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Chapter 5

ELEMENTS OF GROUP 5

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5.1 NITROGEN

5.1.1 Bonds to Hydrogen

Nicholls's review,[1] "Inorganic Chemistry in Liquid Ammonia" surveys the literature up to the end of 1977 and is the first book in English devoted to this subject since Franklin's account published in 1935. The same author, along with his co-workers, has pointed out the value of ammonium cyanide as a reagent for the preparation of cyanometallates in liquid ammonia :[2] excess of this reagent in an ammonia-soluble product can readily be removed by sublimation at room temperature. A study of the NH_4CN-NH_3 system indicates the existence of two ammoniates, $NH_4CN.4NH_3$ and $3NH_3$. A new absorption band associated with the ammoniated electron has been observed at 245nm, $\varepsilon(20^{\circ}C)$ $950\ell mol^{-1}cm^{-1}$, by Belloni et al.[3] In order to avoid interference from decomposition products in the dilute solutions the spectra of NH_3 and ND_3, 210-240nm, and of the amide ion, 230-280nm, were also recorded.

Ammonia is the only product of the reaction between H_2 and N_2 (total pressure < 5 torr) in a microwave discharge (2450MHz).[4] The conversion of H_2 increases up to 100% for high N_2 concentrations : under these conditions the yield of NH_3 is of the order of 10^{-3} mole kwh^{-1}. The presence of a Pd catalyst enhances the yield. After photolysis at wavelengths in the $\tilde{A}$-$\tilde{X}$ region ammonia-d_3 has been shown to produce ^{15}N-enriched N_2 ; the maximum enrichment factor was reported to be 4.8.[5] Flash photolysis of NH_3 in the presence of O_2 has been studied using the intracavity laser spectroscopy technique.[6] The reaction between NH_2 and O_2 was shown to be less significant than that between NH_2 and HO_2. The pyrolysis of NH_3 behind reflected shock waves at temperatures in the range 2500-3000K has been studied mass spectrometrically.[7] The results are consistent with a chain mechanism in which NH_3 is removed by unimolecular decomposition and by attack from H, NH and NH_2. The evidence was consistent with the participation of NH_2 in the reaction which produces N_2.

Ammonia polymers, $(NH_3)_n$, n=2-6, van der Waals molecules produced by beam expansion techniques, have been investigated by the electric deflection method.[8] The results indicate that the dimer is polar whereas the higher polymers are non-polar ; the authors infer that these polymers have cyclic, hydrogen-bonded structures. The absolute proton affinity of NH_3 has been determined by the molecular-beam photoionization method.[9] The result, 203.6±1.3kcal mol^{-1} at 298K is in good agreement with that determined by ion cyclotron resonance experiments. The energies of proton solvation by more than one NH_3 have been determined from the appearance potentials of fragments from larger cluster ions. These energies (kcal $mole^{-1}$), summarized in equations (1) and (2), are considerably smaller than previously reported values.

$$NH_3.NH_4^+ \rightleftharpoons NH_4^+ + NH_3 \quad ; \quad \Delta H_0^o = 13.8\pm1.4 \qquad \ldots(1)$$

$$(NH_3)_2.NH_4^+ \rightleftharpoons NH_3.NH_4^+ + NH_3 \quad ; \quad \Delta H_0^o = 6.4\pm1.6 \qquad \ldots(2)$$

An inexpensive NH_4^+-sensing heterogeneous membrane electrode, consisting of ammonium phosphomolybdate incorporated into a methacrylate matrix, has been described.[10] In a continued study of the i.r. spectra of the ammonium ion in crystals the NH_3D^+ ion has been used as the probe ion.[11] This paper discusses the problem of the fundamental vibrational frequencies of the "free" ammonium ion and reviews the criteria of hydrogen bonding in ammonium halides.

The chloride ion-catalysed rate of oxidation of NH_4^+ in nitric acid mixtures at 100°C can be expressed by the rate equation (3),

$$-d[NH_4^+]/dt = k[H^+]^m[NO_3^-]^n[Cl^-]^p[NH_4^+] \qquad \ldots(3)$$

$m = 2.43$, $n = 3.10$, and $p = 1.30$.[12] The proposed reaction mechanism involves the production of HOCl and NH_2Cl, and is thus consistent with the lack of catalytic activity of fluoride or bromide ions. The oxidation of NH_3 coordinated to osmium has been shown[13] to proceed to the μ-dinitrogen binuclear species. $[(Os(NH_3)_4CO)_2N_2]^{4+}$, almost quantitatively according to equation (4), when Ce^{4+} is the oxidant in acidic solution. The yields of

$$2[Os(NH_3)_5CO]^{2+} \longrightarrow [(Os(NH_3)_4CO)_2N_2]^{4+} + 6H^+ + 6e^- \qquad \ldots(4)$$

the same binuclear cation are also high by electrolytic or persulphate oxidation. The thermal decomposition of a series of nitro ammine complexes of Co(III) has been investigated by gas chromatography.[14] All compounds decompose in two or three stages. In the first stage (ca. 140-240°C) all complexes evolve N_2 with

NH_3 and/or NO. Mainly NH_3 appears at the second stage (210-300°C) and NO at the third stage (275-350°C). ^{15}N FT n.m.r. spectroscopic studies of $[Co(NH_3)_5(^{15}NH_3)]^{3+}$ and $[Co(^{15}NH_2CH_2CH_2{}^{15}NH_2)_3]^{3+}$ have been carried out to determine $^1J(^{59}Co - {}^{15}N)$ and the spin-lattice relaxation time $T_1(^{59}Co)$, 62.5 and 63.8 Hz, 38 and 13 msec, respectively.[15]

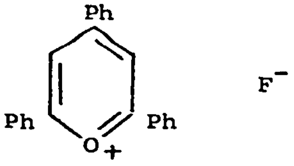
5.1.2 Bonds to Boron

The molecular structure of $Me_3N.BF_3$ in the gaseous phase has been determined from electron diffraction and vibrational-rotational spectroscopic data.[16] The final parameters differ but little from those obtained from a preliminary analysis of diffraction data. The height of the potential barrier to internal rotation about the B-N bond is 4.3kcal mol^{-1}, which is higher than that in $H_3P.BH_3$ (2.47 kcal mol^{-1}) but comparable with that in Cl_3CSiCl_3. The data also reveal that the C-N bond is longer in the $Me_3N.BF_3$ adduct in the gaseous phase than in the solid state.

5.1.3 Bonds to Carbon

Trifluoromethylamine, CF_3NH_2, has been prepared from the corresponding N-chloro compound, CF_3NCl_2, by reaction with HCl at -78°C.[17] The compound is unstable with respect to loss of HF and is a weaker base than quinoline.

A novel and convenient method for the transformation of tertiary amines to secondary amines has been described.[18] The reaction with phenylmethane and benzenethiolates in the presence of a palladium or ruthenium catalyst also produces the alkyl thiolate. Thus Bu_2NMe is converted to BuNHMe (69%) and $BuSCH_2Ph$. Primary alkyl and benzyl amines may be converted into the corresponding fluorides.[19] The process involves the reaction with 2,4,6-triphenylpyrylium fluoride (1) to form the corresponding pyridinium fluoride, which is then thermolysed



(1)

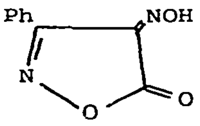
(100-130°C) to generate the alkyl or benzyl fluoride (yield >60%).

The reaction of chlorodimethylamine with excess methyl iodide proceeds according to equation (5).[20] Compound (2) precipitates

$$2Me_2NCl \; + \; 2MeI \longrightarrow \underset{(2)}{NMe_4[Me_2N(ICl)_2]} \qquad \ldots(5)$$

as a fine yellow solid, whose structure was reported in last year's Review.[21] A feature of interest is that the V-shaped anion can be considered as a pseudopolyhalide ion with Me_2N as a pseudohalogen. The use of the tridodecylammonium ion, A^+, as a lipophilic phase transfer reagent in inorganic chemistry has been described by Shukla and Preetz,[22] who have prepared salts of mixed hexahaloosmate(IV) anions, such as $OsFCl_4I^-$, by the exchange reactions between A_2MX_6 and AY in aromatic hydrocarbon solvents. The structure of the first trialkylamine metal cluster compound, $[Os_3(CO)_9(NO)_2NMe_3]$, has been determined by X-ray crystallography;[23] the large steric requirement of the trialkylamine ligand is reflected in the long Os-N distance, 2.22Å.

Cotton et al.[24] have characterised $(n\text{-}Bu_4N)_3[Re_2(NCS)_{10}]$ crystallographically and demonstrated the presence in the anion of a solely N-bonded, bridging thiocyanato ligand. A new synthesis of pure fulminic acid has been described:[25] it is claimed to be both facile and safe, i.e. it does not involve the use of dangerously explosive metal fulminate intermediates. The method is based on the flash thermolysis of 4-substituted isoazol-5(4H)one oximes, equation (6). The fulminic acid was



$$\xrightarrow{450^{\circ}C} CO_2 \; + \; PhCN \; + \; HCNO \qquad \ldots(6)$$

shown to be free of isocyanic acid and HCN. Two homogenous hydrogenation catalysts for nitriles have been developed:[26] $[RhH(i\text{-}Pr_3P)_3]$, and the less active $[Rh_2H_2(\mu\text{-}N_2)(P(C_6H_{11})_3)_4]$ effect the hydrogenation of a number of nitriles to the corresponding primary amines. The first named catalyst was shown to function also as a dehydrogenating agent for amines.

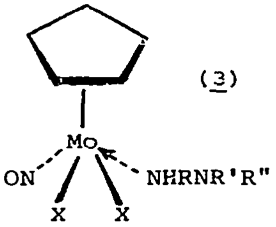
5.1.4 Bonds to Silicon

Silylphosphine, SiH_3PH_2, reacts with liquid NH_3 to form mainly PH_3, SiH_4, $(SiH_3)_2NH$ and $(SiH_3)_3N$.[27] Surprisingly there was no sign of SiH_3NH_2 as an intermediate in this reaction. Among the minor products detected were some previously uncharacterized oligomeric silazane species, $(SiH_3NH)_2SiH_2$ and $(SiH_3)_2NSiH_2NHSiH_3$; the composition of the reaction mixture was shown to be dependent on reaction time, temperature and the reactant ratio.

5.1.5 Bonds to Nitrogen

An electron diffraction study has shown that the inner-outer conformer of 1,2-dimethylhydrazine, with an estimated dihedral angle of 90°, is a major component in the gaseous phase.[28] The presence of a second conformer has now been confirmed whose dihedral angle is smaller. Sutton et al.[29] have reported the preparation and structure of a "side-on", η^2-arylhydrazido(1-) ligand, H_2NNPh, bound to a $(\eta^5\text{-}C_5H_5)_2W^+$ moiety : the W-N distances are,respectively, 2.04 and 2.16Å to the 3- and 4-coordinate nitrogen atoms. Complexes of molybdenum with aryl or alkyl hydrazines, $NHRNR^1R^2$, have been prepared and characterized by McCleverty et al.[30] These include simple hydrazine adducts, e.g. (3), hydrazido(1-) complexes, e.g. (4), and hydrazide(2-) complexes, e.g. (5). Protonation of (4) or (5) with HBF_4 gave the hydrazine adduct (6). Dichloro-6,6'-dihydrazino-2,2'-bipyridyl iron(II), (7), on exposure to O_2 (1 mol) decomposes quantitatively in the solid state to a range of iron(II) polypyridyl complexes and N_2 (2 mol), derived from the hydrazino portions of the ligand.[31] Such a decomposition has not been observed with complexes of this ligand with other metals. Iron(II) halide complexes of hydrazine and its mono- and di-methyl derivatives have been prepared by Nicholls et al.[32] A noteworthy and characteristic property of the bis-hydrazine complexes was their violent spontaneous decomposition during drying or upon standing or when exposed to air. The monoprotonated hydrazinium cation, $N_2H_5^+$, has been shown to act as a ligand in the complex $[(N_2H_5)CuCl_3]$.[33]

Photolysis of Co(III) azido complexes in aqueous or methanolic solution has been shown to give rise to azido radicals. Phenyl-



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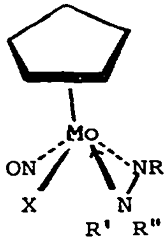

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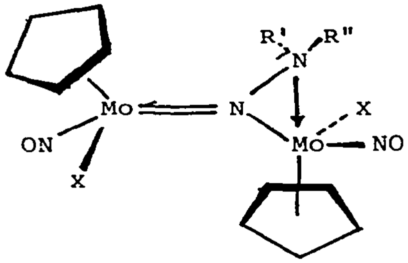

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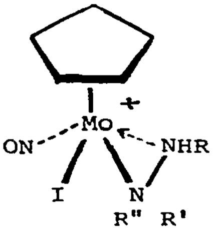

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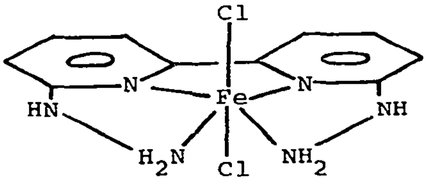


(7)

(N-tertiary butyl) nitrone or, preferably, tetramethylnitrosodurene act as spin traps and have enabled Rehorek and co-workers[34] to observe e.s.r. spectra of the azido adducts. The pulse radiolysis of aqueous hydrazine solutions in the pH range 2-13 has been studied:[35] the decay of a single transient species (observed 1ms after the pulse) has been explained in terms of the formation of triazine, N_3H_3, and its conjugate acid, $N_3H_4^+$, and base, $N_3H_2^-$ or $N_3H_4O^-$. The purification, hydrolysis and pyrolysis of 2,2-dimethyltriazanium chloride, $[Me_2N(NH_2)_2]^+Cl^-$, have been described by Sisler et al.[36] The principal alkaline hydrolysis product is the dimethylhydrazone of formaldehyde, $Me_2N{\cdot}N{=}CH_2$. The same compound is formed on pyrolysis, along with N_2 and a small amount of tetramethyl-2-tetrazene, $Me_2N{\cdot}N{=}N{\cdot}NMe_2$.

Inorganic tetrazenes of the type $(Me_3M)_2N{\cdot}N{=}N{\cdot}N(MMe_3)_2$, M = Si, Ge or Sn, have been synthesised by Wiberg and co-workers.[37] The silicon derivative is formed in almost quantitative yield by the catalytic dimerization of $(Me_3Si)_2N_2$ with SiF_4. Conversion of the silicon compound to the germanium or tin analogues was achieved by the reaction of CF_3CO_2H at low temperatures, followed by treatment with Me_3MCl or Me_3MNR_2. All three tetrazenes have planar M_4N_4 skeletons and a trans configuration. Thermolysis and photolysis of the new compounds were also investigated.

The reaction of $Ag_2N_2O_2$ with Me_3SiCl or (more safely) of $[(Me_3Si)_2NO]Li$ with SO_2Cl_2 generates bis(trimethylsilyl) hyponitrite, $Me_3SiO{\cdot}N{=}N{\cdot}OSiMe_3$.[38] This new compound is metastable up to 50°C and is thus less stable than the known tetrazene, $(Me_3Si)_2N{\cdot}N{=}N{\cdot}N(SiMe_3)_2$. The hydroxytriazene, $Me_3SiO{\cdot}N{=}N{\cdot}N(SiMe_3)_2$, is even less stable : it has been synthesised for the first time by the reaction of $[(Me_3Si)_2N{-}NSiMe_3]Li$ with, successively, RONO and Me_3SiCl. A trans configuration about the N=N link has been assumed for all three compounds.

Berner and McGarrity[39] have reported n.m.r. spectra of protonated diazomethane in HSO_3F/SO_2ClF ; the spectra at −106°C are consistent with the formation of the methyldiazonium ion, MeN_2^+ (80%) and the isomeric methylene diazonium ion, $CH_2{=}N_2H^+$ (20%). Clustering reactions of protonated dinitrogen, N_2H^+ with hydrogen molecules (equation 7) have been studied in a pulsed electron beam mass spectrometer.[40] No cluster ions larger than

$$(n-1,n) \qquad N_2H^+(H_2)_{n-1} + H_2 \rightleftharpoons N_2H^+(H_2)_n \qquad \ldots(7)$$

n = 2 were observed even at −187°C ; the enthalpy changes for the (0,1) and (1,2) reactions were −7.2 and −1.5 kcal mol^{-1} respectively.

Folkesson and Larsson have investigated some aspects of the reduction of N_2 to hydrazine by vanadium(II) in aqueous solution.[41] They have sought to identify the most effective bridging, oxygen-containing ligand in anticipation that a polynuclear complex would facilitate attack on a bidentate N_2 molecule. The highest yields of N_2H_4 were obtained using $(O_2C(CH_2)_nCO_2)^{2-}$, where n is 5 or 6. Dinitrogen uptake by VCl_3 in the presence of Li_2Np, Np = naphthalene, has been shown to be complicated by the presence of metallic lithium.[42]

^{15}N n.m.r. studies of ^{15}N-enriched complexes $[M(N_2)_2L_4]$, M = Mo or W, L = mono- or ½(bis-)tertiary phosphine, have been carried out.[43] The metal-bound nitrogen resonates at higher field than the terminal nitrogen. The two ^{15}N resonances in the relating hydrazido(2−) complexes are more widely separated (ca. 160 ppm) with the metal-bound N appearing to low field. The dinitrogen ligand in $[RhCl(N_2)(Pi\text{-}Pr_3)_2]$ has now been shown to be coordinated end-on (η^1),[44] and not side-on (η^2) as was reported in 1977. This revision is based on a -160°C single crystal X-ray structure determination and on ^{31}P and ^{15}N n.m.r. spectra. Kubota et al.[45] have isolated four new dinitrogen complexes of iridium(I); their i.r. spectroscopic study indicates that ancillary ligands influence the stretching frequencies of both CO and N_2 in the same way. The thermal decomposition of $[Ru(NH_3)_5N_2]X_2$, X = Cl, Br or I, in the solid state have been investigated.[46] It is of interest to note that an ammonia ligand is lost (165-213°C) before the N_2 ligand (243-270°C). The thermal stability of the complexes follows the general sequence, $Cl^- > Br^- > I^-$.

5.1.6 Bonds to Oxygen

Electron diffraction studies have shown that methylated derivatives of NH_2OH exist in two conformations, which differ by 180° rotation about the N-O bond.[47] This had been predicted by M.O. calculations; however, the free energy differences between the conformers, ca. 0.6 kcal mol^{-1} in the trimethyl and NO-dimethyl derivatives, is much smaller than had been predicted. Hydroxylamine itself is oxidised by nitric acid to form N_2O and nitrous acid, in proportions which are dependent on the reaction conditions.[48] Experiments with ^{15}N-enriched hydroxylamine showed that virtually all of the N_2O arises from the reaction between nitrous acid and NH_2OH. The mechanism suggested involves oxidation of unprotonated NH_2OH by N_2O_4 to form the nitroxy diradical HNO; this is then further oxidised to HNO_2, which reacts with NH_2OH to form N_2O. Definitive evidence for the nature of coordinated HNO in a transition metal complex has been obtained by Wilson and Ibers[49] for $[OsCl_2(CO)(HNO)(PPh_3)_2].\frac{1}{2}CH_2Cl_2$. The nitrosyl hydride ligand is coordinated via nitrogen, Os-N 1.92Å. The N-O bond length, 1.19Å, and the ONH angle, 99°, in the ligand are comparable with those established earlier for the thermally unstable molecule, 1.21Å and 108.5° respectively.

The reaction of silver(I) oxide with NO has been studied in the temperature range 333-473K both in flow and batch reactors.[50] The reaction products are $AgNO_3$, Ag, NO_2 and $AgNO_2$, which was shown to be the primary product at temperatures $\leqslant$353K. Alkaline earth metal peroxides have been tested as solid absorbents for the determination of nitrogen oxides in the atmosphere.[51] Nitrate ion formed in the absorber is extracted into water and determined by means of an ion-selective electrode. The equilibrium constant, enthalpy and entropy changes for the reversible reaction of NO with the edta complex of iron(II) in aqueous solution have been determined in the temperature range 38.5 to 70°C (in the absence of O_2).[52] The synthesis and solution behaviour of $[Ir(NO)(\eta^3-C_3H_5)(PPh_3)_2]^+$ have been reported by Schoonover and co-workers.[53] They have found that the tetrafluoroborate hemihydrate in one isomeric form is an η^3-allyl complex containing a bent nitrosyl group, IrNO angle 129°, $\nu(NO)$ $1631cm^{-1}$. At low temperatures in solution a new form appears with $\nu(NO)$ $1763cm^{-1}$ and a p.m.r. spectrum attributable to an η^3-allyl ligand. The authors propose that this compound is subject to a facile linear-bent nitrosyl equilibrium. The addition of silver nitrite (2 mols) to cis-$[W(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$ (1 mol) in CH_2Cl_2 causes the rapid deposition of silver metal:[54] the resulting solution gradually evolves a mixture of CO, CO_2 and N_2O. Connor and Riley propose that the formation of N_2O occurs as a result of an intramolecular nucleophilic attack of coordinated NO on a nitrito ligand.

Nitrosonium salts containing MF_6^-, MF_6^{2-}, MF_6^{3-}, MF_7^- and MF_8^{2-} have been synthesised from NOF or NO, with or without F_2, and the appropriate transition metal or metal fluoride.[55]

Exposure of KNO_2 or $NaNO_2$ to ^{60}Co γ-rays at room temperature generates a radical species previously described as $N_2O_4^-$: Symons[56], now proposes that the species may be $N_2O_4^{3-}$. A new gas chromatographic procedure for the analysis of trace amounts of NO_2^- (0.01 to $0.1\mu g\ ml^{-1}$) in water has been developed.[57] The nitrite is converted via a diazonium intermediate into 3,4-dichlorobromobenzene which is subsequently determined by g.c. using electron capture detection. The kinetics of the elimination of nitrous acid from $p-NO_2C_6H_4CH_2CMe_2NO_2$ have been investigated and compared with those for HCl and HBr eliminations in related compounds.[58] The results indicate that the relative nucleofugacities are $Br^- > NO_2^- > Cl^-$; this is surprising in view of the generally accepted correlation of nucleofugacity with the strength of the conjugate acid of the leaving group.

The rate constant of reaction (8) has been determined as

$$ClO + NO_2\ (+N_2) \longrightarrow ClONO_2\ (+N_2) \qquad \ldots(8)$$

a function of pressure (25 - 612 torr) and temperature (274-339K) because of the interest of the possible involvement of chlorine(I) nitrate in stratospheric ozone depletion.[59] At 50 torr the experimental values of the rate constant were found to be 4.3 x 10^{-33} exp(1085/T) cm^6 $molecule^{-2}s^{-1}$. A new photoelectron, 304Å HeII and 584Å HeI, study of N_2O_4 has been carried out.[60] The N_2O_4 concentration in the reservoir behind the nozzle was ca. 60%. The thirteen bands below 24eV attributable to N_2O_4 molecules have been assigned on the basis of a recent Green's function study.[61]

The photolysis of thionitrites, RSNO, in the presence of compounds containing CC double bonds produces C-nitroso compounds and nitroxides.[62] Nitronium, NO_2^+, and nitrosonium, NO^+, difluorophosphates have been prepared by mixing $F_2P(O)OP(O)F_2$ with N_2O_5 and N_2O_3, respectively.[63] I.r. and Raman spectra of the nitronium salt are consistent with an unperturbed ONO^+ ion and a regular $PO_2F_2^-$.

The standard enthalpy of formation of NH_4NO_3 at 298.15K has been calculated from measurements of the energy of combustion of hydrocarbon oil and polyethylene sheet in the presence of NH_4NO_3.[64] Hence the standard enthalpy of formation of the aqueous nitrate ion has been obtained, -(206.81 ± 0.41)kJ mol^{-1}. Practically all the most accurate published data for the extraction of nitric acid by amine nitrates can be represented by a three parameter equation;[65a] the parameters allow for inductive and steric effects of substituents on the aminonitrogen and for the nature of the diluent. Extraction of nitric acid by neutral organophosphorus compounds can be treated similarly, but by means of a two parameter equation.[65b]

A single crystal neutron diffraction study of $[Rh(C_5H_5N)_4Cl_2]H(NO_3)_2$ at 298K has demonstrated that the anion, $O_2NOHONO_2^-$, although orientationally disordered is nevertheless symmetrical.[66] Contrary to earlier X-ray findings, the hydrogen-bond within this anion is very short, 2.46(2)Å. Beattie and co-workers[67] have reported that the coordination mode of NO_3^- can be determined by noting the number and relative intensities of isotope bands associated with the highest frequency N-O stretching mode in the i.r. spectrum of the ^{18}O-enriched material. The method has been illustrated by reference to the matrix spectrum of molecular KNO_3. The HeII photoelectron spectra for gaseous $Ti(NO_3)_4$ at 24°C and $Cu(NO_3)_2$ at 150°C have been interpreted with the aid of ab initio m.o. calculations.[68] These show that the metal-ligand bonding involves those orbitals which correlate with the 4e′ ligand orbitals. The ionization energies are consistent with the nitrato groups of the Ti(IV) compound having a smaller overall negative charge than those of the Cu(II) compound.

The reduction of NO_3^- by monomeric Mo(V) complexes has been studied in DMF.[69] Several compounds were shown to effect reduction with a one-electron step process, with complex kinetics, producing NO_2 and the corresponding Mo(VI) compound. Possible implications for the enzymatic nitrate reduction were discussed. Rapid reduction of NO_3^- to NH_3 in aqueous solution is effected by the product of the one-electron reduction[70] of $[(\eta^5\text{-}C_5H_4R)(\eta^6\text{-}C_6Me_nH_{6-n})Fe]^+$. The reaction of $[(bipy)_2pyRu(OH_2)]^{2+}$ with nitrate ion in 1M HNO_3 at room temperature is complete within 90min.[71] The principal reaction products are $[(bipy)_2pyRu(OH_2)]^{3+}$, 57±7%, and $[(bipy)_2pyRuNO]^{3+}$, 33±8%. The overall chemistry appears to involve the initial reduction of NO_3^- to HNO_2 followed by the capture of HNO_2 by Ru(II).

Single crystals of sodium orthonitrate, Na_3NO_4, have been grown successfully (240d at 415°C) in silver crucibles.[72] An X-ray structure analysis has shown that the dimensions of the NO_4^{3-} anions are regular in spite of the low site symmetry; the average N-O distance is 1.39Å and the surprisingly short O---O non-bonded contacts are 2.26Å.

5.1.7 Bonds to Sulphur

A series of thionitrosyl complexes of Mo, Re and Os has been synthesised by the reaction of suitable nitrido complexes with elemental sulphur, propylene sulphide or S_2Cl_2.[73] Typical syntheses are summarized in equations (9) and (10). Treatment of

$$[\mathrm{MoN(S_2CNR_2)_3}] \xrightarrow[\text{propylene sulphide}]{\mathrm{S_8}\ \text{or}} [\mathrm{Mo(NS)(S_2CNR_2)_3}] \quad \ldots(9)$$

$$[\mathrm{ReX_2N(PR_3)_3}] \xrightarrow{\mathrm{S_2Cl_2}} [\mathrm{ReClX(NS)(PR_3)_3}] \quad ..(10)$$

the thionitrosyls with tertiary phosphines regenerate the parent nitrido complexes in high yield. The novel organometallic thionitrosyl complex $[(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)]$ has been isolated in

21% yield from the reaction of $Na[(\eta^5-C_5H_5)Cr(CO)_3]$ and $S_3N_3Cl_3$ in THF at -78°C.[74] The coordination of the thionitrosyl group to the Cr has been shown to be essentially linear with Cr-N 1.69 and N-S 1.55Å. In $[Mo(NS)(S_2CNMe_2)_3]$ the Mo-N-S angle is 172° and Mo-N and N-S bond lengths are 1.74 and 1.59Å, respectively.[75] These results are analogous to the corresponding data for NO^+ complexes and thus indicate that in both compounds the coordinated group in NS^+. The Mo-N triple bond in the parent nitride $[MoN(S_2CNEt_2)_3]$ is appreciably shorter, 1.64Å, than in the thionitrosyl.

The crystal structure of $K_3N(SO_3)_2.H_2O$ has been determined by single crystal X-ray methods and has been compared with that of the refined structure of $K_2NH(SO_3)_2$.[76] The values obtained for the S-O and S-N lengths in the two compounds agree well with Cruickshank's dπ - pπ valence bond scheme.

