_5.

The $[Ph_3Bi(MoO_4)_2]^{2-}$ ion and a polymeric species $(Ph_3BiMoO_4)_n$ have been isolated from reactions between triphenylbismuth dibromide and MoO_4^{2-}.[500] From ^{17}O and ^{13}C n.m.r. spectroscopy of the tetra(n-butyl)ammonium salt a trigonal bipyramidally coordinated bismuth atom is suggested with equatorial phenyl groups and unidentate MoO_4^{2-} anions in the axial positions.

X-ray scattering data from solutions of basic bismuth(III) perchlorate are consistent with the presence of the same $Bi_6O_4(OH)_4^{6+}$ unit that is present in the solid state structures of $Bi_6O_4(OH)_4(ClO_4)_6.7H_2O$ and $Bi_6O_4(OH)_4(NO_3)_6.H_2O$.[501] Oxygen atoms are situated above the octahedral faces of a Bi_6 unit in which the Bi-Bi distance is 3.69, and $Bi-O^{2-}$ and $Bi-OH^-$ distances are 2.19 and 2.37Å respectively.

I.r. and mass spectrometry have been used to characterise the triformate, $Bi(O_2CH)_3$, which on heating is converted successively to $BiO(O_2CH)$ and Bi_2O_3 at 157 and 345°C respectively.[502] A number of new higher bismuth oxides has been investigated as the products of reactions in which Bi^{3+} was oxidised with ammoniacol hydrogen peroxide, Na_2O_2 and peroxodisulphate or by hydrolysis of bismuth(V)ates.[503] In addition to BiO_2, four different forms of $BiO_{2.5}$ were identified by thermal and X-ray methods.

The $Bi_2O_3-SeO_2-H_2O$ system at 100°C has been examined and the crystallisation fields and conditions for the formation of $Bi_2(SeO_3)_3$ and $Bi_2(SeO_3)_3.H_2SeO_3$ defined.[504] The products from metathesis reactions between sodium alkyl xanthates and diphenylbismuth bromide are $Ph_2BiSC(S)OR$, where R=Me, Et, n-Pr, i-Pr, n-Bu and i-Bu.[505] A structure determination for the i-propyl derivative showed pyramidal coordination about bismuth (Bi-C 2.26, 2.23, Bi-S 2.66Å, with angles at bismuth of 96.5, 90.9 and 84.9°); the coordination is increased by a sulphur atom from a symmetry related molecule at 3.23Å from bismuth.

The structure of $HgBr_2S_4$ contains two bismuth atoms in the asymmetric unit, the first in distorted octahedral coordination with Bi-S distances lying between 2.63 and 3.09Å and the second at the centre of a distorted mono-capped trigonal prism (Bi-S 2.63 - 3.34Å).[506] In $Bi_3In_5S_{12}$, the third ternary compound observed in the $In_2S_3-Bi_2S_3$ system, two of the bismuth atoms are in eight-fold (distorted bicapped trigonal prismatic) coordination, while the third has monocapped trigonal prismatic coordination similar to that in the mercury compound above.[507]

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