New routes for the preparation of salts containing the bis(chlorosulphur)nitrogen cation, $[N(SCl)_2]^+$ have been reported.[77] The first method involves the reaction of $(NSCl)_3$ in $SOCl_2$ on the chloride ion acceptor, $AlCl_3$, $FeCl_3$ or $SbCl_5$, followed by the addition of SCl_2. The iron(III) compound $[N(SCl)_2][FeCl_4]$ can also be prepared from S_4N_4, SCl_2 and $FeCl_3$. The reactions of S_7NH, S_7NBCl_2, or 1,4-$S_6N_2H_2$ with $SbCl_5$ in liquid SO_2 have yielded dithionitronium hexachloroantimonate, $[NS_2][SbCl_6]$.[78] The crystal structure comprises linear SNS^+ cations (N-S, 1.46Å) and approximately octahedral anions. The NS bond in NS_2^+ is shorter than the CS bond in the isoelectronic species CS_2. I.r. and Raman spectra for the new cation were reported. Ionic compounds containing the thiazate anion, NSO^-, have been synthesised for the first time by means of reaction (11);[79] the starting materials were sulphinylaminotrimethylsilane (<u>12</u>) and potassium tert-butoxide.

$$KOBu + \underset{(\underline{12})}{Me_3SiNSO} \xrightarrow{THF} KNSO + Me_3SiOBu \qquad \ldots(11)$$

The potassium salt precipitates during the reaction and was characterised by its i.r. spectrum, with bands at 1270, 990 and 515cm^{-1}.

Thiazyl trifluoride, NSF_3, displaces the weakly coordinated SO_2 from the dipositive metal hexafluoroarsenates to form

$[M(NSF_3)_4](AsF_6)_2$, M = Mn, Fe, Co, Ni, or Cu, in liquid SO_2.[80] The S-N stretching mode increases from 1515 cm^{-1} in the free ligand to about 1600 cm^{-1} in the metal complexes. Monomeric thiazyl fluoride, NSF, which is unstable at room temperature, can be stabilised as a ligand by a similar reaction, equation (12), to that given above.[81] Excess NSF is required and the temperature

$$6NSF + [M(SO_2)_x](AsF_6)_2 \longrightarrow [M(NSF)_6](AsF_6)_2 + xSO_2 \quad ...(12)$$

should be kept below -20°C to inhibit solvolysis by SO_2. In the crystalline state the $[M(NSF)_6](AsF_6)_2$ salts, M = Co, Ni, are stable at room temperature and the structure of the Co salt has been determined by X-ray structural analysis (see Table 1).

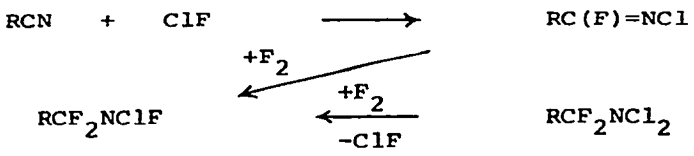
Table 1. Structural parameters for free and coordinated thiazyl fluoride.

	ν_{SN} /cm^{-1}	ν_{SF} /cm^{-1}	d(SN) /Å	d(SF) /Å	∢NSF /°
NSF (gas)	1361	641	1.446	1.646	116.5
$[Co(NSF)_6](AsF_6)_2$	1429	655	1.399	1.569	115.0

5.1.8 Bonds to Halogens

Liquid mixtures of NF_3 and BF_3 show large positive deviations from Raoult's law at 158.95K.[82] The evidence from the vapour pressure data is for no acid-base interaction in their system. The system NF_3-HCl is even more imperfect; the two liquids are only partially miscible at mole fractions 0.1 to 0.9.

Novel N-chloro-N-fluoroamines have been prepared by Sekiya and DesMarteau by the reaction of ClF + F_2 mixtures with some halogenated nitriles.[83] With RCN, R = Cl, CF_3, C_2F_5, the following reaction sequence is reasonably well established. Treatment of



the product when R = Cl with mercury in trifluoroacetic acid yielded CF_2NF, the simplest fluorinated imine, in 90% yield.

Ab initio m.o. calculations show that NH_2Cl^+ is planar in its ground state.[84] Thus the reported description of the orbital associated with the first band of the photoelectron spectrum of NH_2Cl is questionable. The HeI and II spectra for Me_2NCl and Me_2NBr have been obtained by Carnovale et al.[85] The valence p.e. spectra were interpreted with the aid of SPINDO m.o. calculations. Pure, gas-phase samples of the unstable methylbromamines, MeNHBr, $MeNBr_2$ and Me_2NBr, as well as some less pure samples of NH_2Br and $NHBr_2$ (products of the gas-phase reaction of NH_3 and Br_2) have also been studied by p.e. spectroscopy (He I).[86] The unsubstituted bromamines are considerably less stable than their methyl analogues hence their spectra could be obtained completely free of those of their precursors. A summary of the trends in the first ionisation potential is shown below: it includes estimated values for $NHBr_2$

$$\begin{tikzcd}
\begin{array}{c}10.88\\ NH_3\end{array} \arrow[r, "-1.24"] \arrow[d, "-0.70"'] & \begin{array}{c}9.64\\ MeNH_2\end{array} \arrow[r, "-0.67"] \arrow[d, "-0.04"] & \begin{array}{c}8.97\\ Me_2NH\end{array} \arrow[r, "-0.53"] \arrow[d, "+0.17"] & \begin{array}{c}8.44\\ Me_3N\end{array} \\
\begin{array}{c}10.18\\ NH_2Br\end{array} \arrow[r, "-0.58"] \arrow[ur, "-0.54"] \arrow[d, "-0.08"'] & \begin{array}{c}9.60\\ MeNHBr\end{array} \arrow[r, "-0.46"] \arrow[ur, "-0.63"] \arrow[d, "+0.02"] & \begin{array}{c}9.14\\ Me_2NBr\end{array} \arrow[ur, "-0.70"] & \\
\begin{array}{c}10.10\\ NHBr_2\end{array} \arrow[r, "-0.48"] \arrow[ur, "-0.50"] \arrow[d, "-0.0"'] & \begin{array}{c}9.62\\ MeNBr_2\end{array} \arrow[ur, "-0.48"] & & \\
\begin{array}{c}10.10\\ NBr_3\end{array} \arrow[ur, "-0.48"] & & &
\end{tikzcd}$$

and NBr_3. There are a number of discrepancies between the detailed assignments for Me_2NBr in references 85 and 86.

The chemistry of iodine azide, IN_3, a highly labile reagent, which has been prepared in a pure state only recently, has been reviewed by Dehnicke.[87]

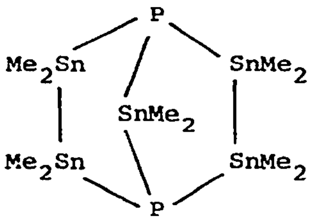
5.2 PHOSPHORUS

5.2.1 Phosphorus and Phosphides

Contrary to previous reports, the blue colour which results when freshly sublimed white phosphorus is dissolved in disulphuric acid can be attributed to S_5^+ arising from sulphur impurity.[88] A previous report had attributed it to a cationic phosphorus species. Red phosphorus samples obtained by polymerisation of white phosphorus under a variety of different conditions have been investigated by X-ray techniques and it seems clear that two distinct allotropic modifications exist.[89] Both are monoclinic but one set of products has lattice parameters close to those of Hittorf's phosphorus while for the other set the a and c parameters are increased by ca. 10%.

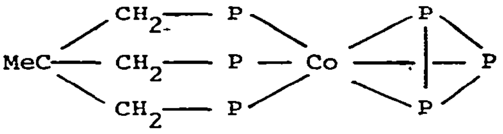
White phosphorus and dimethylstannane react to give pentakis-(dimethyltin) diphosphide (13) with a norbornane-like structure;[90] its n.m.r. spectrum has been measured and discussed in relation to this structure.

The preparation and the structures of the cobalt and nickel complexes containing coordinated P_3 or As_3 units mentioned in last year's review have now been fully reported.[91] The compounds are represented by the general formula $[M_2(D_3)(\text{triphos})_2]X_n$, where M = Co or Ni, D = P or As, X = BF_4^- or BPh_4^-, n = 1 or 2, and full structures are reported for two phosphorus and one arsenic compound. In all cases the Group 5 unit behaves as a 3π system.



(13)

The cobalt compound (14), also mentioned last year, shows Lewis base properties and on irradiation in the presence of $Cr(CO)_6$ up



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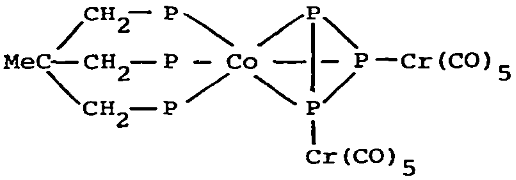
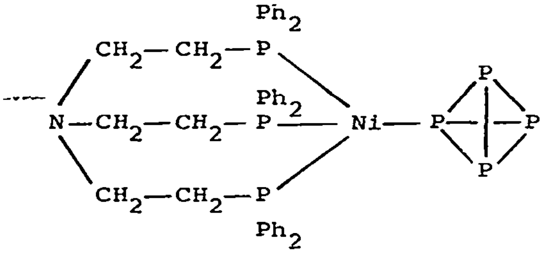
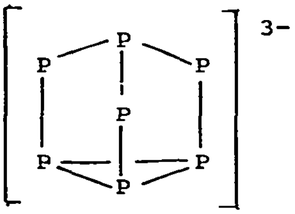


(15)

to two $Cr(CO)_5$ groups can be incorporated as shown in (15).[92] X-ray diffractometry gives 2.42 and 2.14Å for the mean Cr-P and P-P distances respectively. It was not possible even in the presence of an excess of $Cr(CO)_6$ to incorporate a third $Cr(CO)_5$ unit. A similar compound containing a coordinated P_4 unit has recently been obtained, extending the range of this type of compound, by adding a solution of white phosphorus in THF to a solution of tri(2-diphenylphosphinoethylamine)nickel.[93] The compound (16) is diamagnetic and contains a nickel atom in tetrahedral coordination by phosphorus atoms. The Ni-P distance



(16)



(17)

to the P_4 unit is 1.99Å and within the latter the P-P distances are 2.20 and 2.09Å.

An interesting new lithium phosphide, Li_3P_7, solvated with three moles of either THF or monoglyme is the final product of the reaction between diphosphine and either n-BuLi or $LiPH_2$.[94] At -60°C in solution the ^{31}P n.m.r. spectrum shows three sets of signals in the ratio 1:3:3, which can be associated with the atoms occupying the positions in a P_4S_3 cage-type structure (17). The fine structure is lost on heating and finally at 50°C there is a single sharp resonance. This compound is thus the first known polyphosphide with fluctuating bonds. A number of reactions of the compound are reported among which are those with trimethylchlorosilane, methanol and methyl bromide giving respectively $(Me_3Si)_3P_7$, P_7H_3 and P_7Me_3.

The alkali metal monophosphides NaP and KP have been prepared from the elements at temperatures in the region of 750K.[95] Crystals of the former are orthorhombic ($P2_12_12_1$) and consist of one dimensional infinite helices of two-coordinate phosphorus atoms (mean P-P 2.24Å, P-P-P 111.9 and 114.8°). From powder data, the potassium derivative is isostructural and the two compounds are best described as Zintl phases. The P-P bond energy in these compounds is estimated as 248 kJ mol^{-1}.

The chromium compound $Cr_{12}P_7$, in confirmation of an earlier report, is an isotype of Th_7S_{12} with the chromium atoms in both five and four fold coordination (mean Cr-P 2.39Å.[96] Single crystal data for the gold phosphides, Au_2P_3 and $Au_7P_{10}I$, show that the former consists of a polymeric phosphorus anion in which six membered rings are linked into infinite chains while the latter contains a puckered net of six membered rings.[97] In each case the gold is in a formal +1 oxidation state.

Single crystals of ReP_4 have been obtained from the elements in molten tin while a reaction in the presence of iodine led to microcrystalline material only.[98] The compound (orthorhombic, Pbca) contains rhenium atoms in distorted octahedral coordination by phosphorus (mean Re-P 2.40Å), pairs of which share an edge allowing the development of a Re-Re bond. Each phosphorus atom is in distorted tetrahedral coordination to rhenium and phosphorus atoms in such a way that the latter form puckered ten-membered rings which are further condensed to an infinite two dimensional net.

The ternary compounds KMgP, KMgAs, KMgSb and KMgBi result when mixtures of the elements are heated and on the basis of single crystal and powder data they have a modified Cu_2Sb structure.[99] Among other ternaries recently prepared are MgCuP[100] (orthorhombic, Pnma, anti-$PbCl_2$ structure), BaCuP[100] and BaAgP[100] (hexagonal, $P6_3/mmc$, modified Ni_2In structure), and CaAgP[101] and CaAgAs[101] (hexagonal, $P\bar{6}2m$, modified Fe_2P structure). The cadmium compounds $Cd_4P_2X_3$, for X = Cl, Br or I, are obtained when mixtures of Cd, P and CdX_2 are heated to 750 C in quartz vessels;[102] they are isotypes of $Cd_4As_2I_3$ from X-ray, vibrational spectroscopic, and thermal data.

5.2.2 Bonds to Carbon or Silicon

The +3 Oxidation State. Although there is a formal similarity between the Me_3Si group and the $Me_2P(BH_3)$ group, from the lability generally associated with borane derivatives difficulties might be expected in isolating compounds in which Me_3Si groups are replaced by $Me_2P(BH_3)$.[103] However, recent work has shown that such compounds can show surprisingly high thermal and chemical stability, and the chlorophosphane-borane analogue of Me_3SiCl, for example, can be prepared as shown in equation (13) as a distillable,

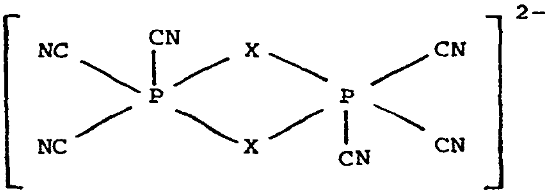
$$Me_2PCl + H_3B.OC_4H_8 \longrightarrow Me_2P(BH_3)Cl + OC_4H_8 \qquad ...(13)$$

slightly moisture sensitive liquid. Controlled hydrolysis or ammonolysis leads respectively to the disiloxane, $[Me_2P(BH_3)]_2O$, and silylamine, $Me_2P(BH_3)NH_2$, analogues, while metallation of the latter followed by reaction with a further molecule of $Me_2P(BH_3)Cl$ gives the disilazane analogue $[Me_2P(BH_3)]_2NH$. Continuing the analogy, the methylene bridged compound, $[Me_2P(BH_3)]CH_2$, has been reported,[104] and, after metallation at the central carbon atom, the bis(N-tetramethylethylenediamine)lithium salt of the $[Me_2P(BH_3)CHPMe_2(BH_3)]^-$ anion can be isolated. Independent ions are present with phosphorus atoms in tetrahedral coordination; the P-C (bridge) bonds are almost equal in length (ca. 1.70Å) and shorter than the terminal bonds (ca. 1.82Å); the P-C-P angle is 128.6°.

The low pressure pyrolysis reaction used to synthesise molecules containing phosphorus-carbon multiple bonds, e.g. $MeC\vdots P$ from dichloroethylphosphine at $900^\circ C$, can be followed better by photoelectron spectroscopy than by microwave spectroscopy as described in earlier work in this area.[105] Both ^{19}F and ^{31}P n.m.r. data confirm that the phospha-alkene $CF_2{:}PH$ and the alkyne $CF\vdots P$ are intermediates in the room temperature reaction between solid potassium hydroxide and CF_3PH_2.[106] Similarly it has been shown that when $(CF_3)_2PH$ replaces CF_3PH_2 an important intermediate is the phospha-alkene $CF_2P{:}CF$.[107]

A sodium dicyanophosphide, $NaP(CN)_2$, stabilised as a crown ether-

THF complex results when $P(CN)_3$ is reduced by [18]crown-6 sodium diethylphosphite in THF.[108] An X-ray structure shows that while the cation consists of a sodium ion coordinated to a crown ether molecule with THF molecules above and below the ring, the anion has a similar structure except that the THF molecules are replaced by two N-coordinated dicyanophosphide ions. Mean molecular parameters are P-C 1.74Å, C-P-C 95.0°, and P-C-N 172°. Pseudo-halogen character has been postulated for the $P(CN)_2^-$ ion and products equivalent to trihalides, e.g. $P(CN)_2Br_2^-$ and $P(CN)_2I_2^-$, have been obtained with bromine and iodine but with chlorine only the neutral compound $P(CN)_2Cl$ was obtained.[109] Analogous reactions occur with BrCN and ICN to give respectively the anions $P(CN)_3Br^-$ and $P(CN)_3I^-$, which from X-ray structures contain the dimeric anions (18).[110] Coordination about phosphorus is pseudo-octahedral and similar to that in $Bi_2Cl_8^{2-}$.



(18 X = Br or I)

Methyl and trifluoromethyl phosphorus, arsenic, selenium and tellurium compounds have been prepared by a number of routes illustrated in equations (14) to (18).[111] The simplest method

$$P_2Me_4 + Me_2S_2 \longrightarrow 2Me_2PSMe \quad ...(14)$$

$$P_2(CF_3)_4 + Me_2Se_2 \longrightarrow 2(CF_3)_2PSeMe \quad ...(15)$$

$$P_2(CF_3)_4 + Me_2Te_2 \longrightarrow 2(CF_3)_2PTeMe \quad ...(16)$$

$$2Me_2PH + As_2(CF_3)_4 \longrightarrow 2Me_2PAs(CF_3)_2 \quad ...(17)$$

$$Me_2AsCl + MeSH \xrightarrow{Me_3N} Me_2AsSMe \quad ...(18)$$

seems to be the redistribution reaction between a diphosphine or diarsine and the appropriate disulphide, diselenide or ditelluride; the products form chromium carbonyl complexes.

Rotational isomerism in Me_4P_2 and the equilibrium between the _trans_ and _gauche_ forms have been investigated by variable temperature photoelectron spectroscopy, showing that the _trans_ isomer is more stable by 0.5 kcal mol^{-1}.[112]

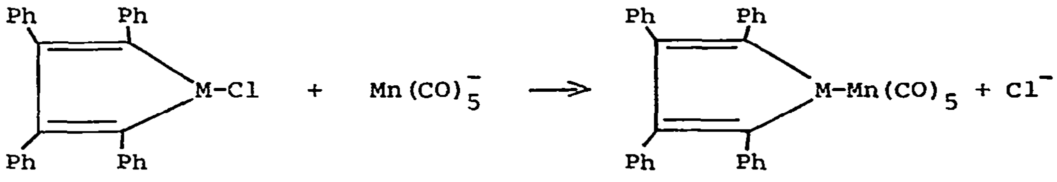
The desulphuration of tetramethyl diphosphine disulphide is the first step in a new simple synthetic route to dimethylphosphine.[113] Treatment of the resulting tetramethyl diphosphine with protonic compounds follows the reactions in equations (19) and (20) leading to an overall yield of ca. 65% of the dimethylphosphine.

$$Me_2PPMe_2 + H_2O \longrightarrow Me_2PH + Me_2PHO \qquad \ldots(19)$$

$$2Me_2PHO \longrightarrow Me_2PH + Me_2POOH \qquad \ldots(20)$$

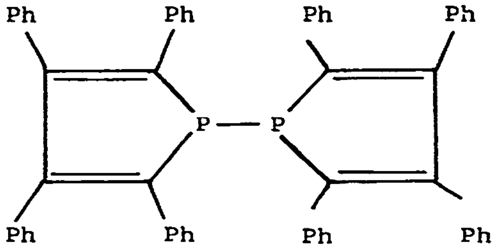
Dialkylchlorophosphines react with secondary and tertiary phosphines to give respectively tetraalkyl- and pentaalkyldiphosphonium chlorides $(R_4P_2H)Cl$ and $(R_3P_2)Cl$, while with primary phosphines the products are polymeric phosphanes, $(RP)_n$ and dialkylphosphonium chlorides, $(R_2PH_2)Cl$.[114] Mercury and dimethylchlorophosphine over a period of several days at 80°C yield a colourless, crystalline product containing the reagents in a 1:2 ratio, which X-ray diffraction has shown to be a coordination polymer of mercury(II) chloride and tetramethyldiphosphane.[115] The Hg-P and P-P distances are 2.49 and 2.19Å respectively and although the product shows considerable stability towards acids it is hydrolysed in alkali hydroxide solutions and decomposed on heating. A number of lanthanide derivatives, $M(t\text{-}Bu_2P)_3$ for M = Y, Ho, Er, Tm, Yb and Lu, have been isolated from reactions between $Li(t\text{-}Bu_2P)$ and the appropriate trichloride.[116]

Reaction between the chlorophosphole (19, M = P) and the manganese pentacarbonyl anion takes place as shown in equation (21)

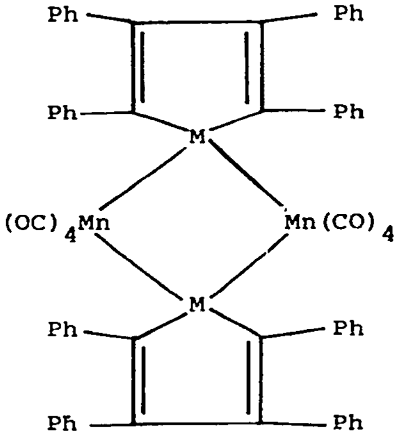


(19, M = P, As, Sb) ...(21)

but quantities of $Mn_2(CO)_{10}$ and the diphosphole (20) are also obtained. This is in contrast to the behaviour of the M-Ph derivatives of (19) which react either by electron donation from the M lone pair or as a diene.[117] When M = As or Sb the reaction in equation (21) is almost quantitative. Similar reactions leading to σ-bonded complexes with Mo, W, Re and Fe have also been reported.

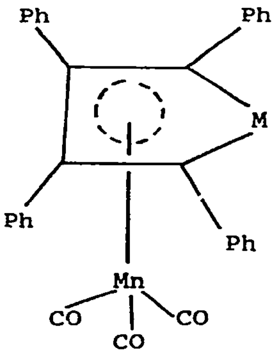


(20)



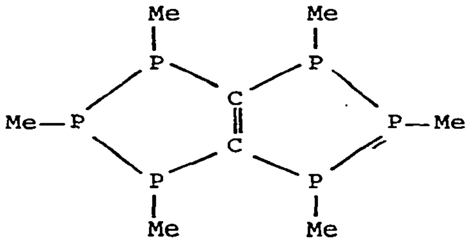
(21, M = P or As)

The manganese and rhenium compounds are stable at room temperature in the solid state and in solution but on heating to ca. 70°C CO is lost giving the dimer (21) containing bridging phosphole groups. FurtherCO loss occurs on heating to ca. 140°C leading to monomeric tricarbonyl derivatives in which the phospholyl or arsolyl groups behave as π-bonded ligands (22).[118]



(22, M = P or As)

Further details in the area of cyclic carbaphosphanes have become available during 1979 with reports on the reaction between $K_2(PMe)_4.2THF$ and tetrachloroethylene which gives the unsaturated compound (23),[119] and reactions which lead to alkyl substituted



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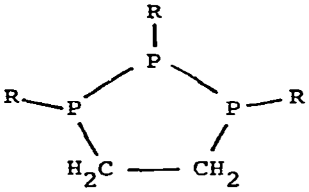


(24, R = Me, Et or t-Bu).

cyclo-dicarbatriphosphanes (24).[120] The latter are analogues of the better known phenyl substituted derivatives and result when either $K_2(PR)_3$ or $K_2(PR)_4$ reacts with 1,2-dichloroethane. Similar reactions with 1,2-dichloropropane are reported. The products in both cases consist of two isomers, identified by n.m.r. spectroscopy, which arise from differences in the relative orientations of the alkyl groups attached to phosphorus. The all trans isomer is preferred.

Good yields of the vinyldifluorophosphoranes, $Ph_nPF_2(CH{:}CH_2)_{3-n}$ n = 1 or 2, and $Ph_2PF_2(C_6H_4CH{:}CH_2)$ are obtained by direct fluorination of the appropriate phosphorus(III) compound in $CFCl_3$ solution.[121] In the presence of t-butoxide in THF, Ph_2PH and $PhPH_2$ add to $Ph_2PF_2(CH{:}CH_2)$ to give respectively $Ph_2PF_2CH_2CH_2PPh_2$ and $(Ph_2PF_2CH_2CH_2)_2PPh$.

Ligands in the series $Me_nM(CF_3)_{3-n}$, for M = P, As or Sb and n = 0 - 3, have been prepared and characterised, and their Lewis basicity with respect to a number of standard acids assessed.[122] The phosphorus compounds (L) form the complexes $M(CO)_5L$ and cis-$M(CO)_4L_2$ for M = Cr, Mo or W,[123] and give addition compounds with boron trihalides.[124]

The chain reaction which leads to spontaneous inflammability of $(CF_3)_3P$ in air has been examined to unravel the reaction paths involved.[125] In the presence of radical traps the oxidation is inhibited pointing to a radical chain process similar to that for the alkylphosphines. In the absence of radical traps but with thermal quenching oxidation leads to good yields of the new compound, tris(trifluoromethyl)phosphate $(CF_3O)_3PO$ together with OCF_2 and $(CF_3)_2P(O)F$. The chain process summarised in equations (22) - (25) is suggested.

$$(CF_3)_3P + CF_3OO^{\bullet} \longrightarrow CF_3OOP(CF_3)_2 + CF_3^{\bullet} \quad ...(22)$$

$$CF_3OOP(CF_3)_2 + CF_3OO^{\bullet} \longrightarrow (CF_3OO)_2P(CF_3) + CF_3^{\bullet} \quad ...(23)$$

$$CF_3^{\bullet} + O_2 \longrightarrow CF_3OO^{\bullet} \quad ...(24)$$

$$(CF_3OO)_2P(CF_3) \longrightarrow (CF_3O)_3PO \quad ...(25)$$

An improved synthesis outlined in equation (26) and a full X-ray structure have been reported for the unusual, air stable, tertiary phosphine $P(CH_2CN)_3$.[126] The compound which crystallises in the space group R3c is propellor shaped with a P-C distance of 1.842Å and a C-P-C angle of 98.6°. t-Butoxyethylphosphine prepared as shown in equation (27) is an important intermediate in the preparation of triethanol-phosphine $P(CH_2CH_2OH)_3$.[127] Subsequent treatment with butyl lithium and t-butoxyethyl chloride gives $P(CH_2CH_2O\text{-}t\text{-}Bu)_3$ which is converted to the product on hydrolysis. Similar reactions with aryl and alkyl phosphines yield the corresponding diethanol derivatives $RP(CH_2CH_2OH)_2$.

$$PCl_3 + 3Bu_3SnCH_2CN \longrightarrow P(CH_2CN)_3 + Bu_3SnCl \quad ...(26)$$

$$NaPH_2 + t\text{-}BuOCH_2CH_2Cl \longrightarrow NaCl + t\text{-}BuOCH_2CH_2PH_2 \quad ...(27)$$

A triacetic acid analogue, $P(CH_2COOH)_3$, has also been reported following the reactions in equations (28) and (29).[128] The phosphine acetic acids $Ph_{3-n}P(CH_2COOH)_n$, with structural similarities

$$P(SiMe_3)_3 + 3ClCH_2COOSiMe_3 \longrightarrow P(CH_2COOSiMe_3) + 3Me_3SiCl \quad ...(28)$$

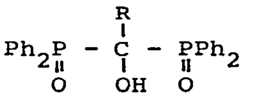
$$P(CH_2COOSiMe_3)_3 + 3MeOH \longrightarrow P(CH_2COOH)_3 + 3Me_3SiOMe \quad ...(29)$$

to complexones, form complexes with a number of divalent metal ions.[129]

Tri-t-butylphosphine reacts in benzene solution with one mole of either $GeBr_4$ or $SnBr_4$ to give two new compounds identified by their n.m.r. and vibrational spectra as the bromo-tributylphosphonium salts $(t\text{-}Bu)_3PBr^+\ MBr_3^-$ where M = Ge or Sn.[130]

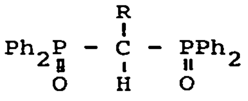
Reactions between alkylthio- and alkylseleno- phosphonium salts and alkylmecaptide ions result in trivalent phosphorus compounds and using this approach it has been possible to produce the optically active phosphine, Me(n-Pr)PhP, with retention of configuration and 59% of the initial optical activity from $[Me(n\text{-}Pr)PhP(SMe)]^+CF_3SO_3^-$ and $t\text{-}BuS^-$.[131]

Oxidation reactions have been investigated for the acyl phosphanes, $PC(O)PPh_2$ where R = Me,[132] CF_3,[132] or Ph.[133] Slow oxidation with molecular oxygen for the methyl and trifluoromethyl compounds leads initially to the cprresponding phosphane oxide $RC(O)P(O)Ph_2$ which on treatment with water gives the alcohol (25) and phosphinate (26).[132] With fast oxidation on the other hand the CO



$$Ph_2\underset{O}{\underset{\|}{P}} - \overset{R}{\underset{OH}{C}} - \underset{O}{\underset{\|}{P}}Ph_2$$

(25)

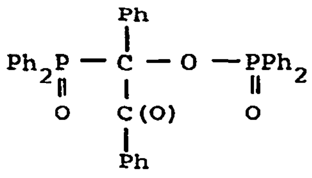


$$Ph_2\underset{O}{\underset{\|}{P}} - \overset{R}{\underset{H}{C}} - \underset{O}{\underset{\|}{P}}Ph_2$$

(26)

groups of the acylphosphane is attacked with liberation of CO_2 and generation of $Ph_2P\cdot$ and R· radicals. Oxidation of the benzoyl derivative $PhC(O)PPh_2$ occurs at both carbon and phosphorus atoms leading to benzoyl diphenylphosphinate, $PhC(O)OP(O)Ph_2$, as an intermediate and the two anhydrides $(Ph_2CO)_2O$ and $(Ph_2PO)_2$ as final products.[133] The phenyl substituted phosphane oxide $PhC(O)P(O)Ph_2$ i.e. the analogue of the intermediates obtained from oxidation of $MeC(O)PPh_2$ and $CF_3C(O)PPh_2$, can be obtained from an Arbusov reaction between Ph_2POMe and PhC(O)Cl, but it readily dimerises to (27). Hydrolysis gives the alcohol (28).

Bis(diorganophosphino)methanes can be readily obtained from diorgano(trimethylsilylmethyl)phosphanes and organochlorophosphanes as shown in equation (30), and a methylene bridged triphosphane, $Ph_2PCH_2PPhCH_2PPh_2$, is the product when $PhPCl_2$ replaces PhR^2PCl in equation (30).[134] P-P coupling, showing that phosphorus rather



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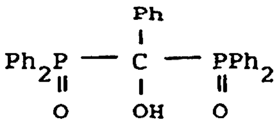
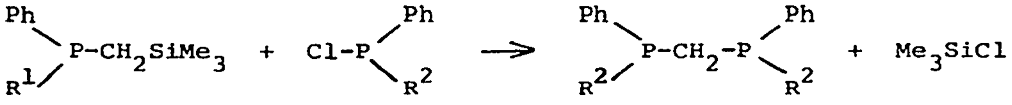


(28)

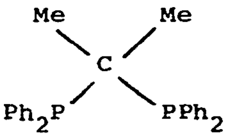
than carbon is the nucleophilic centre, takes place when lithium diphosphino-methanes $Li[R_2{}^1PCHPR_2{}^2]$ react with chlorodiorganophosphanes, $R_2{}^3PCl$.[135,136] The initial product is the ylide $R_2{}^3PPR_2{}^1{:}CH{\cdot}PR_2{}^2$ but its isolation depends on steric effects. For example with R^3 = t-Bu, isolation is possible but in other cases isomerisation to the tris(phosphino)methane $[(R_2{}^1P)(R_2{}^2P)(R_2{}^3P)]CH$ occurs.



R^1 = Me or Ph

R^2 = Me or Ph ...(30)

In general it has been found that the ease of lithiation of phosphinomethanes $(Me_2P)_nCH_{4-n}$ occurs more readily with an increase in n.[137]



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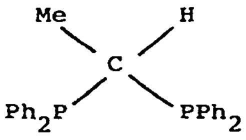

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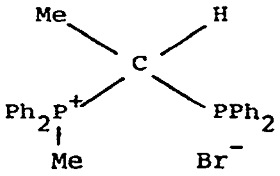
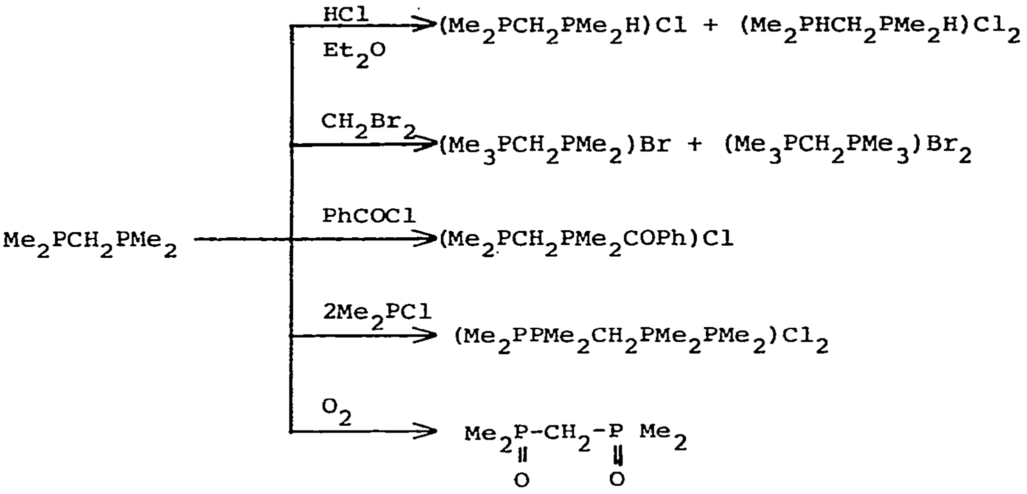


(31)

Substituted 1,3-ditertiary phosphanes such as (29) and (30) react with methyl halides to give the corresponding mono- and di-phosphonium salts, but only for the mono- salt (31) does dehydrohalogenation occur to give the ylide $Ph_2MeP{:}CMe{\cdot}PPh_2$ with retention of the basic skeleton.[138] The corresponding diphosphonium salt undergoes phenyl group migration to produce the benzyl ylide $(PhCH_2)Ph_2P{:}CMe{\cdot}PPhMe$.

A number of reactions summarised in Scheme 1 have been reported for the diphosphinomethane, $Me_2PCH_2PMe_2$, which serve as prototypes for the reactions with unsymmetrical compounds $Me_2PCH_2PR_2$ where R = t-Bu or Ph.[139]

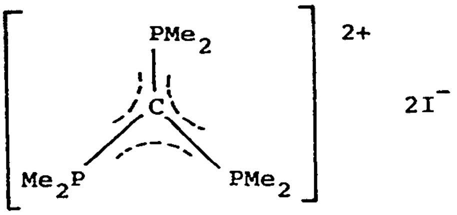


Scheme 1

As mentioned in reference 136, methylidynetris(phosphanes) can be prepared as shown in equation (31).[140] X-ray crystallography

$$Li[HC(PMe_2)_2] + Me_2PCl \xrightarrow{Et_2O} HC(PMe_2)_3 + LiCl \qquad ...(31)$$

shows disorder in the solid state with phosphorus atoms adopting both left handed and right handed arrangements with respect to the CH position. Metallation of this compound to $Li[C(PMe_2)_3]$ followed by treatment with methyl iodide gives in addition to Me_4PI and $Me_3PO.LiI$ a novel phosphorus ylide $[C(PMe_2)_3]I_2$ containing a resonance stabilised sp^2 carbanion.[141] An X-ray study shows the trigonal planar structure (32) with a mirror plane perpendicular to the plane of the cation.[142] The two independent P-C distances are equal (1.75Å) but the P-C-P angles are 116.7 and 126.5°; this difference is ascribed to steric interactions between the methyl



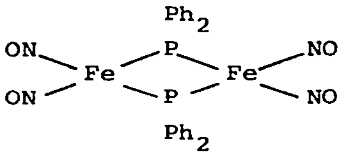
(32)

groups on the symmetry related phosphorus atoms which are in eclipsed positions.

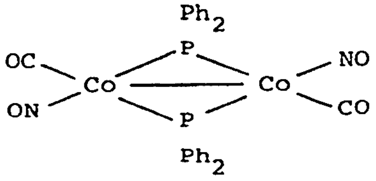
Faraday effect measurements and u.v. spectroscopic data are presented to show that interaction takes place between the π-system of phenyl groups or the lone pair on nitrogen or oxygen substituents with symmetry compatible phosphorus orbitals in the diphosphanes, R^1R^2P P R^1R^2 where R^1, R^2 = Et, Ph, NR_2 or OR, and phenyl phosphanes, Ph_nPX_{3-n} where X = H, Cl or OR and n = 1-3.[143]

The well known ligand, bis(diphenylphosphino)ethane, has been obtained in two crystallographic modifications and although both are monoclinic, $P2_{1/n}$, the cell dimensions are different.[144] Different packing modes are considered to account for these differences and for the small differences in i.r. spectra.

Among structures of transition metal complexes determined during the past year are two compounds, (33) and (34), which contain diphenylphosphino bridging groups.[145]



(33)



(34)

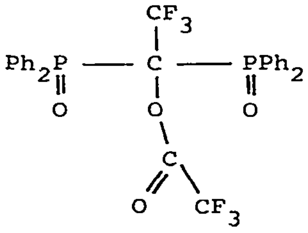
Vibrational data for triallyl phosphine and arsine can be analysed in terms of C_3 overall molecular symmetry for the $M(C-C)_3$ skeletal modes with all the allyl groups in the gauche configuration.[146] The internal allyl modes may then be assigned on the basis of local C_s symmetry.

The CS_2 adducts R_3P-CS_2, for R = n-Bu or C_6H_{11}, give i.r. and Raman spectra in accord with the zwitterion formulation $R_3P^+-CS_2^-$ proposed earlier for the triethylphosphine analogue.[147] Normal coordinate analyses for the borane adducts $Ph_3P.BH_3$, $Ph_3P.BD_3$ and $(C_6D_5)_3P.BH_3$ have been carried out and the data point to a relationship between the P-B valence force constant and the magnitude of $J(^{31}P-^{11}B)$.[148]

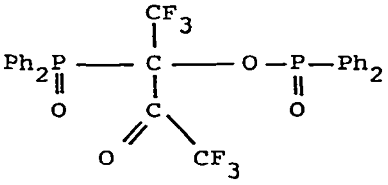
Nucleophiles such as DMF, HMPA, hydrazine and diethylformamide replace the para-fluorine atoms in each of the rings in $(C_6F_5)_3P$ to give $(p\text{-}Me_2NC_6F_4)_3P$ with the first two reagents and $(p\text{-}N_2H_3C_6F_4)_3P$ and $(p\text{-}Et_2NC_6F_4)_3P$ respectively with the latter two.[149] With aniline, phenylhydrazine and formamide, the reaction leads to mixtures of the mono- and di- substituted phosphines.

<u>The +5 Oxidation State</u>. An X-ray structure for bis(diphenylphosphonyl)acetylene, $Ph_2P(O)C⋮CP(O)Ph_2$, shows an almost linear skeleton with P-C-C angles of 178.5 and 178.9°.[150] The C-C distance is 1.197Å and the two bonds from phosphorus to acetylene carbon atoms are 1.798 and 1.789Å and the torsion angle between the two P=O groups is ca. 180°. The sulphur[151] and selenium[152] analogues have similar structures except that the torsion angles between the P=X groups are reduced in each case to ca. 120°.

The phosphane oxide, $CF_3C(O)P(O)Ph_2$, dimerises to the trifluoroacetate (<u>35</u>) at -25°C and on warming to 40°C this is converted irreversibly to the phosphinate (<u>36</u>).[153]



(<u>35</u>)

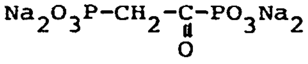


(<u>36</u>)

X-ray powder diffraction and thermal analysis data are reported for the tin(II) and tin(IV) halide adducts each with two moles of di-isopropylmethylphosphonate.[154] The latter on heating loses i-propyl halide to give initially oligomers of the type $\{[(i\text{-}PrO)MePO_2]_2SnX_2\}_n$ in which tin atoms are linked by double $Sn(OPO)_2Sn$ bridges, and finally a higher cross linked polymer $[(MePO_3)_2Sn]_n$. The tin(II) halide complexes give successively

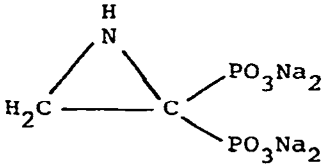
$\{[(i\text{-}PrO)MePO_2]_2Sn\}_n$ and $\{[Me(OH)PO_2]_2Sn\}_n$ on heating.

Phosphorus acid can be benzoylated with either the anhydride $(PhCO)_2O$ or benzoyl chloride; the product in the first case is $PhC(OH)(PO_3H_2)_2$ while a mixture of $PhCCl(PO_3H_2)_2$ and $(p\text{-}Cl\text{-}C_6H_4)CH(PO_3H_2)_2$ results with the chloride.[155] Reaction with nitrous acid replaces the amino group in 1-aminoalkanediphosphonic acids $RC(NH_2)(PO_3H_2)_2$ to give a good yield of $RC(OH)(PO_3H_2)_2$ for R = Ph, p-Cl-C_6H_4, Me, C_3H_7 and cyclohexyl,[156] but the reaction is modified for the aryl derivatives by the presence of concentrated hydrochloric acid to give the C-chloro derivatives $RCCl(PO_3H_2)_2$. Alkane diphosphonic acids carrying substituents in the 2- or 3-positions are relatively unknown but the compound $ClH_2C{\cdot}C(NH_2)(PO_3H_2)_2$ can be prepared by treating $ClH_2CC(O)NH_2$ with a mixture of phosphorous acid and phosphorus trichloride.[157] On neutralisation, the acid loses ammonia to give the salt (37) via (38) as a possible intermediate. Phosphonocarboxylic acids, e.g. $R_2C(CO_2H)(PO_3H_2)$, are interesting mixed compounds and a general preparative approach



$Na_2O_3P\text{-}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}PO_3Na_2$

(37)



(38)

to these compounds is the catalytic addition of P-H and C-H containing acid esters to activated multiple bonds.[158] A number of these products are shown diagramatically in Table 2.

The structure of the bone growth regulator, disodium dihydrogen 1-hydroxyethylidenediphosphonate, $Na_2[HO_3P{\cdot}C(OH)Me{\cdot}PO_3H]$ shows a planar W-conformation for the anion with eclipsed phosphonate groups so that it can behave as a tridentate ligand.[159]

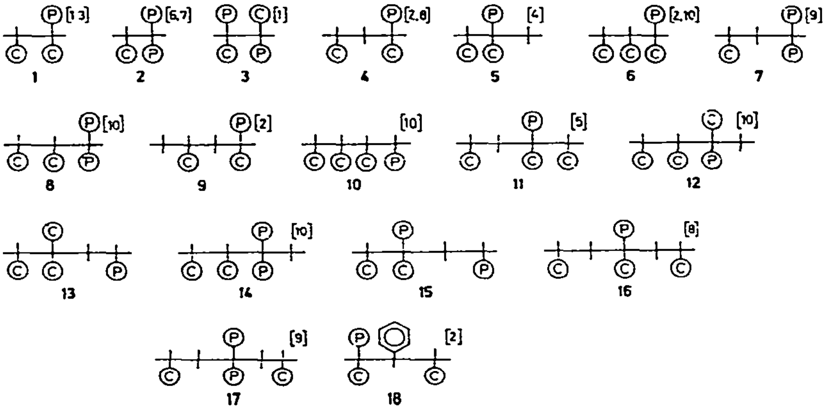
Acetic anhydride and potassium hydrogen fluorophosphate react as shown in equation (32), and on heating to 140°C the product loses

$$K(HPO_3F) + (MeCO)_2O \longrightarrow K[PO_3F(COMe)] + MeCOOH \qquad \ldots(32)$$

acetic anhydride giving the difluorodiphosphate $K_2(P_2O_5F_2)$.[160]

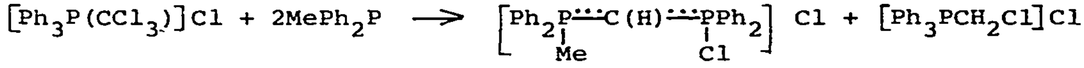
Further chemistry of triphenyl(trichloromethyl)phosphonium

Table 2. Structures of known and new saturated phosphonocarboxylic acids (Ⓒ = CO_2H; Ⓟ = PO_3H_2; $\Sigma\text{-}CO_2H + \text{-}PO_3H_2 \geq 3$)



chloride $[Ph_3P(CCl_3)]Cl$ has been described,[73] showing that with phosphanes, the reaction course depends markedly on the nature of the substituents as shown for two cases in equations (33) and (34).[161] Two new examples of the reaction between a phosphane and

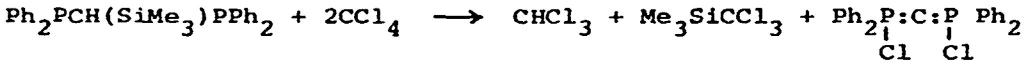
$$[Ph_3P(CCl_3)]Cl + 2Ph_2PCl \longrightarrow [Ph_3P\overset{\cdots}{-}C(Cl)\overset{\cdots}{-}PPh_2Cl]Cl + Ph_2PCl_3 \qquad \ldots(33)$$



$$[Ph_3P(CCl_3)]Cl + 2MePh_2P \longrightarrow \left[Ph_2\underset{Me}{P}\overset{\cdots}{-}C(H)\overset{\cdots}{-}\underset{Cl}{P}Ph_2\right]Cl + [Ph_3PCH_2Cl]Cl \qquad \ldots(34)$$

carbon tetrachloride leading to ylide formation by elimination of chloroform have also been published.[162,163] Both concern silicon substituted phosphanes and are summarised in equations (35) and (36). The products are stable and can be isolated with that from

$$Me_3SiCH_2PPh_2 + CCl_4 \longrightarrow CHCl_3 + Me_3SiCH{:}\underset{Cl}{P}Ph_2 \qquad \ldots(35)$$

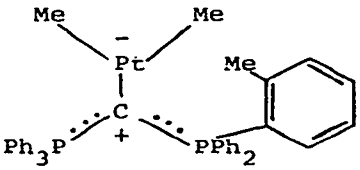


$$Ph_2PCH(SiMe_3)PPh_2 + 2CCl_4 \longrightarrow CHCl_3 + Me_3SiCCl_3 + Ph_2\underset{Cl}{P}:C:\underset{Cl}{P}Ph_2$$

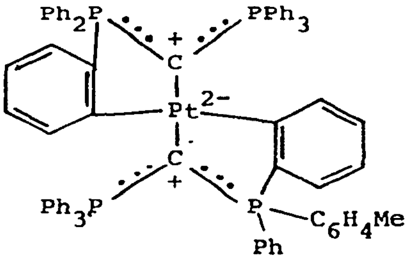
...(36)

equation (35) adding hydrogen chloride smoothly to give $[Ph_2PCl\cdots CH\cdots PClPh_2]Cl$.[163]

Salts of the trimethyl-platinum(IV) cation, Me_3PtX where X = PF_6^-, $OSO_2CF_3^-$ or I^-, react with the bis(ylide) $Ph_3P:C:PPh_3$ to show another facet of the chemical behaviour of these unusual compounds.[164] The actual course of the reaction depends on the amount of ylide used but among the products are methane and $HC(PPh_3)_2^+X^-$, the former arising from combination between a methyl group from platinum and an ortho hydrogen atom from an aromatic group of the ylide. The platinum species isolated include compounds (39) and (40) from reactions with respectively two and three equivalents of the ylide. A full discussion is given of possible reaction sequences with details of the identification of the products.

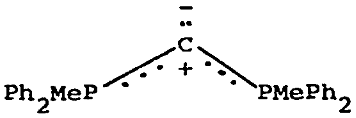


(39)



(40)

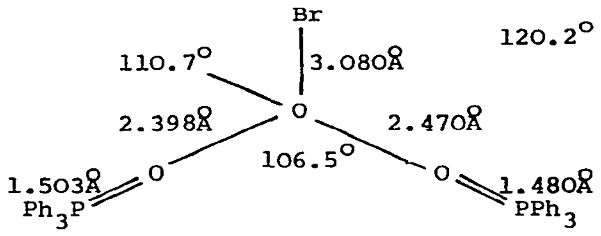
Recent X-ray diffraction data for the deep yellow mixed ylide $Ph_2MeP:C:PMePh_2$ has shown an exceptionally small C-P-C angle (121.8°) and the formulation in (41) is therefore suggested.[165]



(41)

Downfield ^{31}P n.m.r. shifts, observed for Ph_3PO in equimolar mixture with a number of Group 4 compounds in toluene solution, are associated with the formation of weak adducts.[166] Analysis of the concentration dependence gives values of $60M^{-1}$ and $100M^{-1}$ for the formation constants of the 1:1 adducts $Ph_3PO.Me_3SiCl$ and $Ph_3PO.Me_3SnCl$ respectively. Data for the Ph_3PO-$SiCl_4$ system are more complicated and suggest the presence of multiple equilibria involving probably both $Ph_3PO.SiCl_4$ and $2Ph_3PO.SiCl_4$.

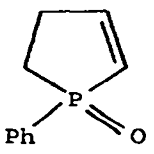
Triphenylphosphine oxide forms adducts with both HF and HBr. The anhydrous HF adduct (monoclinic, $P2_1/c$) contains a short hydrogen bridge with O···H and H-F distances of 1.42 and 1.00Å respectively.[167] The O-H-F angle is 159.8° giving with an O···F separation of 2.38Å. The hydrogen bromide compound analyses as $2Ph_3PO.H_2O.HBr$ and the structure is based on the two phosphine oxide molecules and HBr attached by three short hydrogen bonds to the water molecule in a pseudo-tetrahedral fashion.[168] The principal dimensions are included in (42).



(42)

The structure of Ph_3PSe (monoclinic, $P2_1/c$), contains two independent molecules with very similar dimensions; the phosphorus angles vary between 103.3 and 113.8°, with a P = Se distance of 2.106Å.[169]

On bromination, 1-phenyl-2-phospholene-1-oxide (43) gives two isomeric forms, one of which with a ^{31}P n.m.r. shift of 43.3 ppm has been shown by X-ray diffraction to have the trans structure (44).[170] The second isomer also has the two bromine atoms trans to each other but here that on the carbon atom adjacent to phosphorus is cis to the phenyl group (45).



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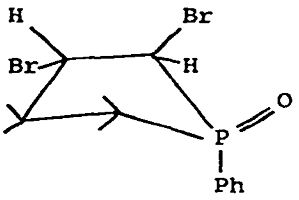
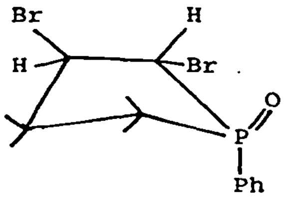
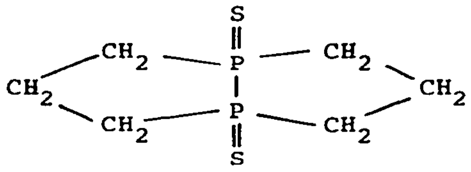


(44)



(45)

X-ray data for the orthorhombic (Pnma) modification of the 1,5-diphosphabicyclo-octane-1,5-disulphide (46) shows close to C_{2v} overall symmetry with the five membered rings in the envelope



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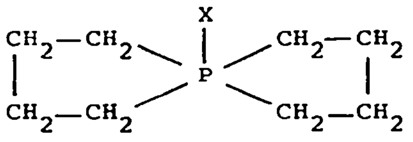

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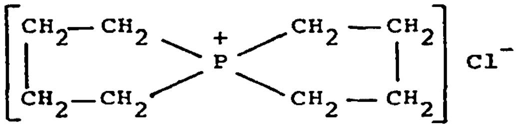
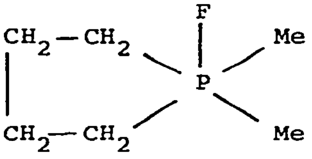


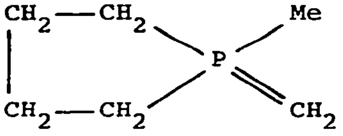
(48)

conformation.[171] The two rings adopt the eclipsed endo-endo conformation similar to that in the monoclinic form and slight differences in molecular packing account for the polymorphism.

A new spirocyclic phosphorane (47, X = Me) has been isolated from a reaction of methyl lithium with spiro-salt (48) and the methoxy derivative (47, X = OMe) can be obtained by successive treatment of (48) with sodium amide and methanol.[172] N.m.r. data for both compounds show pronounced fluxionality and it is not possible to describe the geometry in terms of either the trigonal bipyramid or square pyramidal alternatives. The structure is similar with the fluorophosphorane (49) obtained from the methylene derivative (50).

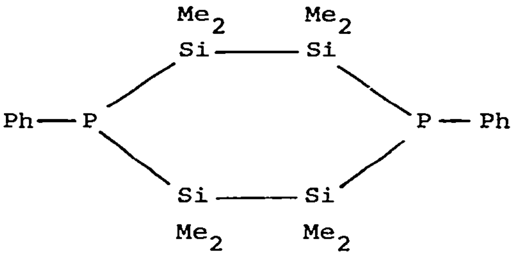


(<u>49</u>)

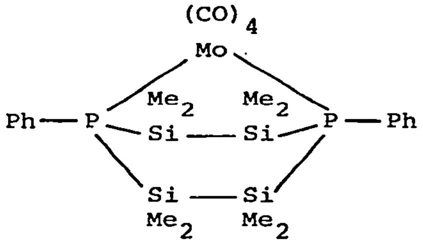


(<u>50</u>)

<u>Silicon Compounds.</u> In the solid state, the diphosphatetrasilahexane (<u>51</u>) lies on a centre of symmetry with the P_2Si_4 ring in the chair conformation.[173] Ring angles at phosphorus and silicon are 104.4 and 104.9° respectively intermediate between those in the cyclic hexaphosphane and hexasilane molecules and the Si-P and Si-Si distances, 2.252 and 2.345Å respectively, show no evidence for (p-d)π bonding. When (<u>51</u>) behaves as a bidentate ligand in the $Mo(CO)_4$ complex (<u>52</u>), the ring is forced to adopt a boat conformation.[174]



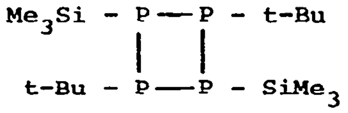
(<u>51</u>)



(<u>52</u>)

The silylphosphine Ph_3SiPPh_2 can be obtained when triphenylchlorosilane and lithium or sodium diphenylphosphide react in THF solution and general methods for the preparation of Ph_2PMR_3 compounds are discussed.[175]

Silyl substituted linear and cyclic polyphosphoranes result from reactions between organodichlorophosphanes and the lithium derivative, $(Me_3Si)_2PLi.2THF$.[176] With the methyl and phenyl dichlorides, the initial products are $(Me_3Si)_2PRP(SiMe_3)_2$, where R = Me or Ph, but on heating to ca. 130°C thermal rearrangement occurs in both cases to give <u>inter alia</u> $(Me_3Si)_3P$, $(Me_3Si)_2PP(SiMe_3)_2$ and $P_5(SiMe_3)_3R_2$. The major product from t-$BuPCl_2$, on the other hand, and two moles of the lithium compounds is the cyclotetraphosphane (<u>53</u>) which on photolysis gives in addition to $(Me_3Si)_3P$, compounds with the formulae $P_5(SiMe_3)_n(t\text{-}Bu)_{5-n}$ where n = 2 or 3; $P_4(SiMe_3)_n(t\text{-}Bu)_{4-n}$ where n = 1 or 3, and $P_3(SiMe_3)_n(t\text{-}Bu)_{3-n}$. An isomeric form of



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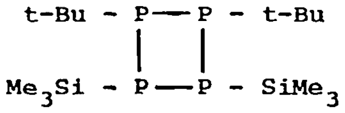
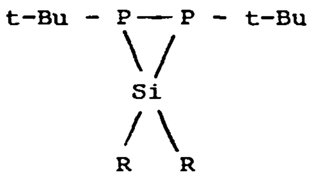


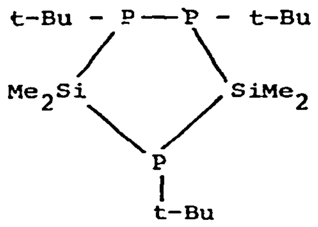
(54)

(53) formulated as (54) is also found among the products obtained from a reaction between $t\text{-}BuPCl_2$ and one mole of the lithium salt.

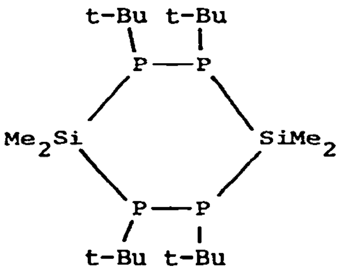
Members of a new class of phosphorus-silicon compounds based on a P_2Si ring system have been isolated from [2+1] cyclocondensation reactions between a diorganodichlorosilane and the dipotassium salt $K_2[(t\text{-}Bu)PP(t\text{-}Bu)]$.[177] Two compounds represented by structure (55) have been identified and the reaction leads also to



(55, R = Me or Ph)



(56)

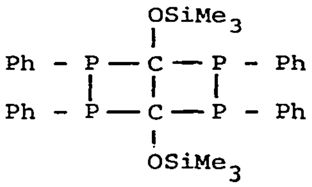


(57)

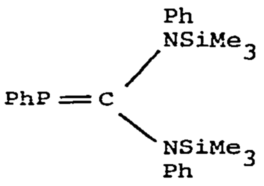
small quantities of larger ring silaphosphanes formulated as (56) and (57).

There is no evidence for the formation of the silylamine Si_3NH_2 as an intermediate in the liquid phase reaction between silylphosphine SiH_3PH_2 and ammonia; the products are PH_3, $(SiH_3)_2NH$ and $(SiH_3)_3N$.[178]

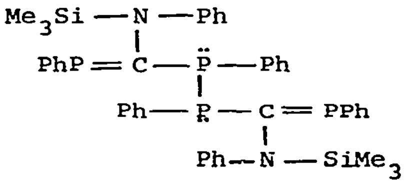
The reaction between $PhP(SiMe_3)_2$ and phosgene has been reexamined.[179] The latter, known to be a good chlorinating agent in phosphorus chemistry gives phenyldichlorophosphine as the final product, but the process is now known to be stepwise yielding $PhP{:}C(OSiMe_3)PPh(SiMe_3)$ as the first intermediate. Reaction with a further mole of $COCl_2$ then gives $[(PhP)_2(COSiMe)]_2$ by loss of Me_3SiCl and carbon monoxide. An X-ray structure for this second compound reveals the unusual tetraphosphabicyclohexane structure (58).[180] The two sets of phosphorus atoms are non-equivalent in agreement with ^{31}P n.m.r. data which are interpretable as an AA^1BB^1 spin system. If $PhP(SiMe_3)_2$ is treated with $Cl_2C{:}NPh$, the nitrogen analogue of phosgene, the first product isolated is (59) which results from a double condensation with a 1,3-silyl shift.[181]



(58)



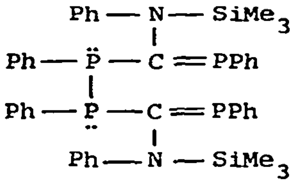
(59)



(60)

On further reaction, PhNC is eliminated and a yellow oil identified from its characteristic ^{31}P n.m.r. spectrum as a tetraphosphahexadiene, present in both the meso (60) and racemic (61) forms.

Carbon disulphide, isocyanates and isothiocyanates can be readily



(61)

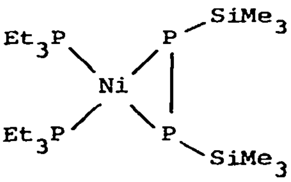
inserted into the Si-P bond of trimethylsilyl-diphenylphosphine as shown in equations (37) and (38).[182]

$$Me_3SiPPh_2 \ + \ CS_2 \ \longrightarrow \ Me_3SiSC(S)PPh_2 \qquad ...(37)$$

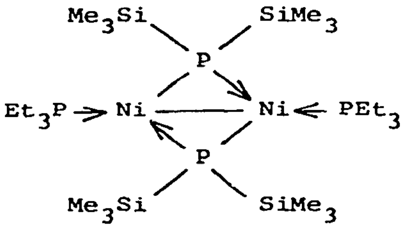
$$Me_3SiPPh_2 \ + \ RNCX \ \longrightarrow \ Me_3SiNRC(:X)PPh_2 \qquad ...(38)$$

(X = O or S)

The lithium salt, $LiP(SiMe_3)_2$ reacts in THF solution at low temperature with the nickel complex $NiCl_2(Et_3P)_2$ giving two new compounds (62) and (63) containing Ni-P ring systems.[183] The



(62)



(63)

reaction sequence is probably complex with $(Et_3P)_2NiClP(SiMe_3)_2$ and $(Et_3P)_2Ni[P(SiMe_3)_2]$ as possible intermediates.

Silyl-substituted polyphosphines such as $P_7(SiMe_3)_3$, $P_{10}(SiMe_3)_4$ and $P_{13}(SiMe_3)_5$ are known as products from reactions between P_4, Me_3SiCl and sodium-potassium alloy but it has now been shown that similar compounds result when a pure phosphide, e.g. Na_3P_{11} or Cs_3P_{11} reacts with Me_3SiCl in toluene.[184] These reactions provide a simple route to $P_{11}(SiMe_3)_3$ and in a similar way Rb_3As_7 has been converted to $As_7(SiMe_3)_3$. The latter has a structure similar to that of $P_7(SiMe_3)_3$ with As-As distances of 2.407, 2.427 and 2.444Å. The photoelectron spectrum of $P_7(SiMe_3)_3$ has been reported and analysed and is used as a model for the unknown hydride P_7H_3.[185]

5.2.3 Bonds to Halogens

The +3 Oxidation State. Although nickel powder reacts slowly with PF_3, such reactions can be enhanced if the nickel is produced with sulphide activators to give, for example, a 62% yield of $Ni(PF_3)_4$ over a 46h period.[186] With PF_2H, the active nickel gives only PF_3H_2 and PF_3 but the elusive $Ni(PF_2H)_4$ complex can be obtained by a low temperature metal atom-ligand condensation reaction.[187]

I.r. and Raman data for PF_2H and PF_2D have been assigned and a normal coordinate analysis carried out.[188]

An improved synthesis for $(\eta^1\text{-}C_5H_5)PF_2$ from PF_2Br and the thallium(I) salt of cyclo-pentadiene at -70°C has been reported together with reactions leading to $(\eta^1\text{-}C_5H_5)_2PF$, $(\eta^1\text{-}CH_3C_5H_4)PF_2$ and $(\eta^1\text{-}CH_3C_5H_4)_2PF$.[189] Each of the compounds is air, moisture and temperature sensitive, the most stable compound being $(C_5H_5)PF_2$, and all react to give the expected borane complexes with B_2H_6.

Reactions based on oxidative addition of alcohols to $PhPF_2$ followed by elimination of hydrogen fluoride lead via formation of the five coordinate phosphoranes $PhPF_2H(OR)$, where R = Me, Et, CF_3CH_3, t-Bu, etc. to the phosphanes PhPF(OR).[190]

Electron diffraction data for $MeNHPF_2$ have been interpreted in terms of a single conformer in which the phosphorus lone pair is <u>trans</u> to the N-C bonds, but the presence of up to 20% of a second conformer cannot be completely excluded.[191] Major parameters are P-F 1.593, P-N 1.648Å, F-P-F 94.1, F-N-P 100.6 and P-N-C 125.3°, the latter value probably indicating that the bonds to nitrogen are coplanar. Such planarity is certainly found in both $(F_2P)_3N$ (see ref.200) and $(H_3Si)_3N$ and in continuation of this work, the two mixed compounds $(F_2P)_2(H_3Si)N$ and $(F_2P)(H_3Si)_2N$ have been synthesised by the reactions in equations (39) and (40).[192] The

$$NH(PF_2)_2 + SiBrH_3 + NMe_3 \longrightarrow (F_2P)_2(H_3Si)N + Me_3NHBr \quad ...(39)$$

$$PF_2[NH(SiH_3)] + SiBrH_3 + NMe_3 \longrightarrow (F_2P)(H_3Si)_2N + Me_3NHBr \quad ...(40)$$

products are stable in the liquid and gas phases at room temperature but react explosively with air. They react with diborane to give adducts but with HBr and water, the P-N and Si-N bonds respectively are cleaved.

The crystal structure of bis(difluorophosphino)amine has been determined at -110°C showing the trigonal planar structure reproduced in Figure 1.[193] P-N and P-F distances are respectively 1.67 and 1.58Å and the P-N-P and F-P-F angles are 120.7 and 95.7° respectively.

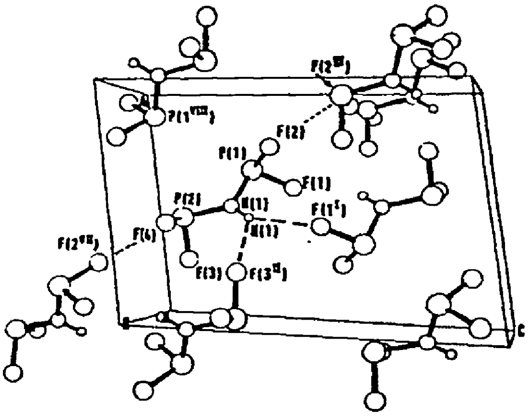
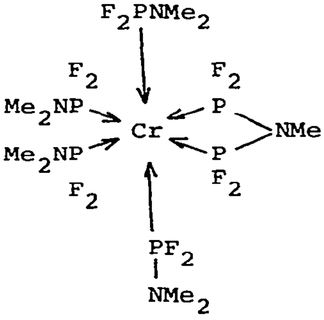


Figure 1. Arrangement of the $(F_2P)_2NH$ molecules in the unit cell (reproduced by permission from J. Chem. Soc. Dalton Trans., (1979)1192).

The ligand properties of the methylamino-difluorophosphines continue to be of interest as, in addition to behaving as neutral donors, there is evidence for cationic behaviour in the complexes between strong transition metal nucleophiles such as $NaMoCp(CO)_3$ and $MeN(PF_2)_2$.[194] Reactions occur in both 1:1 and 1:2 ratios in THF to give complexes formulated as $[F_2PNMePF]^+[MoCp(CO)_3]^-$ and $[F_2PNMeP]^{2+}[Mo_2Cp_2(CO)_4]^{2-}$ on the basis of spectroscopic data, in particular the observation of a highly deshielded phosphorus atom in the ^{31}P n.m.r. spectra. Further details are now available on the complexes formed between metal vapours and Me_2NPF_2 or $MeN(PF_2)_2$ either singly or as a 4:1 mixture that were mentioned in last year's report. In some cases the products parallel those from metal carbonyls but with iron vapour a small amount of Fe$[MeN(PF_2)_2]_4$ not known from carbonyl reactions has been isolated. Its X-ray structure shows a trigonal bipyramidal structure with three mono- and one bidentate ligand. The mixed ligand complex $[Cr(Me_2NPF_2)_4MeN(PF_2)_2]$ has the octahedral based structure (64). U.v. photoelectron spectra of $MeN(PF_2)_2$ (=L) and the ML_3, M = Cr,



(64)

Mo, and W, $(NiL_2)_n$ and Rh_4L_6 complexes have been measured.[196]

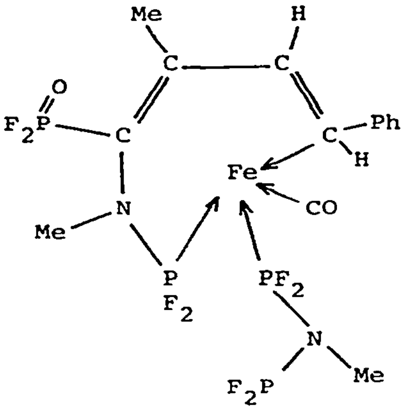
Complexes of the corresponding N-phenyl ligand, $PhN(PF_2)_2$ (=L), have been isolated and in comparison with the N-Me analogues the major effect of phenyl substitution is a stabilisation towards hydrolysis of the bond between nitrogen and an uncomplexed phosphorus atom.[197] Among the compounds isolated were ML_3 where M = Cr, Mo or W, $Fe_2(CO)_5L_2$, $(CpFeL)_2$, $Co_2(CO)_2L_3$, Co_2L_5 and $Co_4(CO)_6L_3$.

The benzalacetone complex $(PhCH{:}CHCOMe)Fe(CO)_3$ reacts with $MeN(PF_2)_2$ in boiling hexane to give a yellow complex $[PhCH{:}CHC(Me){:}C(POF_2)NMePF_2]Fe(CO)(PF_2)_2NMe$, as a result of a series of reactions involving an intramolecular Wittig type reaction as a key step.[198] Its structure (65) is unusual in that the iron is coordinated by a novel tetrahapto-1,3-diene ligand.

The preparation of $Me_3SiN(PF_2)_2$ and $N(PF_2)_3$ by reactions which involve Si-N or Sn-N bond cleavage have been reported following the methods outlined in equations (41) and (42).[199]

$$(Me_3Sn)_2NSiMe_3 + 2PF_2Br \longrightarrow Me_3SiN(PF_2)_2 + 2Me_3SnBr \qquad \ldots(41)$$

$$N(SnMe_3)_3 + 3PF_2Cl \longrightarrow N(PF_2)_3 + 3Me_3SnCl \qquad \ldots(42)$$



(65)

The structure of $N(PF_2)_3$ has been determined from electron diffraction data and is of special interest as the simplest phosphorus analogue of trisilylamine with PF_2 groups free to rotate or oscillate without either steric crowding or restrictions due to H•••F bonding.[200] The molecule has a planar skeleton with C_{3h} symmetry; the important molecular parameters are P-N 1.712, P-F 1.574A°, F-P-N 99.0 and F-P-F 97.1°.

Low temperature X-ray studies on both phosphorus trichloride[201] and tribromide[202] show crystallisation in the orthorhombic space group Pnma with P-Cl distances of 2.034 and 2.019Å and P-Br distances of 2.212 and 2.216Å. The independent angles are 100.04 and 100.19° for the chloride and 101.3 and 99.0° for the bromide. A final difference Fourier synthesis showed residual electron density at 0.8Å from the phosphorus atom in PCl_3, i.e. in the position expected to be occupied by the lone pair of electrons, while by analogy with the $POBr_3$ structure the P- lone pair distance in PBr_3 was estimated to be 1.27Å. If longer contacts are considered, the phosphorus atom in PBr_3 is considered to be at the centre of a bicapped trigonal prism of bromine atoms.

Phosphoryl chloride from atmospheric oxidation is well known to be the major impurity in phosphorus(III) chloride but it now possible to absorb such phosphorus(V) impurities to a level below 0.1% using granulated silica gels.[203]

Phosphorus(III) chloride or bromide in the presence of protonic catalysts, e.g. hydrogen chloride gas, react with dialkylfluorophosphites to give reorganisation products as shown in equation (43),

$$(RO)_2PF + PCl_3 \longrightarrow ROPFCl + ROPCl_2 \qquad ...(43)$$

providing a convenient route to chlorofluoro- and bromofluorophosphites.[204]

Continuing research into the behaviour of phosphorus halides and 100% sulphuric acid or oleum, data have now been obtained for reactions with the phosphorus trihalides.[205] With the chloride, oxidation and protonation occurs to give $PCl_3(OH)^+$ followed on standing by $PCl_2(OH)_2^+$ and $P(OH)_4^+$.[205] Reactions with the bromide and iodide are similar but complications arise owing to the liberation of the free halogen. However, in the bromide system there is ^{31}P n.m.r. evidence for the formation of all cations in the series $[PBr_n(OH)_{4-n}]^+$. In the presence of a halogen tetrahalogenophosphonium cations $[PBr_{4-n}Cl_n]^+$ are formed from PCl_3 or PBr_3 in 25% oleum, fluorosulphuric acid or 100% sulphuric acid,[206] together with solvolysed species, such as $[PBr_{3-n}Cl_n(OH)]^+$ and $PF_3O(HSO_3F)$, and although iodine containing cations, e.g. $[PI_nX_{4-n}]^+$ where X=Cl or Br, were not observed, the partially solvolysed species $[PI_nX_{3-n}(OH)]^+$ could be identified in solution.

Both thiourea (L) and N,N'-diethyldithiooxamide (LL) from complexes with the Group 5 trichlorides and the species $PCl_3L(DMF)_2$, $AsCl_3.L(DMSO)_3$, $AsCl_3.L_3$, $BiCl_3.L_3$, $SbCl_3.L_{2.33}$ and $SbCl_3(LL)_{1.5}$-$(C_2H_4Cl_2)$ have been obtained.[207]

Evidence has been obtained for the formation of monomeric phosphoryl(III) chloride and bromide, OPX, in reactions between PX_3 and quartz at high temperatures.[208] The processes, investigated using a quartz null manometer, showed that at ca. 550°C for PCl_3 and ca. 800°C for PBr_3 there was the start of a reversible process leading to an increase in the number of gas molecules. The equilibrium which was rapidly established is not associated with decomposition of the trihalide itself and the process shown in equation (44) is suggested. From the thermodynamics of the system,

$$2PX_3 + SiO_2 \rightleftharpoons 2OPX + SiX_4 \qquad ...(44)$$

the standard enthalpies of formation for OPCl and OPBr are -65.6 ± 3.6 and -53.7 ± 4.3 kcal mol^{-1} respectively.

A number of new i-propyl and t-butyl esters and thioesters have been prepared from bis(trifluoromethyl)chlorophosphine.[209] The reaction with t-butanol to give $(CF_3)_2P(O)t\text{-}Bu$ has been investigated in some detail to show that it probably proceeds via the processes in equations (45)-(47). Reactions of both $(CF_3)_2P(O)Cl$ and $(CF_3)_2P(S)Cl$ with alcohols in the presence of tertiary amines give

$$(CF_3)_2PCl + t\text{-}BuOH \longrightarrow (CF_3)_2P(O\text{-}t\text{-}Bu) + HCl \quad ...(45)$$

$$(CF_3)_2P(O\text{-}t\text{-}Bu) + HCl \longrightarrow (CF_3)_2POH + t\text{-}BuCl \quad ...(46)$$

$$(CF_3)_2POH + t\text{-}BuCl \longrightarrow (CF_3)_2P(O)t\text{-}Bu + HCl \quad ...(47)$$

phosphinic acid esters, e.g. $(CF_3)_2P(S)OR$, but there is competition particularly with t-butanol from salt forming reactions which lead to isobutene evolution and $[Me_4NH]^+[(CF_3)_2PSO]^-$.

The +5 Oxidation State. Although phosphorus pentafluoride is a well known Lewis acid, in combination with SbF_5 it shows basic properties and a compound with the stoichiometry $PF_5.3SbF_5$ has been characterised as $PF_4[Sb_3F_{16}]$.[210]

A new P(III) - P(V) compound in which the latter is in five-fold coordination has been successfully synthesised following the method in equation (48),[211] but the direct reaction between PF_5 and F_2PNH_2

$$PF_2[NH(SiH_3)] + PF_5 \longrightarrow F_2PNHPF_4 + SiFH_3 \quad ...(48)$$

was not successful. Similarly no success was recorded in reactions between PF_3O and PF_3S and $PF_2[NH(SiH_3)]$ which might have given other mixed valence secondary amines. A detailed n.m.r. investigation for F_2PNHPF_4 showed different fluorine environments in the PF_4 groups, implying that pseudo-rotation is slow on the n.m.r. time scale and rotation about the P-N bond is restricted.

A zwitterion with phosphorus in both four- and sixfold coordination results when methyl bis(tetrafluorophosphorane) and Me_3SiNMe_2 react.[212] The compound is formulated on the basis of n.m.r. data as $F_5\bar{P}\text{-}CH_2\text{-}P\overset{+}{F}(NMe_2)_2$.

Variable temperature n.m.r. data for CF_3MePF_3 show that the axial and equatorial fluorine atoms can be resolved at 163K and the pseudo-rotation barrier is calculated to be ca. 8.8kcal mol^{-1}.[213] The equivalent barrier in $(CF_3)_2PF_3$ is considered to be 1 - 3 kcal thus accounting for the non-observation of distinct fluorine environments in this compound. Line shape analysis of the proton decoupled ^{31}P and ^{19}F n.m.r. spectra shows that Berry pseudorotation and rotation of the MeS group are important in understanding the fluxional behaviour of $CF_3PF_3(SMe)$.[214]

A Raman spectral study shows that PCl_4AsCl_6 and $AsCl_4SbCl_6$ decompose in the melt to $AsCl_3$, Cl_2 and either PCl_5 or $SbCl_5$ but at 500°C for PCl_4SbCl_6 there is evidence for PCl_4^+ and $SbCl_6^-$ ions.[215] A similar investigation for $(PCl_4)_2Ti_2Cl_{10}$ is summarised in equation (49) and the mono phosphonium salt $(PCl_4)Ti_2Cl_9$ loses $TiCl_4$ on heating to give PCl_4TiCl_5.[216]

$$(PCl_4)_2Ti_2Cl_{10} \xrightleftharpoons{185^\circ C} 2PCl_4TiCl_5 \rightleftharpoons 2PCl_4^+ + 2TiCl_5^- \qquad \ldots(49)$$

In liquid sulphur dioxide solution, both OPF_3 and $OP(NCO)_3$ form weak manganese or nickel complexes with the formula $[ML_n](AsF_6)_2$ for M = Mn or Ni and n = 2 or 4.[217]

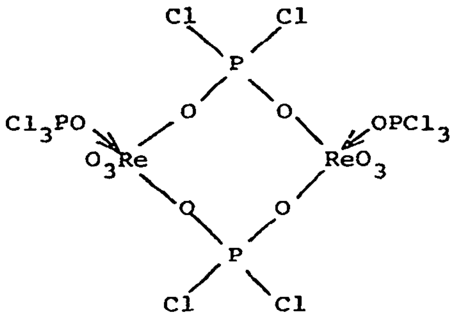
On reaction with $OPCl_3$, uranium pentachloride is reduced to the +4 state and $UCl_4.2(OPCl_3)$ can be isolated.[218] A bromine analogue can also be obtained and their i.r. spectra assigned on the basis of octahedral geometry with the two phosphoryl halide molecules in cis positions. Further chlorine evolution occurs when chlorine monoxide and the UCl_4 complex react and a solvated dichlorophosphate, $UO_2Cl(O_2PCl_2).OPCl_3$ can be isolated.

Tungsten nitride chloride, $WNCl_3$, can be isolated from an excess of $OPCl_3$ as the solvate $(WNCl_3.OPCl_3)_4.2POCl_3$ whose structure is based on a planar W-N eight membered ring.[219] The $OPCl_3$ molecules are weakly coordinated to each metal atom completing a distorted octahedral environment. Phosphoryl chloride is also the solvent in reactions of WCl_6,[220] $ReCl_5$,[221] or $MoCl_5$[222] with chlorine and either cyanogen chloride or trichloroacetonitrile. The products are N-chloroalkyl nitride chlorides as shown for $MoCl_5$ in equations (50) and (51). The product in the former is also obtained when a

$$MoCl_5.POCl_3 + CNCl + \tfrac{1}{2}Cl_2 \longrightarrow Cl_3PO \rightarrow Cl_4Mo{\vdots}NCCl_3 \qquad \ldots(50)$$

$$MoCl_5.POCl_3 + Cl_3CCN + \tfrac{1}{2}Cl_2 \longrightarrow Cl_3PO \rightarrow Cl_4Mo{\vdots}NC_2Cl_5 \qquad \ldots(51)$$

mixture of $MoCl_5$ and potassium cyanide is chlorinated at 80°C in $OPCl_3$ solution; an X-ray structure has been obtained for the product of equation (51). A dichlorophosphate (66) is considered to be the product from a reaction between Cl_2O and rhenium



(66)

pentachloride in $OPCl_3$ solution.[223]

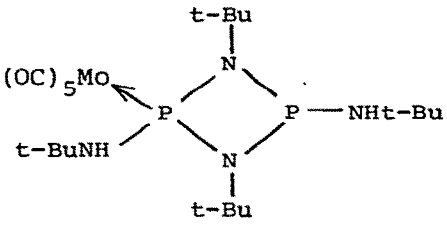
Hydrolysis of the adduct $PBr_3.CHBr_3.AlBr_3$ is a convenient route to dibromomethylphosphic dibromide, $CHBr_2P(O)Br_2$ and the bromines attached to phosphorus can be replaced by OR, NMe_2 and F groups on reaction with respectively alcohols, dimethylamine and antimony(III) fluoride.[224]

Although hydroxylamine and diphenylphosphinic chloride, Ph_2POCl, react in benzene to give the O- substituted derivative $Ph_2P(O)ONH_2$ rather than the N- substituted isomer,[225] the latter, $Ph_2P(O)NHOH$, can be obtained using O-trimethylsilyl hydroxylamine.[226] The reaction probably proceeds via $Ph_2P(O)NHOSiMe_3$ from which the product can be released by treatment with methanol.

5.2.4 Bonds to Nitrogen

Vibrational spectra for $P(NR_2)_3$ where R = Me or Et and for the arsenic analogues have been analysed in terms of overall C_3 molecular symmetry and C_s symmetry for the isolated NR_2 units.[227] In an attempt to define more clearly the conformation of ligated tris(dimethylamino)phosphine, molecular orbital calculations for the model compound $P(NH_2)_3$ and an X-ray structure determination for $[(Me_2N)_3P]_2Fe(CO)_3$ have been carried out.[228] The latter shows the iron atom in trigonal bipyramidal coordination but interestingly the two phosphine groups occupying the axial positions adopt different conformations with ca. C_s and ca. C_3 symmetry respectively. These conformations are in fact related to the two considered to be of lowest energy from the m.o. calculations.

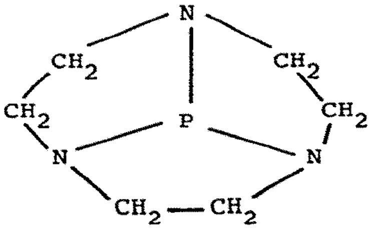
Substituted phosphines such as $P(NHR)_3$ where R = H, Me, i-Pr, Ph and PhNH are generally unstable but it has been possible to stabilise them as molybdenum carbonyl complexes.[229] The compounds are obtained by treating $(OC)_5MoPCl_3$ with either ammonia, the appropriate primary amine or phenyl hydrazine in hexane solution, but when t-butylamine was used the products were $(OC)_5Mo(H_2Nt\text{-}Bu)$ and the phosphazene complex (67).



(67)

Reactions between $(Me_2N)_3P$ and Br_2, I_2, ICl and IBr have been followed by conductometric titrations in acetonitrile showing that both 1:1 and 1:2 complexes are formed.[230] The high molar conductances point to ionic formulations such as $[(Me_2N)_3PX]X$ and $[(Me_2N)_3PX]X_3$.

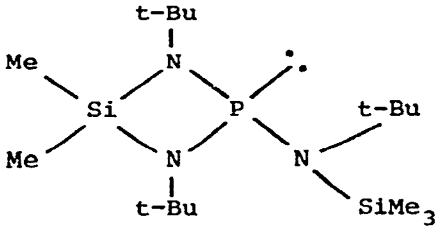
A transamination reaction between $P(NMe_2)_3$ and the cyclic amine $(CH_2CH_2NH)_3$ has been used to obtain the unstable symmetrical tricyclic aminophosphine (68).[231] The compound does not form a



(68)

borane adduct nor can it be oxidised to the phosphoryl derivative, but reactions with sulphur and selenium readily give the P=S and P=Se compounds. An X-ray structure for the former shows that the angles at nitrogen average 109° in contrast to the planarity often observed at nitrogen in systems of this type; the N-P-N angles have values of ca. 100°.

The hindered aminodichlorophosphine, $Cl_2PN(t\text{-}Bu)(SiMe_3)$, reacts with $Me_2Si(N\text{-}t\text{-}BuLi)_2$ to produce a PN_2Si system in the form of two rotamers (69) and (70).[232] Initially (69) predominates but on



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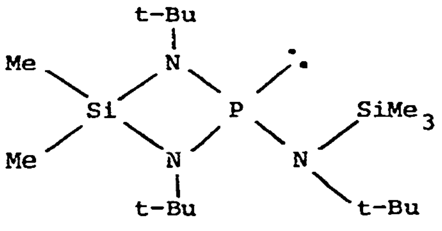
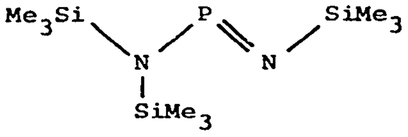


(70)

distillation this is converted into the thermodynamically more stable form (70). The two rotamers which can be separated by fractional crystallization differ in melting points and ^{31}P n.m.r. spectra; structure (69) has been confirmed by a full X-ray determination.

X-ray structures have also been reported for four compounds (71-74) each containing a two-coordinate phosphorus(III) atom.[233] The P-N bonds in (71) and (72) are respectively 1.545, 1.674 and 1.544,



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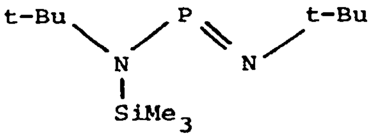

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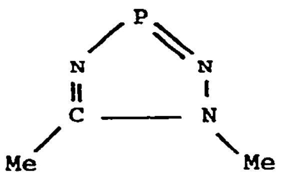

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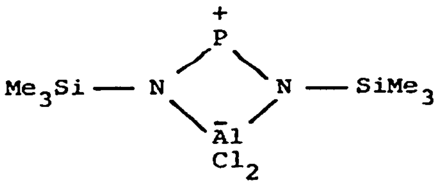
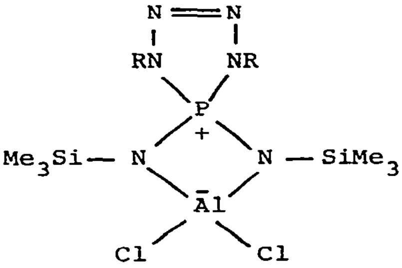
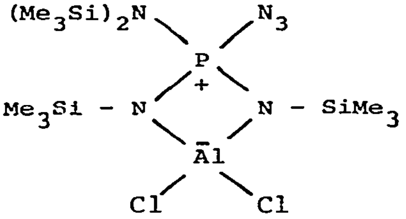


(74)

1.658Å while in the cyclic compounds the π-bond is delocalised and the two P-N distances are equal, i.e. 1.637 for (73) and 1.614Å for (74). Compound (74), which was prepared from $AlCl_3$ and $(Me_3Si)_2NP{:}NSiMe_3$ via the zwitterion $(Me_3Si)_2N{\cdots}\overset{+}{P}{\cdots}N(SiMe_3)AlCl_3^{-}$, can be oxidised to the phosphorus(V) state by free halogens, while with alkyl azides the bicyclic spiro-compounds (75) are obtained.[234] A reaction with azidotrimethylsilane, on the other hand gave a monocyclic isomer (76).

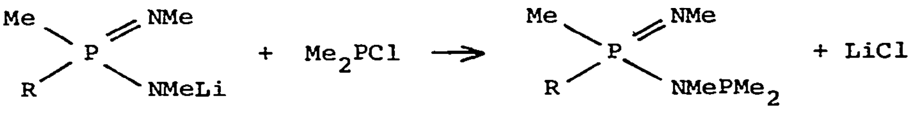


(75, R = Et or t-Bu)



(76)

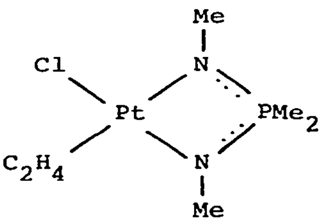
Two new members of the phosphorus amine/imine series of compounds have been obtained in good yields by the reaction in equation (52),[235] and the lithium salt, $Me_2P(:NMe)(NMeLi)$, reacts



...(52)

R = Me or t-Bu

with Zeise's salt to give compound (77).[236] A second platinum complex (78) with a monomeric metathiophosphate group as a ligand



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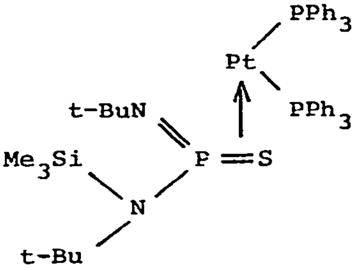
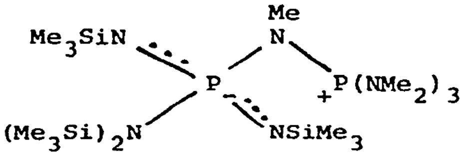


(78)

results from $(Ph_3P)_2Pt(C_2H_4)$ and the amino(imino)thiophosphorane $Me_3Si(t\text{-}Bu)NP(:S)(:N\text{-}t\text{-}Bu)$.[237] Finally in this area addition of the amino(imino)phosphorane $(Me_3Si)_2NP(:NSiMe_3)_2$ to $(Me_2N)_3P:NMe$ gives an open chain compound (79) in which each phosphorus atom is in distorted tetrahedral coordination to four nitrogen atoms.[238]



(79)

P-N bond distances vary between 1.54 and 1.79Å with the P-N-P bridge being highly unsymmetrical.

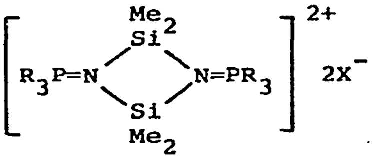
The skeleton in N-trimethylsilyliminotrimethylphosphorane $Me_3P:NSiMe_3$ is bent (P-N-Si 144.6°) from electron diffraction measurements.[239] The high value is related to steric effects from the six methyl groups; the barrier to inversion is estimated as ca. 10 $kJmol^{-1}$.

Trans-silylation reactions using the N-trimethylsilyl derivative have been used to prepare the corresponding N-bromo- and N-iodo-dimethylsilyl compounds as shown in equation (53) and, as shown in equation (54), an alternative approach uses the bis(trialkylphosphinimido)dimethylsilanes.[240] However, unless the substituents at phosphorus are bulky, the products dimerise to the cationic Si_2N_2 systems shown in (80).

$$R_3P{:}NSiMe_3 + Me_2SiX_2 \longrightarrow R_3P{:}NSiMe_2X + Me_3SiX \qquad ...(53)$$

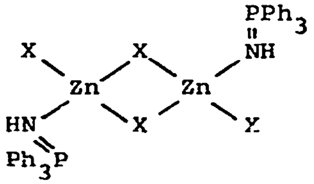
$$X = Br \text{ or } I$$

$$(R_3P{:}N)_2SiMe_2 + Me_2SiX_2 \longrightarrow R_3P{:}NSiMe_2X \qquad ...(54)$$



(80)

(81)



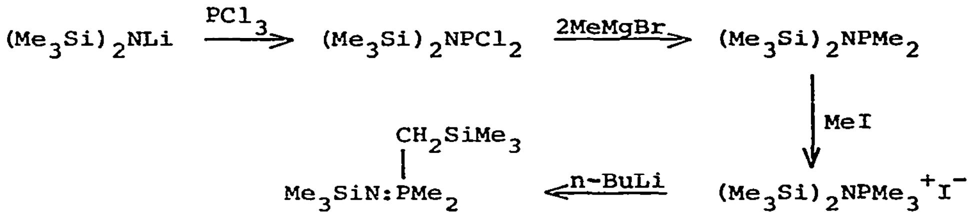
Triphenylphosphinimine complexes of zinc, cadmium, and mercury are the products when alcoholysis of $Ph_3P{:}NSiMe_3$ is carried out in the presence of anhydrous halide.[241] Dimeric structures, (<u>81</u>), are proposed for the zinc compounds, ZnX_2L for X = Cl, Br or I, while $CdBr_2$ and HgI_2 form the complexes $Cd_2Br_4L_3$ and $Hg_2I_4L_3$ respectively. With CdI_2 the product is CdI_2L_2 with molecules linked into dimers by N-H···I bonding.

A new method for the preparation of phosphazenophosphanes is summarised in equation (55).[242] Gas phase p.e.s. have been reported

$$R^1_3P{:}NSiMe_3 + P(OR^2)_2 \longrightarrow R^1_3P{:}N{\cdot}P(OR^2)_2 + Me_3SiOR^2 \qquad \ldots(55)$$

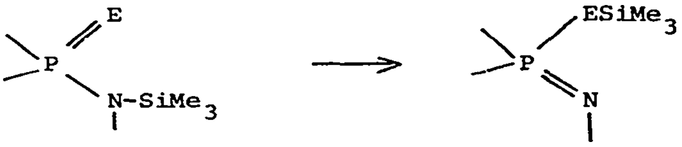
for 13 monomeric iminophosphoranes, $R_3P{:}NX$ where R = Me or Ph and X = H, Me, Et, i-Pr, t-Bu, $SiMe_3$, Ph etc., and the change in ionisation energy with type of substituent discussed.[243] In conjunction with CNDO calculations, interrelationships with the isoelectronic ylide and azomethine $>$C=N- systems are considered.

Reactions leading to the formation of some (silylmethyl)phosphinimines are outlined in Scheme 2, in which the last step with n-BuLi leads to dehydrohalogenation and an N → C silyl migration.[244]



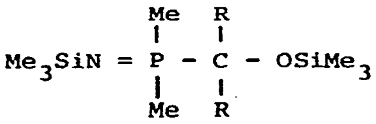
<u>Scheme 2</u>

An analogous series of reactions can be carried out using $PhPCl_2$ in place of PCl_3 in the first step. A specific feature in the chemistry of these Si-N-P compounds is the ready migration of silyl substituents as noted above. The rearrangement shown below



is irreversible for E = O or CR_2, but in silylaminophosphinimines

(E = NR) it is possible to study reversible [1,3] shifts.[245] Such shifts have been investigated for $(Me_3Si)_2NP(:NSiMe_3)PhX$ (X = Me or F), $(Me_3Si)_2NP(:N\text{-}t\text{-}Bu)Me_2$, etc. using n.m.r. spectroscopy. A related [1,5] silyl migration from nitrogen to oxygen has been observed in the reaction between acetone or hexafluoroacetone and $Me_2PN(SiMe_3)_2$ when the products are the P–C bonded phosphinimines (<u>82</u>).[246]



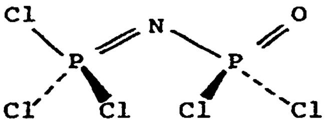
$$Me_3SiN = \overset{Me}{\underset{Me}{P}} - \overset{R}{\underset{R}{C}} - OSiMe_3$$

(<u>82</u>, R = CH_3 or CF_3)

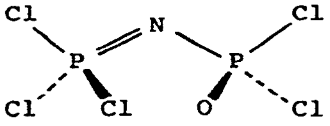
A number of new Si–N–P compounds, including $(t\text{-}Bu)Me_2SiN(Me)PX_n$ where X = F and n = 2 or 4 or X = Cl and n = 2, result from reactions between the appropriate phosphorus halide and the lithium derivative $(t\text{-}Bu)Me_2SiN(Me)Li$,[247] but when phosphorus pentachloride reacts with $(t\text{-}Bu)Me_2SiN(SiMe_3)Li$, trimethylsilyl chloride is liberated with formation of the trichlorophosphinimine $(t\text{-}Bu)Me_2SiN:PCl_3$.

Hexachlorodiphosphazonium chloride $[Cl_3P:N{\cdot}PCl_3]Cl$ can be reduced to the phosphorus(III) compound $Cl_3P:N{\cdot}PCl_2$ on reaction with 2-chloroacrylonitrile in the presence of a small amount of aluminium chloride and phosphorus(III) chloride as solvent.[248]

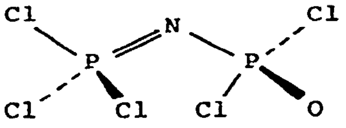
^{31}P n.m.r. data point to the presence of three rotational isomers in the melt of $Cl_3P:N{\cdot}P(O)Cl_2$ which are probably those shown in (<u>83</u>)



(<u>83</u>)

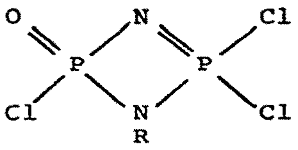


(<u>84</u>)



(<u>85</u>)

to (<u>85</u>), but in solution they either undergo fast exchange or are converted to a single conformer.[249] Reactions of this compound with the primary amines, $MeNH_2$ and $t\text{-}BuNH_2$ lead to substitution at the PCl_3 group and both $(RNH)Cl_2P:N{\cdot}POCl_2$ and $(RNH)_2ClP:N{\cdot}POCl_2$ can be isolated.[250] The reactions however give no evidence for the formation of the cyclic phosphazene (86). Structures have been obtained for two phenyl-substituted derivatives, i.e. $Ph_3P{:}N{\cdot}POCl_2$

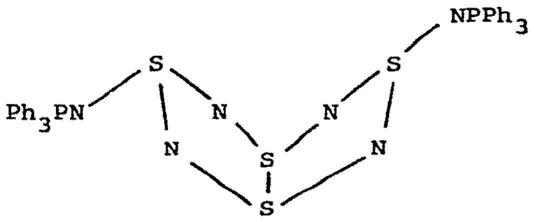


(86)

and $Ph_3P{:}N{\cdot}P(O)Ph_2$, showing significant differences.[251] The P-N bond lengths are short as expected for this type of compound but in the first the formal P=N double bond is longer (1.582Å) than the single bond (1.558Å) whereas the reverse is true for the second, i.e. 1.556Å for the double bond compared with 1.605Å for the single bond. The P-N-P angle is large probably reflecting steric effects and the conformation adopted is that where the formal P=N double bond is approximately parallel to the P=O double bond.

Under U.V. irradiation, the triazidocarbenium salt $[C(N_3)_3]^+SbCl_6^-$ undergoes a Staudinger reaction with phosphorus trichloride to give $[C(N{:}PCl_3)_3]^+SbCl_6^-$, and from X-ray data, the cation has close to C_{3h} symmetry.[252] The azido group in $NbCl_4N_3$ reacts similarly when treated with triphenylphosphine in 1,2-dichloroethane solution and $Nb(NPPh_3)Cl_4$ can be isolated.[253]

A reinvestigation using acetonitrile as solvent shows that the major product from the $Ph_3P\text{-}S_4N_4$ reaction is $(Ph_3P{:}N)_2S_4N_4$ shown by X-ray crystallography to have the structure (87).[254] In addition



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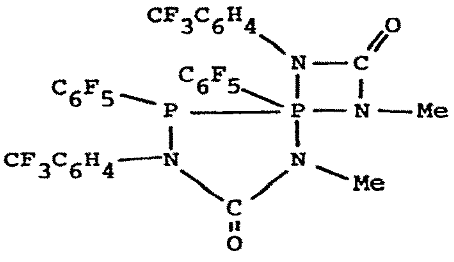
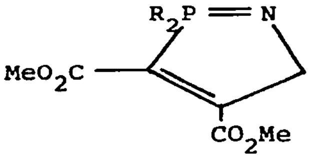


(88)

smaller quantities of the $S_4N_5^-$ salt of the novel sulphonium cation $(Ph_3P{:}N)_3S^+$ were also isolated.

A novel spirocyclic phosphorane (88) which contains both three and five coordinate phosphorus results when $C_6F_5PCl_2$ reacts with two moles of the substituted urea, $(Me_3Si)MeN{\cdot}C(O){\cdot}N(SiMe_3)C_6H_4CF_3$.[255] Coordination about the central phosphorus atom is basically trigonal bipyramidal but distorted some 20% towards the square pyramid. The three coordinate phosphorus occupies an equatorial position and the P-N axial bond distances are 1.867 and 1.743Å for the four- and five-membered rings respectively.

In contrast to the behaviour of cyclic phosphinimines, cyclic compounds such as the azaphosphole (89) readily undergoes cyclo addition reactions with, for example, arylnitrile oxides,[256] diphenylnitrileimines,[256] bromoacetophenone,[257] and syrene oxide[257]



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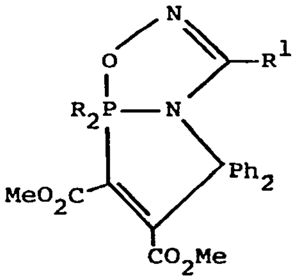

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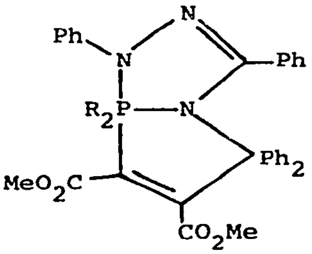

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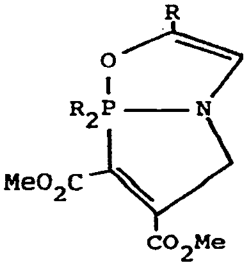
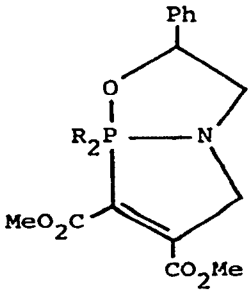


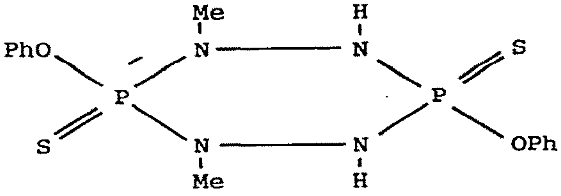
(92)



(93)

to give the stable bicyclic phosphanes (90) - (93) respectively.

Nickel(II) complexes, NiL_4X_2 where X = Cl or Br, have been obtained with hydrazidothiophosphorus ligands such as $[P(NHNH_2)(OR)_2S]^-$ where R = Et or Ph,[258] and an X-ray structure for $NiBr_2[P(NHNH_2)(OEt)_2S]_4$ shows attachment of the ligands via the terminal nitrogen atom of the hydrazine group. Variable temperature ^1H n.m.r. spectroscopy has been used to investigate the ring conformations of the *cis* and *trans* forms of the hydrazide (*94*);[259] with the *cis* form the twist conformation prevails while



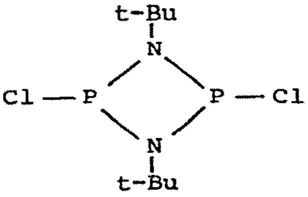
(*94*)

the *trans* isomer is predominantly in the chair conformation.

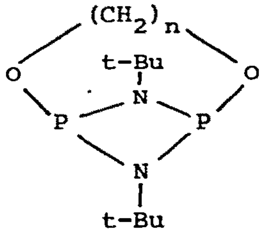
Disubstituted phosphinic acid azides, $R_2P(X)N_3$ where R = Ph, Et or CD_3 and X = O, S, or Se, have been prepared,[260] and investigated particularly by vibrational and n.m.r. spectroscopy using ^{15}N labelled compounds.[261] Azidochlorophosphanes in the series $[PCl_{6-n}(N_3)_n]^-$ where n = 0 - 6 have been identified in reactions of lithium azide with $(n\text{-}C_5H_{11})_4NPCl_6$ in dichloromethane.[262]

The tridentate ligand, $(Me_2N)_2P(O)NMeP(O)NMeP(O)(NMe_2)_2$ forms lanthanide metal complexes with the general formula $[LnL_3](ClO_4)_3$ in which the central atom is in nine fold coordination.[263]

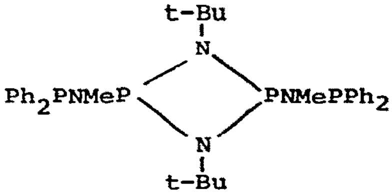
P-N Ring Compounds. Reactions between alcohols and the cyclodiphosphazane (*95*) in the presence of triethylamine lead to the



(*95*)

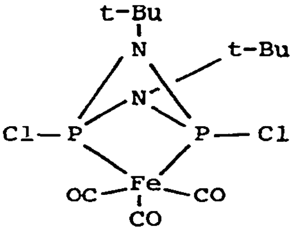


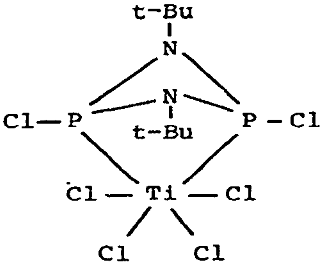
(*96*, n=2 or 3)



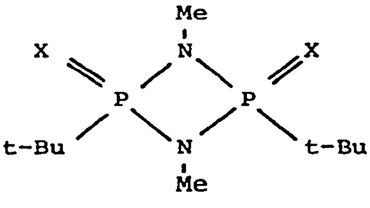
(*97*)

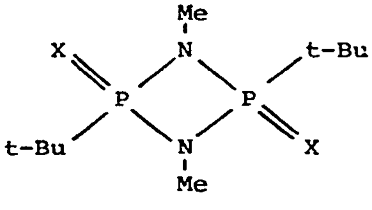
corresponding dialkoxy derivatives, in *cis* and *trans* forms,[264] which differ markedly in their ^{31}P n.m.r. shifts and in their reactivity towards sulphur, selenium and methyl iodide. With diols, the cage compounds (96) were obtained in addition to polymeric material. Reaction with two moles of $Ph_2PNMeLi$ converts the cis isomer of (95) to (97) which can be separated into the cis and trans forms by fractionation from a petrol-dichloromethane mixture.[265] An X-ray determination shows that the lower melting, more soluble, isomer has a crystallographic mirror plane normal to the ring and is thus the cis form. Compound (95) is potentially a bidentate phosphorus donor and its reactions with $Fe_2(CO)_9$, $[RhCl(CO)_2]_2$, $Mn_2(CO)_{10}$ and $TiCl_4$ have been investigated.[266] The products with $Fe_2(CO)_9$ are $Fe(CO)_3[(ClPNt\text{-}Bu)_2]$ with structure (98) and $Fe_2(CO)_7[(ClPNt\text{-}Bu)_2]$ in which the diphosphazane is a bridging group. The rhodium product, $PhCl(CO)[(ClPNt\text{-}Bu)_2]$, on the other hand is considered to have a dimeric structure and that from $TiCl_4$ to have the cis octahedral structure (99).


(98)

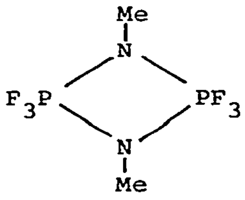

(99)

The diphosphazanes $(Et_2NPNR)_2$ with R = $CF_3\cdot C_6H_4$, $C_6H_3F_2$ etc. have been prepared.[267] Structures for the cis- and trans-diphosphazanes (100) and (101) point to planarity of the rings in the trans isomers but to significant deviations in the cis-forms, probably as a result of steric crowding.[268]

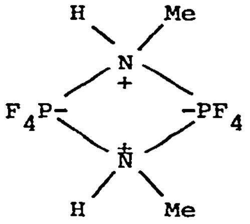

(100, X = S or Te)


(101, X = S, Te or lone pair)

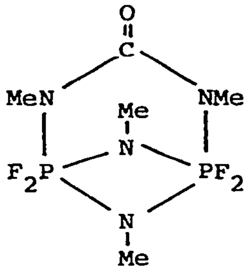
Gaseous hydrogen fluoride converts the fluorodiphosphazane (<u>102</u>) to methylammonium hexafluorophosphate and a new zwitterionic derivative (<u>103</u>),[269] while on photochemical chlorination the $N-CH_3$ groups are converted successively to $N-CH_2Cl$.[270] Reaction with a silylated N,N'-dimethylurea occurs with loss of trimethylsilyl fluoride to give (<u>104</u>) which then dimerises to a cubane-type derivative, $(MeNPF_2)_4(MeNCONMe)_2$.[271] The high resolution mass spectrum of the latter has been investigated.[272]



(<u>102</u>)

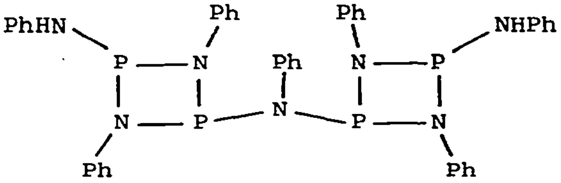


(<u>103</u>)



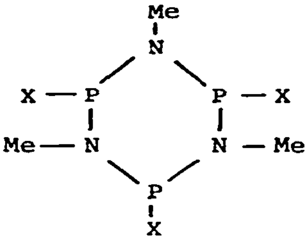
(<u>104</u>)

A dinuclear diphosphazane (<u>105</u>), isolated from a refluxing mixture of aniline and phosphorus(III) chloride, has rather surprisingly from X-ray crystallography the substituents at phosphorus in <u>cis</u> positions.[273] This calls into question an earlier report on the isolation of the monomer $[(PhNH)PNPh]_2$ from this reaction.

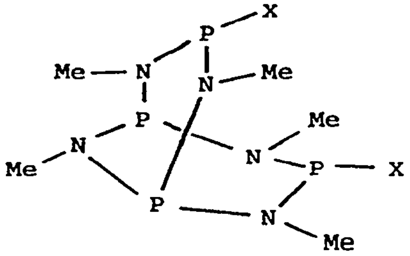


(<u>105</u>)

Phosphorus trihalides react with either heptamethyldisilazane or the methylated cyclo-trisilazane, $(Me_2SiNMe)_3$ to give intermediates such as $X_2P\cdot NMe\cdot SiMe_2X$, $X_2P\cdot NMe\cdot PX_2$ or $X_2P\cdot NMe\cdot PBr\cdot NMe\cdot SiMe_3$ but with an excess of the trihalide under reflux the final product is the cyclo-triphosphazene (<u>106</u>).[274] If this compound is treated with heptamethyldisilazane, a 1,5-bridging system can be added to



(106, X = Cl or Br)



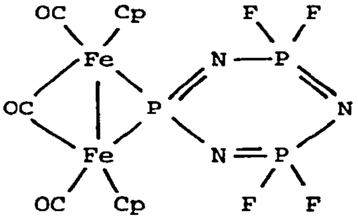
(107, X = Cl or Br)

give the bicyclic (107).[275]

Confirmation of a trans structure for the product, $[(PhNH)P(S)NPh]_2$, obtained from reactions between aniline and β-$P_4S_3I_2$ has been obtained from X-ray crystallography.[276] The compound contains two independent centrosymmetric molecules with conformations approximating to C_i and C_{2h} respectively.

A zone melting technique has been described for preparing ultrapure samples of $N_3P_3Cl_6$ and $N_4P_4Cl_8$.[277]

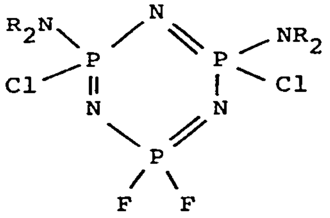
An unusual spirocyclic fluorotriphosphazene (108), whose structure has been confirmed by an X-ray determination, is the product of a reaction between $N_3P_3F_6$ and sodium dicarbonylcyclo-



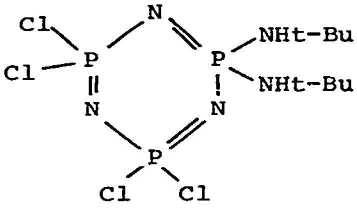
(108)

pentadienyl-ferrate.[278] Only one fluorine atom per phosphorus can be substituted in reactions of the fluorophosphazenes $(NPF_2)_{3\text{ and }4}$ with amines giving compounds of the type $N_3P_3F_4(NR^1R^2)_2$, $N_4P_4F_5(NR^1R^2)_3$ and $N_4P_4F_4(NR^1R^2)_4$; the difference in reactivity compared with the chlorine analogues is associated with the poor leaving ability of fluorine combined with the low nucleophilicity of the free amines.[279] Two kinetically stable azides, $N_3P_3F_5N_3$ and $N_4P_4F_7N_3$ result when the corresponding chlorides are treated with sodium azide in acetone, and the analogous monocyanides can be similarly obtained using KCN in acetone.[280]

^{19}F n.m.r. spectroscopy is a useful technique in assigning cis or trans configurations to the non-geminally substituted $N_3P_3Cl_4(NR_2)_2$ isomers.[281] The method depends on conversion of the compound to the geminal difluoride (109), a reaction shown to take



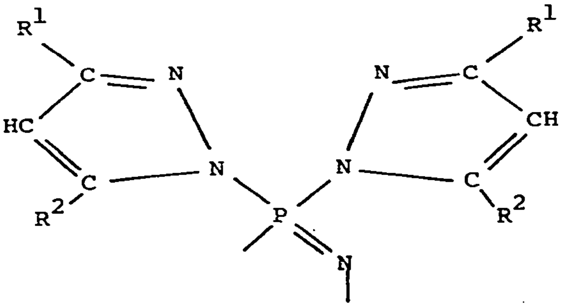
(109)



(110)

place with retention of isomer configuration; the trans isomers then give simpler spectra (δ ca. −68ppm) from the equivalence of the two fluorine atoms while more complex spectra (δ ca. −70 and −66ppm) result from the cis isomer where the two fluorine atoms are differentiated. The geminal isomer (110), obtained on substitution of two chlorine atoms in $N_3P_3Cl_6$ with t-butylamine, unusually shows two sharp i.r. peaks at 3440 and 3280 cm^{-1} associated with N-H stretching.[282] To investigate this an X-ray structure has been carried out showing that in the solid state two independent molecules are joined by a double hydrogen bonding system (N···N 3.14, 3.16Å) between an amine nitrogen atom and a ring nitrogen atom adjacent to the $P(NHt\text{-}Bu)_2$ group. Each of the N_3P_3 rings is in a slight boat conformation.

A series of 1-pyrazolyl-phosphazenes containing the repeating unit (111) has been prepared using $(NPCl_2)_{3-6}$ and an excess of the



(111, R^1, R^2 = H or Me)

appropriate pyrazole in THF.[283] I.r. and n.m.r. data indicate that π-donation to the PN ring is weak. A full structure determination for the tetrameric octa(dimethylpyrazole) derivative shows that the unit cell contains two independent molecules with similar molecular parameters. The mean P-N (ring) bond length, 1.557Å, implies that the pyrazoyl substituent behaves more like a chlorine atom than a methyl group.

The structure of $N_3P_3Cl_5(NPPh_3)$ indicates a non-planar ring with P-N bond lengths which vary between 1.58 and 1.62Å; the exocyclic group adopts a conformation (designated as type 1) in which its N-P bond is perpendicular to the adjacent P-Cl bond.[284]

Water soluble phosphazene polymers containing amino groups, i.e. $[NP(NHMe)_2]_n$ and the 3-(1-imidazolyl)propylamino analogue and up to 1500 repeating units, in conjunction with iron(II) and (III) protoporphyrin have been investigated as models for potential hemoglobin substituents.[285]

Relativelyllow yields of compounds in the series $N_3P_3Br_{6-n}(NHEt)_n$, where n = 1, 2, 4 and 6, together with resinous prodocts are obtained when $N_3P_3Br_6$ reacts with ethylamine in ether solution.[286] Two isomeric non-geminal forms exist for the compound with n = 2 but the tetrasubstitution product has a geminal structure. In addition the hydrogen bromide adducts $N_3P_3Br_2(NHEt)_4.HBr$ and $N_3P_3(NHEt)_6.HBr$ were obtained.

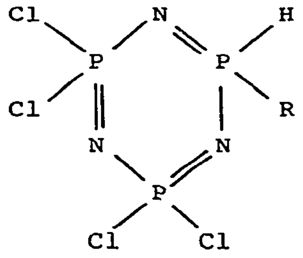
Kinetic data are now available for the reactions between $N_3P_3Cl_6$ and a variety of amines in THF solution[287] and for the $N_3P_3Cl_6$- and $N_4P_4Cl_8$-t-BuNH$_2$ reactions in acetonitrile.[288] From the first study, reactions with straight chain amines gave very similar second order rate constants but with both branched primary amines and secondary amines reaction occurs at a much lower rate. A detailed analysis of the rate data supports a two step mechanism in which the amine attacks perpendicular to the ring giving a trigonal bipyramidal intermediate, followed by inversion with departure of a chlorine atom from an axial position. The second paper[288] provides further quantitative evidence for the higher reactivity of the tetramer, ca. 200 times faster than the trimer, which is associated with a reduction in the enthalpy of activation from 20.3 kJ mol^{-1} for the trimer to 8.2 kJ mol^{-1}.

As a means of preparing triphosphazenes not accessible by other routes, the hexalithiated derivative $N_3P_3(OC_6H_4Li)_6$ has been prepared from the p-bromo derivative and n-BuLi.[289] Reactions with electrophiles such as D_2O, CO_2, Ph_2PCl and Ph_3SnCl then lead to $N_3P_3(OC_6H_4X)_6$ where X is respectively D, COOH, PPh_2 and $SnPh_3$.

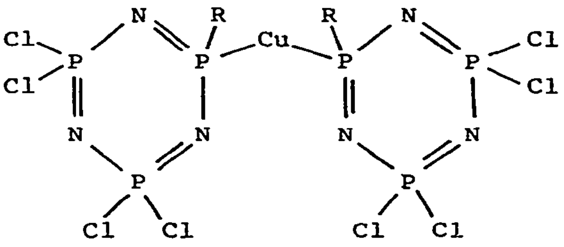
An n.m.r. investigation of $N_3Me_3P_3O_3(OMe)_3$, obtained by thermal rearrangement of $N_3P_3(OMe)_6$, showed that there were two OMe and two NMe environments which are related to the retention in solution of the solid state boat structure.[290] The geminal compounds $N_3P_3Ph_2(OMe)_4$ and $N_3P_3(NHt\text{-}Bu)_2(OMe)_4$ also readily rearrange to the N-methyl isomers but isomerisation is very slow with the non-geminal compound $N_3P_3(NMe_2)_2(OMe)_4$.

Reactions between $(NPCl_2)_3$ and 4 and NaSEt have been reinvestigated with the isolation of compounds in the series $N_3P_3Cl_{6-n}(SEt)_n$, where n = 1 - 6, and $N_4P_4Cl_{8-n}(SEt)_n$, where n = 2 - 6 and 8.[291] Both reactions follow strictly geminal paths but pairs of isomers were obtained in the tetrameric reactions for n = 3, 4 and 5. N.m.r. data, in particular ^{15}N measurements, have been obtained for the ^{15}N labelled thiophosphazenes[291] and the chlorophosphazenes, $(NPCl_2)_{3-5}$.[292]

Full details are now available on the formation of the hydridophosphazene (<u>112</u>) from $N_3P_3Cl_6$ and an alkyl Grignard reagent in the presence of $(n\text{-}Bu_3PCuI)_4$, suggesting that the reaction involves a metallophosphazene intermediate such as (<u>113</u>) which is converted to the hydride by 2-propanol.[293] This intermediate (<u>113</u>) is of broad synthetic utility and gives, for example, in the presence of alkyl halides R^2Cl the previously inaccessible geminal dialkylphosphazene $N_3P_3R^1R^2Cl_4$.[294]



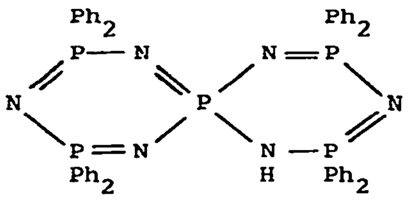
(<u>112</u>)



(<u>113</u>)

Although the hydride (<u>112</u>) itself will not react with thiophosphinyl chlorides, $R_2P(S)Cl$, its lithium derivative undergoes ready substitution by $R_2P(S)$ groups and similarly, reactions giving P-Si and P-Sn substituted phosphazenes occur with, for example,

Me_3SiCl and Me_3SnCl.[295] An X-ray structure on the spirocyclic phosphazene (114) shows that the hydrogen atom is localised on a



(114)

nitrogen atom adjacent to the spiro centre; P-N distances to the central phosphorus are 1.60, 1.60, 1.62 and 1.72Å the latter being to the NH position.[296] Friedel-Crafts reactions with a number of amino-substituted chlorotriphosphazenes point to more ready phenylation at $PCl(NR^1R^2)$ and PClPh groups than at PCl_2 groups.[297] The amount of $AlCl_3$ required is discussed and it is pointed out that an increase in reaction time leads to increased competition from C-phenylation processes. The crystal structure of one of the three known forms of $N_3P_3Ph_3Br_3$ - the c-form - melting between 162 and 164°C contains two independent molecules with both the rings in a slight chair conformation.[298] Contrary to an earlier assignment the compound has a cis arrangement of the phenyl groups.

A number of iron trimetaphosphimate complexes, including $Na_3Fe(O_6P_3N_3H_3)_2.13H_2O$, $NaFe(O_6P_3N_3H_3).8H_2O$, and $K_4Fe(O_6P_3N_3H_3)_2.5H_2O$, have been isolated from aqueous solution.[299]

Crystal structures are now available for the two platinum-phosphazene compounds cis-$PtCl_2(N_4P_4Me_8)$, MeCN and the related N,N-dihydro(octamethylcyclotetraphosphazenium)tetrachloroplatinate.[300] As shown in Figure 2, the N_4P_4 ring in the former is in the saddle conformation and is coordinated to platinum by two trans-annular nitrogen atoms. From the Pt-N distances ca. 2.03Å and the relative orientations of the heavy atom and the ring there is evidence that platinum is also partially coordinated to the π-electrons of the phosphazene ring. In the second compound, protonation has occurred at two antipodal nitrogen atoms and the ring adopts a distorted chair conformation.

Bicyclic phosphazenes (115) are the products when an excess of dimethylamine reacts in either acetonitrile or chloroform solution

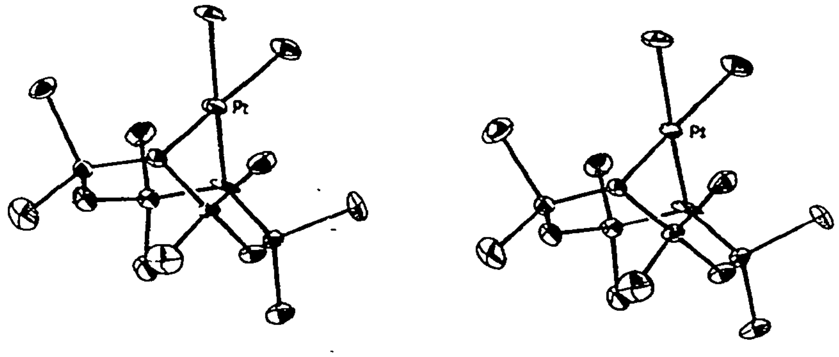
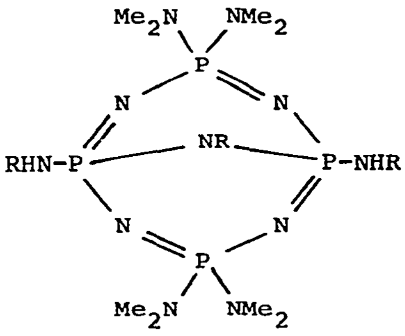


Figure 2. Stereoview of $(N_4P_4Me_8)PtCl_2$ (reproduced by permission from Inorg. Chem., 18(1979)2230).

with the non-geminally disubstituted compounds $N_4P_4Cl_6(NHR)_2$ where R = Me, Et, n-Pr, n-Bu or CH_2Ph.[301] When the amine substituent

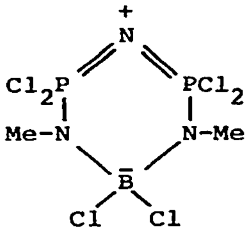


(115)

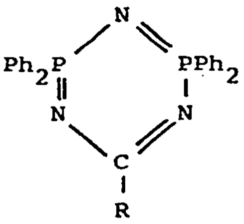
is α-branched however, no bicyclic product is formed. A similar compound but carrying four methylamino groups is obtained together with $N_4P_4(NHMe)_8$ when the tetrameric chloride reacts with methylamine in chloroform.[302] Its structure is unusual as the ring segments on either side of the bridge are planar and inclined at 122.4° and the P-N bridge bonds (ca. 1.71Å) are long.[303]

Two further tetrameric structures have been reported. In $N_4P_4Cl_7(NPPh_3)$, the ring adopts the crown-saddle conformation and the orientation of the $NPPh_3$ with respect to the adjacent P-Cl bond is intermediate between the two previously described.[304] The ring in the octapyrrolidinyl derivative has the saddle conformation with $\bar{4}$ symmetry and equal bond lengths (1.575Å) but the P-N distances to the substituents are 1.656 and 1.679Å.[305]

New members of the boradiphosphatriazene series can be prepared by reactions of the chloride (116) with, for example, SbF_3 to give B-mono- and difluorides, PBr_3 which substitutes the chlorine atoms at phosphorus, and dimethylamine which substitutes all six chlorine atoms.[306] And new derivatives of the carbon containing system P_2CN_3 (117), are the products when perfluoroalkylamidines $R_fC(:NH)NH_2$ react with the phosphazene $Ph_2PCl:N \cdot PPh_2Cl_2$.[307]

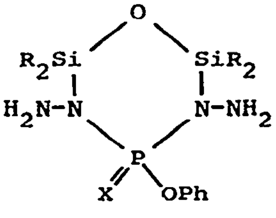


(116)

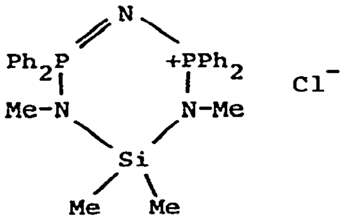


(117)

A number of new P-N-Si-O compounds based upon (118) have been isolated and fully characterised as the products of reactions between 1,3-dichlorodisiloxanes $(R_2ClSi)_2O$, where R = Me or Et, and the phosphoryl dihydrazides $PhOPX(NHNH_2)_2$, where X = O or S.[308] A P-N-Si compound (119) results when the diphosphazonium chloride $(Ph_2PCl \cdot N:PClPh_2)Cl$ and $Me_2Si(NMeSiMe_3)_2$ react in dichloromethane



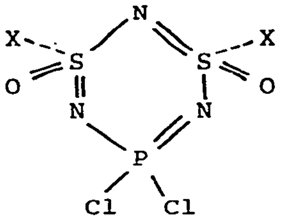
(118)



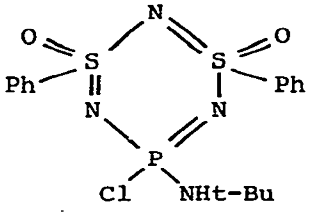
(119)

solution.[309]

Reactions between the *cis*-isomer of the mixed S-N-P species (120) where X = Cl or F and either methyl- or ethylamine led to reaction



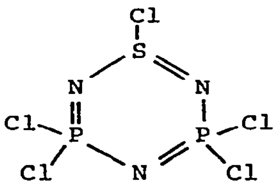
(120)



(121)

at the phosphorus centre, giving a mono substitution product, as a mixture of isomers depending on whether the amine group is *cis* or *trans* to the oxygen atoms at sulphur, and the disubstituted compound.[310] Attempts to force reaction at the sulphur centres using a more polar solvent led to resinous materials. Compound (120) where X = F, Cl or Ph reacts with triphenyl phosphinimine to give stable mono(triphenylphosphazenyl) derivatives which in some cases appear to be present as a mixture of two isomeric forms.[311] Three isomeric forms of the diphenyl derivative (121) have been isolated from a Friedel-Crafts phenylation of the corresponding P,S,S'-trichloride showing that activation of the phosphorus centre, expected from phosphazene chemistry, is not realised with these mixed heterocycles.[312] An excess of $AlCl_3$ does lead to phenylation at phosphorus but the t-butyl group is displaced giving two isomeric forms of $[NP(NH_2)Ph(NSOPh)_2]$ as the product.

A new method based on the reaction between phosphorus pentachloride and bis(trimethylsilyl)sulphur diimide in carbon tetrachloride gives the S(IV) heterocyclic (122) which on reaction with $SbCl_5$ gives the cationic complex (123).[313] An X-ray



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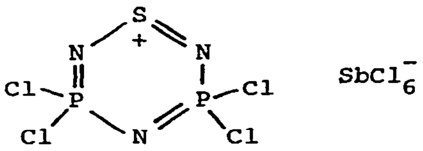


(123)

investigation points to the cation being planar, lying on a mirror plane.

5.2.5 Bonds to Oxygen

Both P_4O_6 and P_4O_7 can be oxidised by either P_4S_{10} or P_4Se_{10} to give products with an adamantane-type structure in the series $P_4O_6X_n$, where n = 1-4 for X = S, n = 1-3 for X = Se, and $P_4O_7X_n$, where n = 1-3 for X = S, n = 1 for X = Se.[314] In addition redistribution reactions in the P_4O_{10} - P_4S_{10}, P_4O_6 - P_4O_{10}, P_4O_6 - $P_4O_6S_4$ and P_4O_6S - P_4Se_{10} systems have been followed with, for example, P_4O_6S, $P_4O_6S_3$ and P_4O_7 being observed in the P_4O_6 - $P_4O_6S_4$ system. An improved synthesis of P_4O_7 from P_4O_6 at room temperature makes use of the catalytic properties of triphenylphosphine oxide.

I.r. spectra for hypophosphorous, phosphorous, phosphoric and arsinic acids and their aqueous solutions contain strong continuous absorptions which have been correlated with the ready polarisability of the P-OH···OP hydrogen bonds.[315]

A number of hypophosphite structures including $Mn(H_2PO_2)_2.H_2O$, $Zn(H_2PO_2)_2.H_2O$, $Zn(H_2PO_2)_2$,[316] $GeCl(H_2PO_2)$ and $SnCl(H_2PO_2)$[317] have been determined. Extended three dimensional structures, in which the water molecule as well as the oxygen atoms of the anion is involved (P-O distances 1.463 - 1.514Å), are observed for the two hydrates. For the isostructural germanium and tin compounds the Group 4 element is at the apex of a trigonal pyramid and is bonded to chlorine and two oxygen atoms of different hypophosphite groups in chains parallel to the c axis.

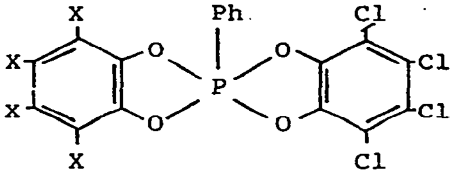
Hydrogen bonding in a range of vanadium,[318] chromium,[318,319] manganese,[318] and iron(II)[320] phosphites has been investigated by i.r. and other methods. A complex containing the tautomeric trihydroxyphosphane form of phosphorous acid, i.e. $(OC)_5Cr.P(OH)_3.H_2O$, has recently been isolated as the product of cation exchange on the triethylammonium salt $Et_3NH[(OC)_5CrP(OH)_2O]$, itself a hydrolysis product of $(OC)_5Cr.PCl_3$ in THF solution.[321] The compound shows a sharp, single ^{31}P n.m.r. signal at 156.0 ppm confirming the $P(OH)_3$ rather than the more usual $OP(OH)_2H$ structure.

A phosphoryl O-cyanate is described as the product from reaction (56) at -25°C, but especially in the presence of cyanate ions there

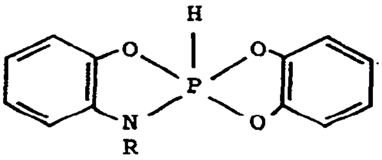
$$(PhO)_2P(O)OH + BrCN + Et_3N \longrightarrow (PhO)_2P(O)OCN + Et_3NHCl \qquad ...(56)$$

is a slow isomerisation to the well known isocyanate.[322]

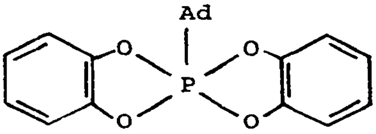
Interest is still high in the factors associated with distortions of the stereochemistry about a five coordinate phosphorus atom toward square pyramidal geometry, and a number of compounds containing chelating oxygen,nitrogen and sulphur ligands have been investigated crystallographically. Among these compounds are (124) with an apical phenyl group which has an almost perfect square pyramidal structure,[323] and (125) with the hydrogen atom in an equatorial position and structures distorted only 5.5 and 11.2% for R = H and Me respectively from the trigonal bipyramidal extreme.[324] Further examples are provided by compounds (126) - (131); the figure following the structure number is the percentage



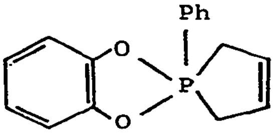
(124, X = H or Cl)



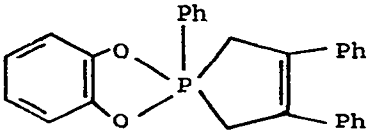
(125, R = H or Me)



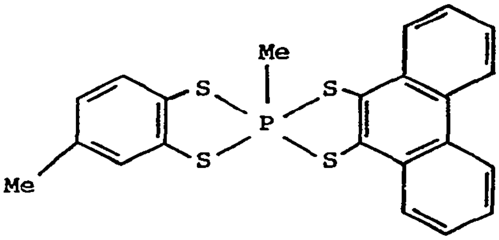
(126, Ad= 1 -adamantyl)[325] (73%)



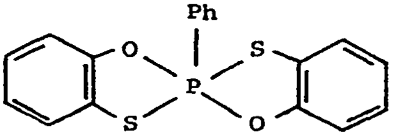
(127)[326] (82%)



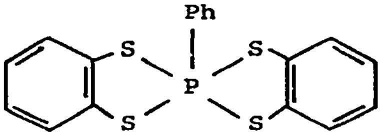
(128)[326] (86%)



(129)[327] (93%)



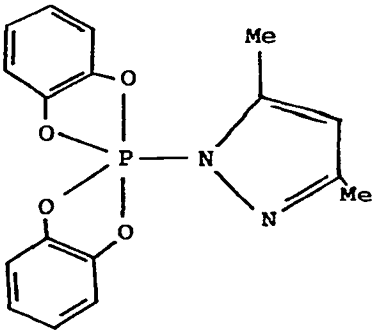
(130)[327] (43%)



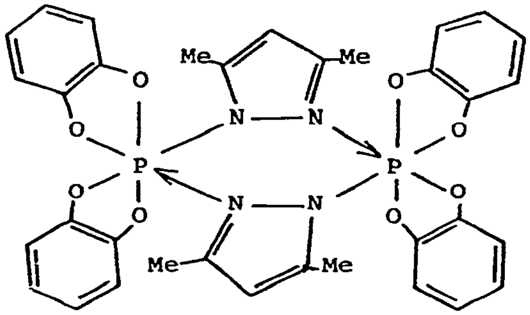
(131)[327] (35%)

distortion along the Berry pseudo-rotation coordinate toward the square pyramidal extreme.

Bis(o-phenylenedioxy)chlorophosphorane and 3,5-dimethylpyrazole react to give the spiro-phosphorane (132) which dimerises in acetonitrile solution to (133); the process can be followed by a



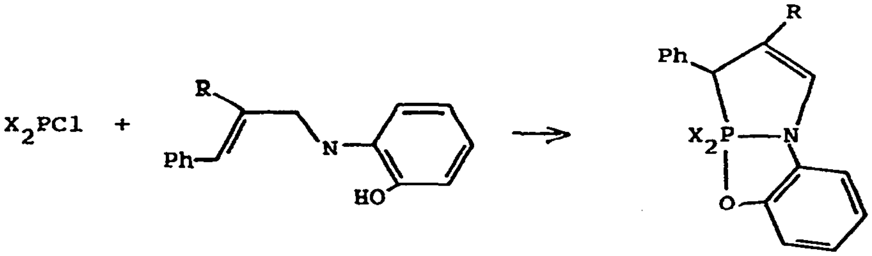
(132)



(133)

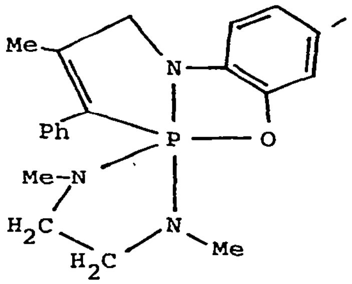
change in ^{31}P n.m.r. shift from -28 ppm for (132) to -84 ppm, characteristic of an octahedral structure for (133).[328]

A combined substitution and oxidative-addition reaction occurs when the chlorophosphines, X_2PCl where X = Me, Ph, OMe or NMe_2 or X_2 = $O(CH_2)_2O$, OC_6H_4O or $NMe(CH_2)_2NMe$, react with the o-hydroxyanil of cinnamicaldehyde (equation 57).[329] With amine substituted

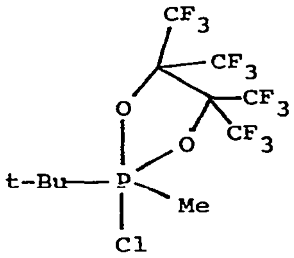


+ HCl ...(57)

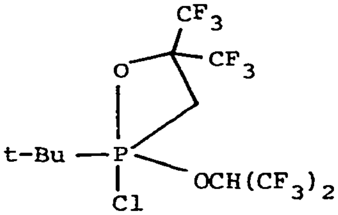
phosphines, the primary product as shown in equation (57) undergoes a 1,3-proton shift in the cinnamic aldehyde moiety and products such as (134) can be isolated. A structure determination for this compound shows two independent molecules in the asymmetric unit which are distorted 13 and 22% respectively from trigonal bipyramidal geometry along the Berry coordinate.



(134)

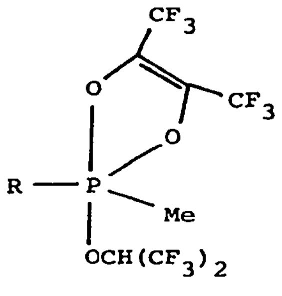


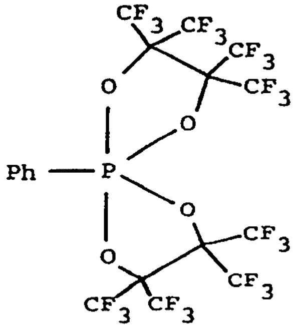
(135)



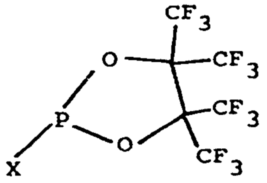
(136)

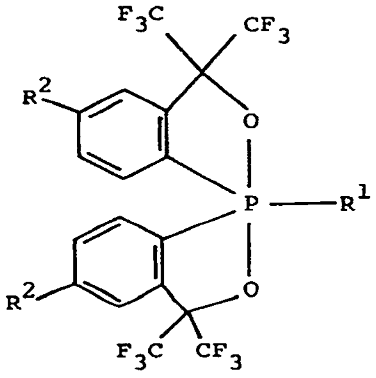
Continuing investigations on the reactivity of phosphorus(III) compounds with hexafluoroacetone now show that the t-butyl derivatives t-BuPR^{1}R^2, for R^1 = Me, t-Bu etc. and R^2 = Cl, OCH(CF$_3$)$_2$ etc., react to give compounds such as (135) or (136),[330] while fluorobiacetyl reactions with phosphinous esters RMePOCH(CF$_3$)$_2$ give the phospholes (137). The new spirophosphorane (138) can be obtained either by the oxidative addition of perfluoroacetone to phenylperfluoropinacolyl phosphine or by a reaction between difluorophenylperfluoropinacolylphosphorane and the appropriate dilithium derivative.[331] The dilithium perfluoropinacolate also reacts with phosphorus(III) halides giving (139), which yield the corresponding trihalides on treatment with chlorine or bromine.[332]


(137)


(138)

Reactions are also described using phosphoryl halides as starting materials.


($\underline{139}$, X = F, Cl or Br)


(140)

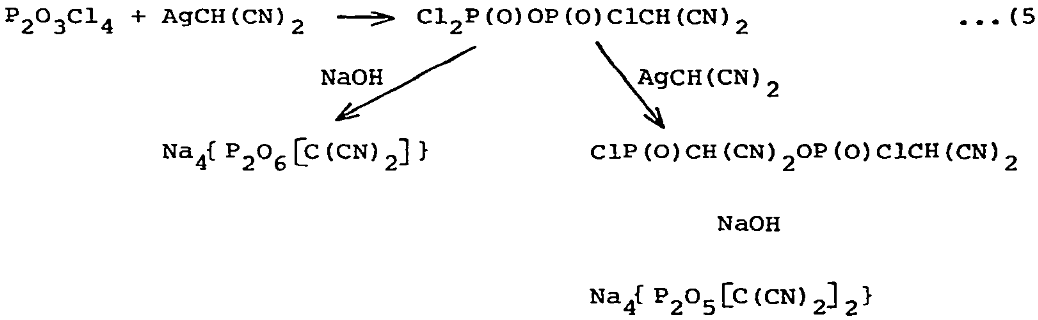
Derivatives of the bicyclic phosphorane (140) can be obtained by a number of routes including, for R^1 = OK and R^2 = H, the interaction between $POCl_3$ and the dilithium salt of hexafluorocumyl alcohol,[333] and for R^1 = OH and R^2 = Me, the reaction of $POCl_3$ and a bifunctional alkoxy Grignard reagent.[334] In addition, two very stable compounds with R^1 = H have been reported.[335]

The monomeric metaphosphate ion PO_3^- has been directly observed in the negative ion mass spectra of a number of organophosphorus insecticides,[336] and a report has now been published on the isolation of $NaPO_3$ in an argon matrix from the vapour above Na_3PO_4

at 1600K.[337] By ^{18}O enrichment techniques the product was shown to have a C_{2v} structure with a bidentate O_2PO group.

The cyclotriphosphate ion opens on reaction with cyanamide in alkaline solution to give the substituted triphosphate $P_3O_9NCN^{5-}$ which can be hydrolysed in acid solution to the ureido derivative $P_3O_9NHCONH_2^{3-}$.[338] Analogues of such cyanamides, e.g. $[PO_3C(CN)_2]^{3-}$ and $P_2O_{7-n}[C(CN)_2]_n^{4-}$ where n = 1 or 2, can be obtained from respectively $POCl_3$ or $P_2O_3Cl_4$ as shown in equations (58) and (59).[339]

$$POCl_3 + AgCH(CN)_2 \longrightarrow Cl_2POCH(CN)_2 \xrightarrow{NaOH} Na_3[PO_3C)CN)_2] \quad ...(58)$$



...(59)

Both linear and cyclic phosphate salts with formulae such as $(C_3H_6N_6)_n.H_{n+2}P_nO_{3n+1}$ where n = 2 or 3, and $(C_3H_6N_6.HPO_3)_n$, where n = 3, 4, 6 and 8, can be obtained from melamine hydrochloride and the appropriate phosphate in aqueous solution.[340]

Polymeric phenyl-phosphonate and -arsonate salts of the divalent metals Mg, Mn, Co, Ni, Zn and Cd have been prepared and diffuse reflectance measurements point to octahedral structures with bridging groups for the $M(PhMO_3).H_2O$ and anhydrous compounds.[341]

Details of the $Na_2O-P_2O_5-H_2O$ system at ca. 300°C have been elucidated by following the evaporation of sodium phosphate solutions with Na:P ratios ranging between 1.6 and 9.[342] Among the phases identified were $Na_3PO_4.NaOH$, three forms of $Na_{3-x}H_xPO_4.xH_2O$, $Na_{2.5}H_{0.5}PO_4.2H_2O$ and a new polymorph of $Na_2HPO_4.NaH_2PO_4$. The $Al_2O_3-P_2O_5-H_2O$ system contains a new phase represented as $Al_2O_3.2P_2O_5.9H_2O$, which X-ray crystallography shows to be best formulated as $[Al_2(H_{1+x}PO_4)_3(H_2O)_6][H_{3-3x}PO_4]$ where $0 \leqslant x \leqslant 1$.[343] The structure contains both isolated PO_4 tetrahedra and aggregates consisting of two AlO_6 octahedra connected by common vertices to $3PO_4$ tetrahedra.

An X-ray structure has been reported for K_2PO_3F which crystallises in the orthorhombic space group Pnma.[344] Reaction between $P_2O_3F_4$ and N_2O_5 and N_2O_3 give respectively $NO_2PO_2F_2$ and $NOPO_2F_2$ for which i.r. data are interpreted to show tetrahedral geometry of the $PO_2F_2^-$ ion and no anion-cation interactions.[345]

The new lead silver phosphate, $Pb_8Ag_2(PO_4)_6$, has an apatite structure with unoccupied halide positions and forms solid solutions with a number of other lead phosphates including $Pb_{10}(PO_4)_6O$ and $Pb_{10}(PO_4)_6Cl_2$.[346] Stoichiometric quantities of $Te(OH)_6$ and the appropriate hydrogen phosphate salt lead to $Te(OH)_6.2(NH_4)_2HPO_4$ and $Te(OH)_6.Na_2HPO_4.H_2O$, for which structures were determined.[347]

Stepwise decomposition occurs on heating $VO(H_2PO_4)_2$ and the newly prepared arsenate analogue giving for the former $VO_2P_2O_5$ at ca. 300°C and $(VO)_2P_4O_{12}$ at 540°C.[348] A new cubic modification of $V(PO_3)_3$ shown to be the cyclotetraphosphate $V_4(P_4O_{12})_3$ has been obtained by heating together a 1:6 mixture of V_2O_5 and H_3PO_4 and seeding the melt with the cubic form of either Al or $Cr(PO_3)_3$.[349] Conditions have been defined for the formation of the A and B forms of $Fe(H_2PO_4)_3$,[350] and a crystalline niobium(V) phosphate, $NbOPO_4.3H_2O$ has been isolated.[351]

Reactions between a number of lanthanide oxides and phosphoric acid leading to orthophosphates $LnPO_4.0{\cdot}5H_2O$ and $LnPO_4$, chain polyphosphates $Ln(PO_3)_3$ and ultraphosphates LnP_5O_{14}, for Ln=La, Pr, Nd and Sm, have been carried out but with CeO_2 similar reactions give both Ce(III) and Ce(IV) salts such as $CePO_4$, $Ce(PO_3)_3$, $Ce(PO_3)_4$ and CeP_5O_{14}.[352]

The indium species $InH(P_2O_7)_2^{4-}$ and $In(P_2O_7)_2^{5-}$ have been identified in aqueous solution in the pH range 6.92 - 8.27 and their formation constants evaluated.[353] The diphosphate ion in the complex $Ba[Coen_2P_2O_7]_2.4H_2O$ behaves as a bidentate ligand from solid state i.r. data and electronic spectroscopy in solution.[354]

The structure of SiP_2O_7 obtained from a P_2O_5-SiO_2 mixture at 1220K has been refined; PO_4 groups are linked in pairs to give diphosphate groups with each PO_4 group sharing three oxygen atoms with different SiO_6 octahedra to generate a three dimensional framework.[355] A crystal structure for β-$CaNa_2P_2O_7.4H_2O$ has been obtained and is of interest as such species are thought to be important in certain kinds of degenerative arthritis.[356]

Stability constants for complex formation between Ce^{3+} and the cyclic phosphates $(PO_3^-)_n$ where n = 3, 4, 6 and 8 have been evaluated by ion exchange and spectrophotometric methods,[357] and a series of UO_2^{2+} complexes with tripolyphosphate have been investigated by vibrational spectroscopy and thermal methods.[358]

The molybdenum compound, $Mo_2O_5.2P_2O_5$, from a full structure determination is the tetraphosphate $(MoO)_2P_4O_{13}$.[359] A 4:1 mixture of Kurrol's salt KPO_3 and $Pb(PO_3)_2$ heated to 700°C gives the pure cyclotriphosphate $K_4Pb(P_3O_9)_3$ whereas under different conditions two glassy phases and a highly polymeric species $[K_2Pb(PO_3)_4]_n$ can be obtained.[360] A crystal structure determination on α-$RbNd(PO_3)_4$ shows the presence of an infinite $(PO_3)_n$ chain.[361]

There is continued active investigation into the chemistry of zirconium phosphates and related inorganic ion exchanges. Alkanols and glycols can be intercalated into the layer structure of $Zr(HPO_4)_2.H_2O$ by regenerating salts formed between the exchanger and the protonated alcohols or glycols.[362] The former appear to give a double layer of extended molecules inclined at an angle ca. 55° with respect to the sheet while the latter are intercalated as a unimolecular layer. The alcohols are held by weak forces only and can readily be replaced by other polar molecules such as water, DMF, acetonitrile, etc. simply by contact with the liquid. Amine molecules can also be intercalated into α-zirconium phosphate,[363] while intercalation of ethylene oxide[364] or propylene oxide[365] into the γ-form leads to ring opening and formation of $Zr(HOCHRCH_2OPO_3)_2.H_2O$, where R = H or Me. Similar organic derivatives substituted with, for example, butyl and lauryl groups have been synthesised and show good potential for a number of chromatographic applications including reversed phase liquid chromatography.[366] Space does not permit a full discussion of other aspects of zirconium phosphate chemistry but further information is contained in references 367-373.

Decomposition of titanium-fluoride complexes in the presence of phosphoric acid gives crystalline $Ti(HPO_4)_2.2H_2O$ which can also intercalate organic molecules;[374] the compound is considered to have a structure analogous to that of γ-zirconium phosphate. The ion exchange behaviour of $Ti(HPO_4)_2.0.5H_2O$, obtained by refluxing a solution of $TiOSO_4$ in a mixture of phosphoric acid and sulphuric acids, has been investigated,[375] and a new exchanger with a variable Zr:Ti ratio results when hydrochloric acid solutions of $ZrOCl_2$ and $TiCl_4$ are added dropwise to phosphoric acid at 60°C.[376] A mixed tin(IV)-chromium(III) arsenophosphate with potential ion exchange properties has also been synthesised.[377]

5.2.6 Bonds to Sulphur or Selenium

Specific heats, melting, transition and decomposition temperatures together with enthalpies are reported from differential scanning calorimetry for P_4S_3, P_4S_4, P_4S_5, P_4S_7, P_4S_9, P_4S_{10} and the selenides P_4Se_3 and P_4Se_4, and new preparative methods have been devised for the three P_4S_4 isomers.[378] The form with an exocyclic double bonded sulphur atom results when a 1:1 mixture of P_4S_3 and P_4S_5 is slowly cooled after being heated to 770K, the α-form results from a reaction between α-$P_4S_3I_2$ and bis(trimethyltin)-sulphide and the β-form by treatment of P_4S_5 with triphenylphosphine in CS_2 solution.

P_4S_{10} is the starting material for the preparation of O,O'-diethylphosphorochloridothionate by the reactions outlined in equation (60)[379] and for the dithiophosphoric acids derived from

$$P_4S_{10} \xrightarrow{EtO H} (EtO)_2PS_2H \xrightarrow{S_2Cl_2} [(EtO)_2PS_2]_2S_2 \xrightarrow{S_2Cl_2} (EtO)_2P(S)Cl \qquad \ldots(60)$$

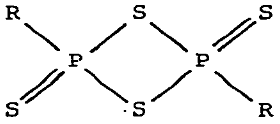
α- and β-naphthol, o-toluidine, o-aminophenol and o-phenylenediamine.[380] In the diethyldithiophosphate derivative of triphenyltin(IV), the ligand is monodentate (P-S 1.931 and 2.054Å) with the tin atom in distorted tetrahedral coordination,[381] while in the nickel(II) complex $Ni[S_2PEt(Oi\text{-}Pr)]_2$ the molecule lies on an inversion centre and has a trans arrangement of the ethyl groups of the two ligand molecules.[382] Coordination about the metal atom is square planar with Ni-S distances of 2.116 and 2.261Å.

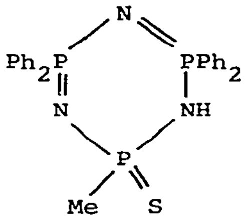
Structures for the hypodiphosphate, $Hg_2P_2S_6$ and the selenium analogue, consist of P_2X_6 groups connected by mercury atoms into layers parallel to the ab plane,[383] in a structure closely related to that for $Fe_2P_2S_6$. The mean P-P distance is close to 2.26Å with mean P-S and P-Se distances of 2.03 and 2.20Å respectively.

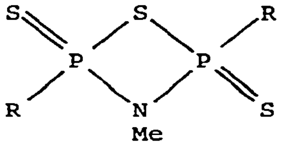
Intercalation of cobaltocene and dibenzene chromium into the lamellar structure of the phosphorus trisulphides, $M(II)PS_3$ for M = Mn, Fe or Zr, shows a marked dependence on the solvent, and the fact that metallocenes with a low first ionisation potential undergo these reactions indicates that charge transfer from guest to host is the driving force.[384] The iron and nickel compounds which have low optical band gaps can also intercalate lithium from n-BuLi to give with the latter the final composition $Li_{3.6}NiPS_3$, but with $CdPS_3$ or $MnPS_3$ which have gaps >2.5eV no intercalation takes place.[385]

Diethylammonium fluoride reacts in a $CHCl_3$-CS_2 mixture with trithiophosphite PHS_3^{2-} in the presence of sulphur or selenium to give compounds with the formulae $(Et_2NH_2)_3(PS_3F_2)$ and $(Et_2NH_2)_3(PS_2SeF_2)$ respectively.[386] An X-ray structure on the latter indicated that rather than being a salt of the $PS_2SeF_2^{3-}$ ion, the compound was a double salt $(Et_2NH_2)_3(PS_2SeF)F$. Isolated PS_4^{3-} units with P-S distances ranging between 2.029 and 2.061Å are found in the structure of $K_3PS_4.H_2O$.[387]

The perthiophosphonic anhydride (<u>141</u>, R = Me) has been shown to convert the 2-hydrido-cyclotriphosphazene to the 2-thione (<u>142</u>),[388a]

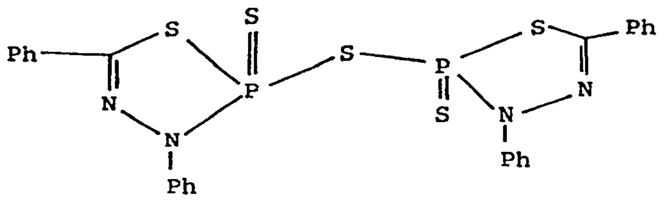

(<u>141</u>)


(<u>142</u>)

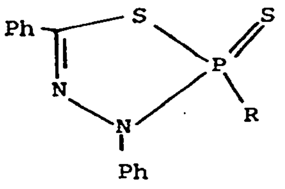

(<u>143</u>)

and with heptamethyldisilazane, (<u>141</u>, R = Me, Et or $MeOC_6H_4$) gives a series of new thiazadiphosphetidines (<u>143</u>) by elimination of hexamethyldisilthiane.[388b] N.m.r. spectroscopy shows the presence of both <u>cis</u> and <u>trans</u> isomers for the compounds with R = Me or Et, but with the methoxyphenyl derivative only the <u>trans</u> isomer is found in the solid state. An X-ray structure for the latter reveals a high degree of disorder in which the organic groups are fixed while the P_2NS ring has two statistical arrangements.

Either P_4S_{10} or the thiophosphonic anhydrides (<u>141</u>) will react with benzo-phenylhydrazonyl chloride PhCCl:N·NHPh to give the thiones (<u>144</u>) and (<u>145</u>) respectively.[389] Alkynyl substituted dithiophosphinic acids $R^1C\vdots C-PR^2(S)SH$ are the products from reactions between Grignard reagents $R^1C\vdots CMgBr$ and perthiophosphonic anhydrides;[390] both the free acid and its salts behave as chelates and complexes with Cr(III), Co(II), Ni(II) and Zn(II) have been isolated. The methyl ester gives a Pt(0) complex on treatment



(144)

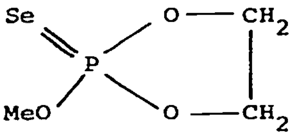


(145, R=Me, Et or $MeOC_6H_4$)

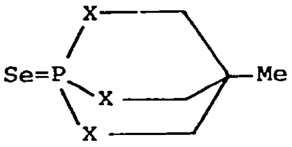
with $Pt(Ph_3P)_4$.

Although tetramethyldiphosphine disulphide, $Me_2P(S)P(S)Me_2$ (=L) coordinates in the *trans* conformation to Cu(II) and the *gauche* form to Cu(I), the complexes obtained with more typical metals, e.g. $(ML_2)^{2+}$, MLX_2 and $MX_4.L$, have i.r. spectra consistent with either D_2d or C_{2v} symmetry and a planar *cis* chelate structure for the ligand.[391]

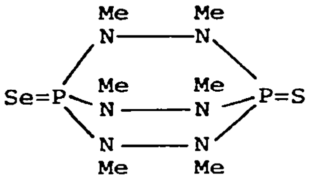
The relationship between P-Se coupling constants and constraint at the phosphorus atom by being part of a ring or cage has been investigated further using the newly synthesised compounds (146)-(148).[392] Values of J(P-Se) for the compounds $SeP(OMe)_3$,



(146)



(147, X = O or NMe)



(148)

$SeP(NMe_2)_3$ and $SePR_3$ etc. decrease on changing solvent from dichloromethane to liquid sulphur dioxide and together with deshielding of the selenium, this is attributed to the formation of 1:1 complexes with SO_2.[393]

In the structures of $(Me_2N)_3PSe$ and the tri(morpholino) and tri(piperidino) analogues there are two short P-N bonds (1.65 - 1.66Å) and one slightly longer one (1.68Å).[394] This effect is associated with the fact that the lone pair associated with the Sp^3 hybridised nitrogen atom of the longer bond is orientated *anti* to the P-Se bond while the other two nitrogen atoms are in close to Sp^2 hybridisation with the lone pairs roughly orthogonal to the

P-Se bond.

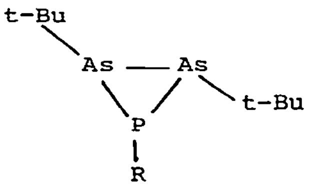
On reaction with SeO_2, trialkyl phosphites give the corresponding phosphate $(RO)_3PO$ and either free selenium or the phosphoroselenate $(RO)_3PSe$ depending on the mole ratio of reactants.[395] Corresponding reaction between $(RO)_3As$ and both SO_2 and SeO_2 are slow giving arsenic(III) oxide and respectively dialkyl sulphides or selenites, while a polymeric material formulated as $(ROSbO)_n$ is the product from the antimony analogues.

Trifluoromethylselenyl compounds, $(CF_3Se)_3M$, are the products of low temperature reactions between PBr_3 or $AsBr_3$ and $Hg(SeCF_3)_2$ in carbon disulphide solution; with P_2I_4, the product is $P_2(SeCF_3)_4$.[396]

5.3 ARSENIC

5.3.1 Arsenic and Arsenides

Compounds containing the As_2P heterocyclic system analogous to the well known P_3 derivatives can be obtained as a mixture of diastereoisomers (149) and (150) from a [2+1] cyclocondensation between $K_2(As_2t\text{-}Bu_2)$ and $RPCl_2$ where R = Et or i-Pr.[397] In addition the four-membered heterocycles $(t\text{-}BuAs)_3PR$, $(t\text{-}BuAs)_2(PR)_2$ and $(t\text{-}BuAs)(PR)_3$ were also isolated. The synthesis and reactivity of substituted alkali arsenides has been reviewed.[398]



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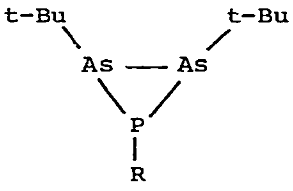


(150)

The europium arsenide Eu_3As_4 (orthorhombic, Fdd2) consists of a continuous network of Eu_6 trigonal prisms, two thirds of which contain an arsenic atom at the centre (mean Eu-As 3.19Å), while the arsenic atoms form As_4 chains (As-As 2.47, 2.56Å, As-As-As 115.9°).[399] In Ta_3As and $(Nb,Ta)_3As$, on the other hand, the basic unit is an $M_{10}As$ bicapped square antiprismatic unit (M-As 2.74, As-As ca. 3.90Å).[400]

A new ternary Cd_2As_3I has been isolated as single crystals during an investigation into the $CdAs_2$-CdI_2 system;[401] its structure consists of arsenic atoms connected by short bonds (mean As-As 2.42Å) into a helix parallel to the c axis.[402] Each arsenic is also connected to two cadmium atoms in a distorted tetrahedral arrangement and the structure is completed by five fold coordination by three arsenic and two iodine atoms about cadmium.

Stoichiometric mixtures of the elements heated to 1000K lead to the new ternaries NaCdAs and TlCdSb, both of which have the modified anti-$PbCl_2$ structures.[403] In the latter the antimony atom is at the centre of a distorted trigonal prism of four thallium and two cadmium atoms. Similar preparative routes give $K_3Ag_3As_2$ and the corresponding copper compound which are isotypes of $K_3Cu_3P_2$,[404] and K_2PdAs_2 (orthorhombic, Cmcm) which contains infinite $PdAs_2$ zig-zag ribbons (Pd-As 2.498, As-As 2.408Å).[405] The cerium compound, Li_2CeAs_2 crystallises with the $CaAl_2Si_2$ structure.[406]

5.3.2 Bonds to Carbon

Organo-arsenic chemistry for 1976 and 1977 has been reviewed.[407] Biological methylation of a number of elements including arsenic has been investigated using reactions between mono- and di-organo haloarsines with $Bu_3PCo(dmgH)_2$ (dmg is the monoanion of dimethylglyoxime).[408] Solutions containing the air sensitive $Bu_3PCo(dmgH)_2 \cdot R^1R^2As$ can be prepared and when R^1=R^2=Me, the compound reacts with MeI to give trimethylarsine and methyl cobalt containing complexes. A compound formulated as $[MePhAs(O)Co(dmg_2H)PBu_3]_2Co \cdot 2H_2O$ has also been isolated and from a crystal structure determination the cobalt atom is bonded to two $PhMeAsO(dmg_2H)PBu_3$ units through the arsenyl oxygen and two adjacent dmg oxygens. Further data is provided by the observation that a variety of micro-organisms can transfer a methyl group intact from L-methionine to arsenic.[409]

New arsenic and antimony cyclopentadienes have been synthesised following the reactions in equations (61)-(63).[410]

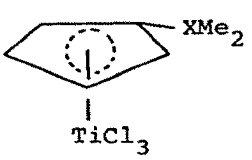
$$C_5H_5Li + t\text{-}Bu_2AsCl \longrightarrow C_5H_5As(t\text{-}Bu)_2 + LiCl \quad \ldots(61)$$

$$C_5H_4(Ast\text{-}Bu_2)Li + Me_3SiCl \longrightarrow C_5H_4As(t\text{-}Bu)_2(SiMe_3) + LiCl \quad \ldots(62)$$

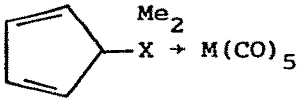
$$C_5H_5SbMe_2 + Me_3SnNMe_2 \longrightarrow C_5H_4SbMe_2(SnMe_3) + C_5H_4(SbMe_2)_2$$

$$+ C_5H_4(SnMe_3)_2 \quad ...(63)$$

Their subsequent reaction with titanium tetrachloride[411] in pentane solution and the chromium and molybdenum carbonyls $M(CO)_5.THF$[412] gave respectively compounds (151) and (152).

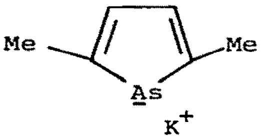


(151, X = As or Sb)



(152, X = As or Sb)

The products obtained when the potassium salt (153) reacts with either $FeCl_2$ or $CpFe(CO)_2I$ are the arsaferrocenes (154) and (155) respectively.[413]



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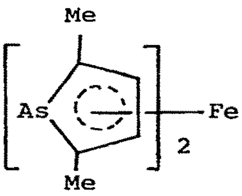

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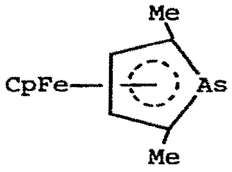
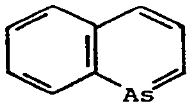


(155)

The synthesis of 1-arsanaphthalene (156) from arsabenzene and benzenediazonium-2-carboxylate has been announced,[414] and three new compounds with an adamantane structure (157) result when 1,1,1-tri(diiodoarsinomethyl)ethane reacts with respectively water, hydrogen sulphide and methylamine.[415] A notable feature of the structure of (157, X = S) is the large As-CH_2-C angle (124°), the As-S distances are 2.242Å and the S-As-S and As-S-As angles 104.7 and 108.8° respectively. The cyclotriarsine (158) (=L) under u.v. irradiation reacts with the Group 6 hexacarbonyls giving $M(CO)_5L$ for Mo and W, $M(CO)_4L_2$ for Cr and W and $[Mo(CO)_4L]_n$.[416]



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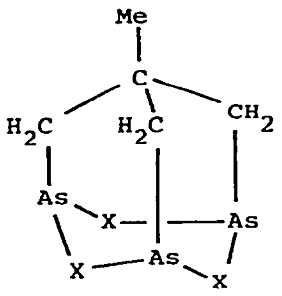
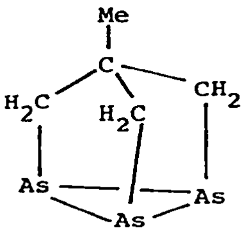
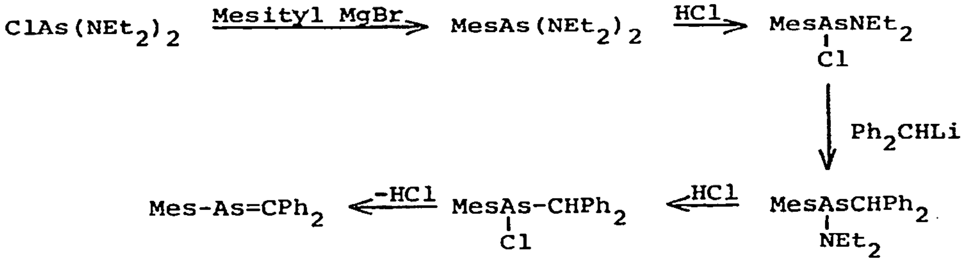


(157, X=O, S or NMe)



(158)

Two coordinate arsenic (III) compounds are less stable and less well known than the phosphorus analogues but a new compound has been synthesised following the reaction in equation (64).[417]

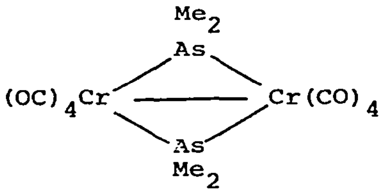


$$\begin{tikzcd}
\mathrm{ClAs(NEt_2)_2} \arrow[r, "\text{Mesityl MgBr}"] & \mathrm{MesAs(NEt_2)_2} \arrow[r, "\mathrm{HCl}"] & \underset{\mathrm{Cl}}{\mathrm{MesAsNEt_2}} \arrow[d, "\mathrm{Ph_2CHLi}"] \\
\mathrm{Mes{-}As{=}CPh_2} & \underset{\mathrm{Cl}}{\mathrm{MesAs{-}CHPh_2}} \arrow[l, "-\mathrm{HCl}"'] & \underset{\mathrm{NEt_2}}{\mathrm{MesAsCHPh_2}} \arrow[l, "\mathrm{HCl}"']
\end{tikzcd} \quad \ldots(64)$$

A related compound $\mathrm{PhAs{:}C(NRSiMe_3)t\text{-}Bu}$ is the rearrangement product which is in equilibrium with the primary product, an iminoacylsilylarsine $\mathrm{Ph(Me_3Si)AsC(:NR)t\text{-}Bu}$, from reactions between phenyl bis(trimethylsilyl)arsine and pivaloyl imidechlorides, t-BuCCl:NR where R = Ph or p-tolyl.[418]

Oxidation of triphenylarsine occurs in the presence of iron(III) chloride, as observed previously for $\mathrm{Ph_3P}$, but temperatures in the region of 80°C are required.[419] The products isolated were $\mathrm{FeCl_3\text{-}(OAsPh_3)_2}$ and possible structures were discussed on the basis of magnetic and spectral data.

Structures for the new $\mathrm{Me_2As}$ bridged complexes (159) and (160) show planarity for the $\mathrm{M_2As_2}$ framework in the former but strong folding in the latter.[420] This together with the M-M bond length is considered to be governed by geometrical requirements of the ligands.[420] The arsinidene complex, $\mathrm{(OC)_5Cr{\cdot}AsCl{\cdot}Cr(CO)_5}$, is



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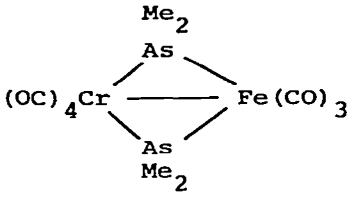

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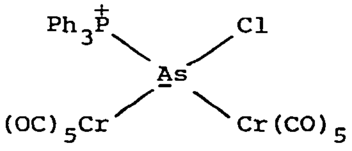


(161)

susceptible to attack at arsenic by Lewis bases and triphenylphosphine, for example, gives a stable 1:1 adduct (161) containing the novel arsanediylphosphorane ligand.[421] With weaker nucleophiles such as esters or ketones adduct formation is readily reversed.

A structure determination on Ph_4AsClO_4 shows isolated ions lying on special positions with $\bar{4}$ symmetry,[422] and in a second polymorphic modification of Ph_4AsBr_3 there appears to be a symmetrical Br_3^- ion.[423]

5.3.3 Bonds to Halogens

Reactions between arsenic(III) fluoride and sulphur trioxide lead to the compounds $AsF_{3-n}(OSO_2F)_n$ where n = 1-3,[424] but corresponding reactions with selenium trioxide give polymeric products, the specific type depending on the solvent used.[425,426]

Addition compounds containing one, two or three moles of the ligand, 1,3-dimethyl-2(3H)-imidazolethione, can be obtained from the Group 5 halides MX_3 for M = As, Sb and Bi and X = Cl, Br and I.[427] Structures were proposed on the basis of vibrational data.

The pentachlorophenyl derivatives, $(C_6Cl_5)_3M$ for M = Sb or Bi, can be prepared from the appropriate trichloride and C_6Cl_5Li, but even with a large excess of the reagent, arsenic trichloride gives only $(C_6Cl_5)_2AsCl$.[428] The lithium derivative of di(t-butyl)amine reacts similarly to give $(t\text{-}Bu)_2NAsX_2$, where X = F, Cl or Br and $(t\text{-}Bu)_2NSbCl_2$ and the barrier to rotation about the As-N and Sb-N bonds can be assessed by temperature dependent ^1H n.m.r. spectroscopy.[429] Reactions of $PhAsCl_2$ or the corresponding mesityl compound with bis(trimethylsilyl)sulphur diimide give $As_2S_2N_4Ph_2$ and $As_2S_2N_4(mesityl)_2$, respectively which are possible precursors to $(RAsNSN)_x$ polymers isoelectronic with the superconducting $(SN)_x$ polymer.[430] X-ray crystallography showed that both compounds contain a boat shaped $As_2S_2N_4$ ring with the arsenic atoms occupying positions at the prow and helm.

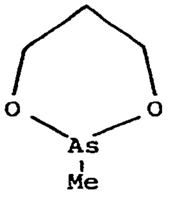
Evidence is now available to show that the dramatic increase in electrical conductivity of polyacetylene $(CH)_n$ on treatment with arsenic pentafluoride arises from oxidation of the chain and formation of AsF_6^- ions which can intercalate between the poly-olefinic cation chains.[431]

The formation of weak 1:1 oxygen-bridged adducts between AsF_5 or SbF_5 and POF_3, SO_2, SOF_2 or COF_2 has been investigated by Raman spectroscopy at -160°C.[432] Unexpectedly, there was no evidence for an adduct between SbF_5 and SO_2F_2 while the arsenic pentahalide was apparently formed; this represents a reversal of the usual Lewis acidities of the arsenic and antimony compounds at low temperature.

I.r., Raman and n.m.r. spectra for R_3AsX_2, where R = i-Pr or $PhCH_2$ and X = F, Cl, Br or I, have been interpreted in favour of trigonal bipyramidal structures.[433]

5.3.4 Bonds to Oxygen

Arsenic, antimony and bismuth chlorides react in refluxing trichloracetic acid to give $As(O_2CCHCl_2)_3$, $SbCl_2(O_2CCHCl_2)$ and $BiCl_2(O_2CCHCl_2)$ respectively.[434] A reinvestigation of the preparative route to the 1,2,3-dioxarsenane (162) has shown that a cyclic dimer (163) and a trimer, each as a mixture of two isomers, are also produced.[435] ^1H[436] and ^{13}C[437] n.m.r. data for over 20



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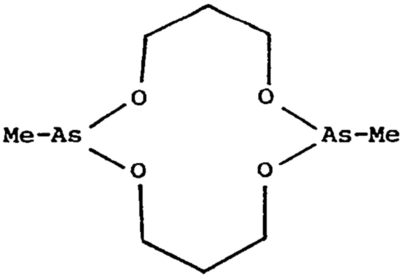

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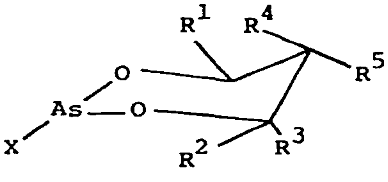
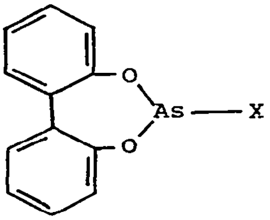


(164)

cyclic arsenites represented by the general formula (164) have been fully analysed; the data show that the substituent at arsenic occupies an axial position and the ring is in a chair conformation.

The chlorine atom in (165, X = Cl) can be replaced on treatment with ammonia or ethylamine but two molecules of the arsenic compound react with aniline to give the bridged compound (166, Y = NPh).[438] Similar bridged species with Y = O or S result when the monochloride is treated with Ag_2O or Ag_2S respectively, and on boiling with sodium in toluene the diarsine (166, Y absent) is the product.



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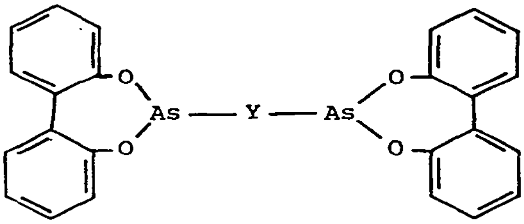
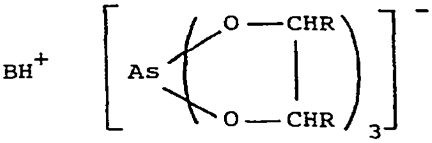


(166)

Displacement of methanol from either $As(OMe)_5$ or $RAs(OMe)_4$ with diols and related compounds is a useful route to cyclic derivatives of arsenic(V). In the first case, if reaction occurs in the presence of a base, salts such as (167) are obtained[439] while the neutral spirocyclic orthoarsonic acid derivatives (168, R = Me or Ph, X = O, S or NH) are produced with the tetramethoxide.[440] A monomer-dimer equilibrium is the best model for solutions of dicyclohexylarsinic acid and dicyclohexyldihydroxychloroarsane in chloroform according to vapour phase osmometry.[441]



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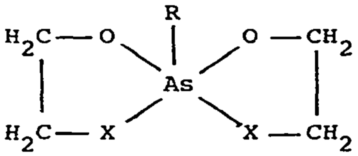


(168)

Mean pK values for the second and third dissociation constants of arsenious acid evaluated from potentiometric and spectrometric methods are 13.59 and 13.87 respectively.[442] Periodate shows a remarkable catalysis of the ^{18}O exchange between arsenate and water, interpreted in terms of the reversible condensation of periodate and arsenate to an arsenatoperiodate.[443]

The Cs_2O-As_2O_5 system shows evidence for $CsAsO_3$ (m 690°C), $Cs_4As_2O_7$ (m 960°C) and Cs_3AsO_4 (m 1190°C).[444] Solid state reactions between M_3AsO_4, where M = K, Rb or Cs, and As_2O_5 in a 4:1 ratio give the diarsenates $M_4As_2O_7$ but when the ratio is changed arsenic-richer phases with variable composition, i.e. $K_3As(III)_xAs(V)_{4-x}O_{11.5-x}$, are produced.[445] Reaction between As_2O_5 and $Fe(OH)_3$ in different ratios gives only $FeAsO_4.2H_2O$, which on heating to 900°C is converted to crystalline $Fe_4(As_2O_7)_3.Fe_2O_3$,[446] while on heating to 800°C the hydrogen arsenate, $Fe(H_2AsO_4)_3$ is converted to $Fe_2[As(III)(As(V)O_4)_3]$.[447] A structure for this species shows Fe_2O_9 groups, formed by face sharing between two FeO_6 octahedra, connected to pyramidal $As(AsO_4)_3$ groups to form a three dimensional network. The arsenic unit is formed by sharing the oxygens of an AsO_3 pyramid (As-O 1.73, 1.85, 1.85Å) with three $As(V)O_4$ tetrahedra (mean As-O 1.679Å).

Full structures are available for $Co(HAsO_4).H_2O$, obtained from $CoSO_4$, As_2O_5 and water at 150°C,[448] and for $KNiAsO_4$ which crystallised as mica-like plates from a K_2O-NiO-As_2O_5 melt.[449] The thermal dehydration of $VOAsO_4.nH_2O$ where n = 0 - 3 has been studied;[450] new phases with the general formula $A_2Mn_3B_2O_2$, where A = Sr or Ba and B = As, Sb or Bi, have been isolated and examined by X-ray diffraction.[451]

Ion exchange properties of crystalline $Zr(HAsO_4)_2.H_2O$ in aqueous solution and molten $NaNO_3$-KNO_3 mixtures at 400°C have been investigated,[452] and two new phases, $Zr(HAsO_4)_2.10H_2O$ and $Zr(NH_4AsO_4)(HAsO_4).H_2O$, have been isolated during an examination of the NH_4^+/H^+ exchange using α-zirconium arsenate.[453]

A new tetraphosphate like anion, i.e. $O_3AsOSiO_3OSiO_3OSiO_3$, has been identified by X-ray crystallography in the manganese arsenatosilicate mineral $Mn_4[AsSi_3O_{12}(OH)]$.[454] Mean As-O and Si-O distances are 1.693 and 1.627Å respectively and the As-O-Si angle is 123.2°. A related, mixed chromium-arsenate, anion occurs in $BaH[AsCr_2O_{10}]$, which can be obtained from CrO_3 and arsenic acid in the presence of barium carbonate, and has a structure based on two CrO_4 tetrahedra sharing common points with the central AsO_4

tetrahedron.[455] Finally a new arsenic substituted polyvanadate structure consisting of a double pair of edge-sharing VO_6 octahedra linked by AsO_4 tetrahedra occurs in the structure of $(NH_4)_4H_6(As_6V_4O_{30}).4H_2O$.[456]

5.3.5 Bonds to Sulphur or Selenium

One of the iodine atoms in $MeAsI_2$ can be replaced on treatment with sodium dimethyldithiocarbamate and the product, $MeAs(S_2CNMe_2)I$, converted to $MeAs(S_2CNMe_2)I_2$ on reaction with a chloroform solution of iodine.[457]

From a structure determination, chains of I_2-I-As-I-I_2-I-As atoms are present in the latter, which are linked into a two dimensional network by I-As-I-As bridges giving square pyramidal coordination about each arsenic atom. Mixed ligand arsenic and antimony dithiocarbamates $M(S_2CNR^1_2)_2(S_2CNR^2_2)$ where M = As or Sb have been isolated.[458]

A number of techniques including wide angle X-ray diffraction, vibrational, electronic and photoelectron spectroscopy have given results consistent with the presence of short range order in amorphous As_2S_5.[459] Each arsenic is attached to three bridging sulphur atoms at 2.30Å and one terminal atom at 2.12Å in a structure derived from that of the unknown As_4S_{10} cage.

The As-S bond distance in Ph_3AsS (2.08Å) is consistent with the presence of a double bond; the arsenic atom is in distorted tetrahedral coordination but the possibility of C_3 molecular symmetry is not realised due to unequal rotation of the phenyl groups.[460]

Sulphur and selenium react with the α,ω-alkane-bis(dimethylarsanes), $Me_2As(CH_2)_nAsMe_2$ where n = 1 - 4, to give the corresponding di-arsenic(V) oxidation product which can behave as chelating ligands with, for example, cobalt(II)halides.[461]

A review with 82 references covering the preparation and properties of ternary compounds with the formula ABX_2 where A is an alkali metal, B = As, Sb or Bi and X = S, Se or Te has been published.[462] A number of such compounds, including, $NaAsSe_2$, $NaSbSe_2$, $NaSbTe_2$ and $NaBiTe_2$, have been prepared and examined by X-rays; the last three compounds have cubic NaCl-type structures while for $NaAsSe_2$ (orthorhombic, Pbca) the structure consists of chains of corner sharing distorted $AsSe_3$ trigonal pyramids.[463]

5.4 ANTIMONY

5.4.1 Antimonides

High molecular weight organo-antimony catenates are of interest on account of their thermal and photoconductive properties and it has now been possible to obtain polymeric $(RSb)_n$ species with a metallic lustre by treating primary alkyl stibines, $RSbH_2$ where R = Me, Et or n-Bu, with organochlorosilanes.[464] Reaction occurs without chlorine incorporation by catalytic loss of hydrogen by a mechanism involving HCl produced via an H-Cl exchange reaction.

RbSb and CsSb can be isolated as orthorhombic $(P2_12_12_1)$ crystals by heating the elements to >500°C.[465] The compounds have the NaP structure with infinite $(Sb^-)_n$ chains (Sb-Sb 2.852, 2.864Å, Sb-Sb-Sb 116.9, 109.7°) parallel to the b axis. The new compound Sr_2Sb_3 prepared from the elements at ca. 1350K is a Zintl phase and is the first alkaline earth antimonide to contain an Sb_6 chain anion.[466] Distances in the chain range between 2.887 and 3.006Å with values for the Sb-Sb-Sb angle lying between 103.3 and 108.7°.

In contrast to the Eu-As system where EuAs can be prepared, the system with antimony gives Eu_2Sb_3 and $Eu_{11}Sb_{10}$; the latter stoichiometry is also found in the related Ca-Sb, Ca-Bi and Yb-Sb systems. All the compounds are isotypic (tetragonal, I4/mmm) and have the $Ho_{11}Ge_{10}$-type structure.[467]

Among the new antimony ternaries investigated recently are $BaMn_2Sb_2$ ($ThCr_2Si_2$ - structure),[468] $BaZnSb_2$ ($BaCu_2S_2$ - structure),[468] $BaCd_2Sb_2$ (Ce_2O_2S - structure),[468] $SrZnSb_2$ (orthorhombic, Pnma),[469] K_5CuSb_2 (space group $R\bar{3}m$) which contains linear $(SbCuSb)^{5-}$ units isoelectronic with $HgCl_2$,[470] and Na_2AgSb (orthorhombic, Cmcm) containing zig-zag Ag-Sb chains (Ag-Sb 2.887Å, Sb-Ag-Sb 180° and Ag-Sb-Ag 64.9°).[471] (The two latter values are interchanged in the abstract).

5.4.2 Bonds to Carbon

Organo-antimony chemistry for 1978 has been reviewed.[472] Tris(trimethylsilyl)stibine on reaction with up to three moles of t-butyl iodide is converted to the orange red solid distibine $(Me_3Si)_4Sb_2$ together with mixed derivatives such as $(Me_3Si)_2Sb(t\text{-}Bu)$ and $Me_3SiSb(t\text{-}Bu)_2$, but with an excess of t-BuI complete reaction occurs giving $t\text{-}Bu_3Sb$ and Me_3SiI.[473] The corresponding reaction with methyl iodide is more vigorous and only the products of complete reaction can be isolated. Both mono- and bi-nuclear chromium and tungsten complexes, i.e. $(OC)_5MSbR_2SbR_2$ where R = Me,Et, t-Bu and Ph and $(OC)_5MSbR_2SbR_2M(CO)_5$ where R = t-Bu and Ph, have been prepared from the distibine and the appropriate $M(CO)_5THF$ complex.[474]

Attempts to prepare Ph_2SbF by a variety of methods known to be successful for the corresponding chloride were unsuccessful, e.g. fluorination of Ph_2SbCl with either AgF or AsF_3 gave Ph_3SbF_2 by oxidative fluorination accompanied by phenyl group migration, while phenylation of SbF_3 with phenyl lithium or phenylmagnesium bromide gave Ph_3Sb.[475] The compound, prepared as previously described from SbF_3 and $(NH_4)_2$ $PhSiF_5$, shows in its mass spectrum a strong peak for the $Ph_2SbF_2^+$ ion suggesting that the compound is strongly fluorine bridged. X-ray diffraction confirms the presence of infinite chains of fluorine-bridged Ph_2SbF units (Sb-F 2.166 and 2.221Å) with the antimony in pseudo-trigonal bipyramidal coordination. Bromination of this monofluoride in dichloromethane has also been reported when it leads to a compound with the empirical formula $Ph_2SbBr_{2.5}F_{0.5}$.[476] An X-ray structure shows that the product is, in fact, a new dimeric mixed halide $Ph_2SbBr_3.Ph_2SbBr_2F$ with a fluorine bridged structure as shown in Figure 3.

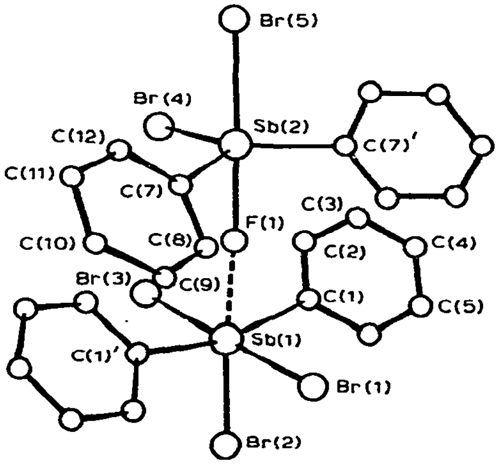


Figure 3. Structure of $Ph_2SbBr_2F.Ph_2SbBr_3$ (reproduced by permission from J. Organomet. Chem., 165(1979)C47).

The simple tribromide, Ph_2SbBr_3, can be obtained by bromine oxidation of Ph_2SbBr at low temperatures and the mixed halides, Ph_2SbBr_2Cl and $Ph_2SbBrCl_2$, are similarly prepared from the appropriate halogen and diorgano-halide.[477] The three compounds are isostructural and contrary to the situation with Ph_2SbCl_3, the antimony here is in distorted trigonal bipyramidal coordination, with two phenyl groups and a bromine atom in equatorial positions.[478] Distances to the axial atoms in all three cases are different as a result of weak intermolecular interaction involving one of these and a neighbouring antimony atom. The major effect of this interaction is an increase in the angle between the two phenyl groups from the expected 120° to ca. 154°.

A similar increase in an equatorial Ph-Sb-Ph angle occurs in the basically trigonal bipyramidal $Ph_3Sb(OAC)_2$ when, in this case, weak Sb···O intramolecular interactions (Sb···O 2.779Å) cause an increase to 148.2°.[479] In the related Ph_4SbO_2CH structures on the other hand, there is little if any secondary Sb···O bonding and the geometry is closely trigonal bipyramidal with an axial formate group.[480] A structure determination for the tri(p-tolyl)antimony (rhombohedral, $R\bar{3}$) gives values of 97.3° and 2.141Å for the C-Sb-C angle and the Sb-C distance.[481]

New air stable antimony(V) diamides $Ar_3Sb(NR_2)_2$ have been obtained by treating the dibromide with, for example, succinimide, phthalimide and benzimidazole in the presence of triethylamine.[482] The compounds are considered to have trigonal bipyramidal structures with axial amido groups. Simpler amines such as piperidine and morpholine do not react.

Sb-O-Sb bonds in both $(Ph_3SbCl)_2O$ and Ph_3SbO are readily cleaved by methanol giving respectively $Ph_3Sb(OMe)Cl$ and $Ph_3Sb(OMe)_2$, while with acetylacetone the products are $Ph_3Sb(acac)Cl$ and $Ph_3Sb(acac)OH$.[483]

The antimony atom in the oxygen bridged species $\{[(NC)_2C{:}C(CN)O]Ph_3Sb\}_2O$ has approximately trigonal bipyramidal geometry with the bridging oxygen and the oxygen of the 1,1,2-tricyanoethenoxo group in axial positions.[484] The Sb-O-Sb angle is 140° and the ligand results by replacement of a cyanide group in TCNE by oxygen.

^{121}Sb Mössbauer data for $Me_3Sb(N_3)_2$, Me_3SbIN_3, Me_3SbI_2, Ph_3SbIN_3, $K(SbCl_5N_3)$ and $(Cl_4SbNCO)_2$, all showing positive isomer shifts, have been obtained and discussed in conjunction with vibrational and X-ray data.[485]

5.4.3 Bonds to Halogens

The structure of the SbF_3.urea adduct consists of trihalide molecules linked into chains by the oxygen atom of urea; Sb-O distances are 2.54 and 2.61Å with the O-Sb-O angle being 124.2°.[486] Coordination about the antimony is probably best described in terms of a distorted capped octahedron from three fluorine atoms at 1.92, 1.93 and 1.96Å, a further fluorine interaction at 2.98Å, the two oxygen atoms, and the seventh position occupied by the lone pair.

Reactions between SbF_3 and SO_3 or SeO_3 are similar to those discussed earlier for arsenic trifluoride.[487] The former gives, depending on the mole ratio of reactants, compounds in the series $SbF_n(SO_3F)_{3-n}$ for n = 0 - 2 while SeO_2F_2 and polymeric products result with the latter. The related antimony(V) fluorosulphates can be prepared by the methods outlined in equations (65) - (68),[488]

$$SbF_3 + S_2O_6F_2 \longrightarrow SbF_3(SO_3F)_2 \qquad ...(65)$$

$$SbF_3 + FOSO_2F \longrightarrow SbF_4(SO_3F) \qquad ...(66)$$

$$SbF_3 + SbF_5 + S_2O_6F_2 \longrightarrow SbF_4(SO_3F) \qquad ...(67)$$

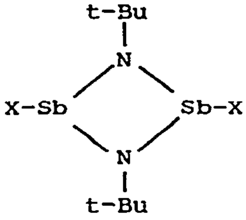
$$SbF_4(SO_3F) + SbF_5 \longrightarrow Sb_2F_9(SO_3F) \qquad ...(68)$$

and are formulated from vibrational data as polymers with fluorosulphate bridges.

Redetermination of the $SbCl_3$ structure (orthorhombic, Pnmc) confirms the mirror symmetry with slightly different Sb-Cl distances (2.340 and 2.368Å) and shows an increase to effective eight fold coordination about antimony in the form of a bicapped trigonal prism by longer interactions (3.457 - 3.736Å) with five other chlorine atoms.[489]

Both 1:1 and 1:2 complexes have been reported for $SbCl_3$ and $SbBr_3$ with trimethylamine,[490] and i.r. and Raman spectroscopy has been used to investigate the stability of the weak $SbCl_3$ adducts with aliphatic and aromatic amides.[491] Adducts between SbX_3 and 1,4-dithiacycloheptane have 1:1 stoichiometry for X = Cl or Br but two moles of SbI_3 react with the ligand.[492] In the trichloride compound each antimony has been found by X-ray diffraction to be bonded at distances of 3.13, 3.23 and 3.40Å to sulphur atoms of three different molecules.

Although $SbX_2N(SiMe_3)t\text{-}Bu$ is presumably formed initially when the trichloride or tribromide reacts with $t\text{-}Bu(Me_3Si)NLi$, there is ready loss of one mole of trimethylsilyl halide giving the diazadistilbetidine (169).[493] In contrast, corresponding reactions with two moles of either $t\text{-}Bu(Me_3Si)NLi$ or $(Me_3Si)_2NLi$ lead to



(169)

$[t\text{-}Bu(Me_3Si)N]_2SbX$ or $[(Me_3Si)_2N]_2SbX$ from which no silylhalide is lost even on heating to 200°C.

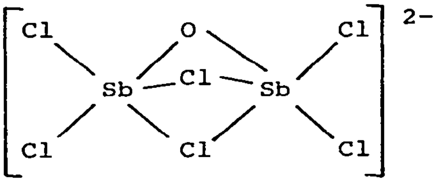
Reactions between pyridine and Sb_2O_3 in aqueous HF give pyridinium salts of the anions SbF_4^-, $Sb_2F_7^-$ and $Sb_3F_{10}^-$ for which preliminary X-ray data have been obtained.[494] A redetermination of the $KSbF_4$ structure (orthorhombic, Pmmn) shows each antimony is coordinated to three fluorines at ca. 1.98Å, two symmetry related bridging halogens at 2.21Å and completion of the SbF_6E polyhedron by a longer fluorine contact at ca. 3.00Å.[495] In $RbSb_2F_7$ (monoclinic, $P2_1/c$) there are polymeric layers parallel to the bc plane in which antimony is again coordinated to six fluorines (Sb-F 1.90 - 2.90Å);[496] but the Sb_2F_7 unit can be recognised if fluorine distances to 2.3Å only are considered. A further point of interest is that in the series KSb_2F_7, $RbSb_2F_7$ and $CsSb_2F_7$ the fluorine bridge becomes more symmetrical showing a specific cation influence on the $SbF_4^- \cdots SbF_3 \rightarrow Sb_2F_7^-$ process.

The complex salts $Cs(SbClF_3)$, $M(SbBrF_3)$ where M = NH_4^+, Rb^+ and Cs^+, $Na(SbBrF_3).H_2O$ and $M_2[C_2O_4(SbF_3)_2]$ all show negative ^{121}Sb Mössbauer isomer shifts and positive quadrupole coupling constants typical of compounds in which the antimony lone pair is stereochemically active.[497] The trends in these parameters have been discussed in relation to known structures.

Salts of the $Sb_2Cl_9^{3-}$ ion can be obtained from antimony trichloride and trimethylamine hydrochloride in concentrated hydrochloric acid whereas in dichloromethane solution the product is $(Me_3NH)_2SbCl_5$.[498] An X-ray structure for the $Sb_2Cl_9^{3-}$ compound shows a polymeric structure based on sheets of condensed singly chlorine bridged Sb_6 units, rather than a discrete dimeric structure. The effect of cation on the type of chloro- and bromo-antimony(III) anions obtained has been investigated by vibrational spectroscopy for a range of substituted ammonium cations.[499,500]

A number of new mixed antimony(III)-antimony(V) species with the general formula $(RH)_8Cl_4[Sb(III)Cl_6][Sb(V)Cl_6]$, where R = $MeCHMeNH_2$, $n\text{-}PrNH_2$, $MeCHMeCH_2NH_2$ etc., have been isolated,[501] and Mössbauer data point to the presence of regular octahedral anions.[502]

An unusual oxychloroantimony(III) anion results from the partial hydrolysis of $(pyH)_3Sb_2Cl_9$.[503] The compound, which shows an i.r. band at 515 cm^{-1} associated with an Sb-O-Sb stretching mode, has the triply bridged structure (170) resulting from face sharing between two $SbCl_4O$ pseudo-octahedral units. The oxygen and one of the chlorine bridges are symmetrical (Sb-O 1.95, Sb-Cl 2.88Å) whereas in the third bridge the Sb-Cl distances are 2.83 and 2.95Å. A more highly condensed analogue, based on a tetrameric unit, $Sb_4Cl_{12}O^{2-}$ (171), is obtained as the ferrocenium salt when $SbCl_3$ and ferrocene are photolysed in benzene solution in the presence of oxygen.[504] X-ray diffraction data however indicate that the compound is best represented as a dimer of (171) as a result of further chlorine bridging.



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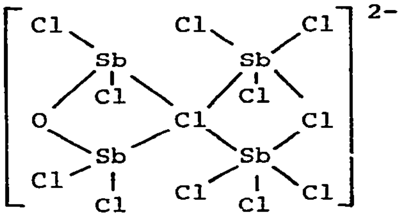
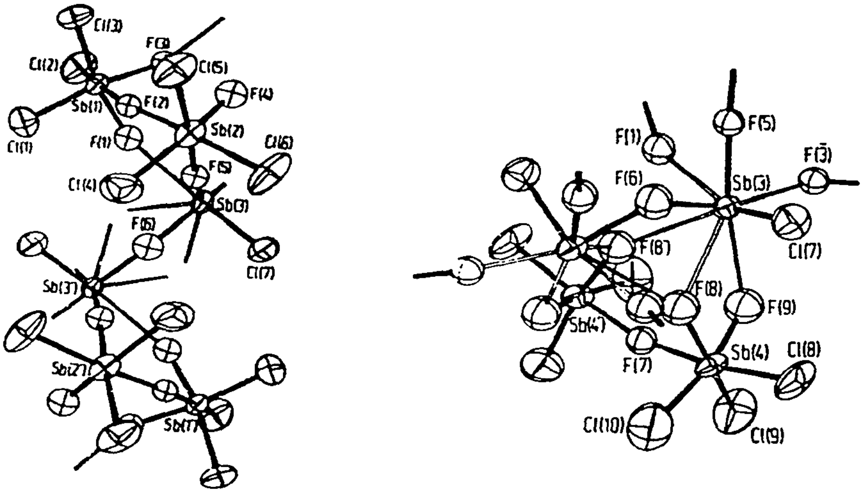


(171)

Various antimony(V) mixed chloride fluorides have already been isolated from reactions between $SbCl_5$ and SbF_5 or related species but two new compounds, the first, represented by the formula $Sb_4Cl_{13}F_7$ and melting between 49 and 54°C, was prepared from a reaction between SbF_5 and $SbCl_4F$ in liquid sulphur dioxide,[505] while the second, $Sb_4Cl_{13.6}F_{6.4}$ with a melting point of 70-71°C was isolated from an SbF_5-$SbCl_5$ reaction.[506] Both compounds have structures related to that of the <u>cis</u> fluorine bridged tetramer found for $SbCl_3F_2$. In the former,[505] two antimony atoms opposite to each other have a chlorine atom replaced by fluorine while in the latter,[506] the four axial groups on one side of the ring are statistically occupied by fluorine and chlorine in the ratio 0.6:0.4. It has been suggested[505] that compounds of this type belong to the series, $Sb_4Cl_{12+x}F_{8-x}$ where x = 0 - 4, and result from the progressive replacement of the terminal fluorine atoms in $(SbCl_3F_2)_4$ to give $(SbCl_4F)_4$.

On long standing, $(SbCl_3F_2)_4$ undergoes a substantial change and a new chloride fluoride with the empirical formula $Sb_2Cl_5F_4$ can be isolated.[507] From X-ray diffraction, the compound should be formulated as $(Sb_6Cl_{14}F_{11})^+(Sb_2Cl_6F_5)^-$ with the structure shown in Figure 4.[507] Two of the antimony atoms in the cation have been reduced to the +3 state and there is weak fluorine bridging between these atoms and a terminal fluorine in the anion leading to

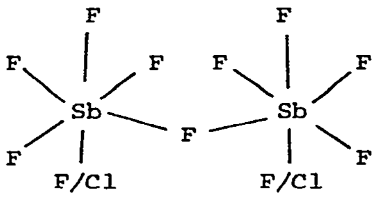


(a) (b)

<u>Figure 4</u>. (a) The structure of the $Sb_6Cl_{14}F_{11}^+$ cation; (b) the structure of the $Sb_2F_5Cl^-$ anion (reproduced by permission from Z. Anorg. Allgem. Chem., 447(1978)171).

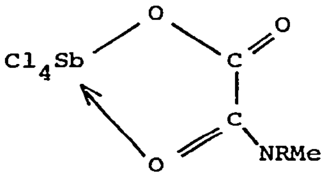
infinite chains parallel to the c axis.

Trimeric compounds represented by the formula $SbCl_4{}^+[Sb_2F_{11-x}Cl_x]^-$ can also be isolated from $SbCl_5$-SbF_5 mixtures and a new member with x = 0.5 has recently been identified by X-ray crystallography.[508] The structure (<u>172</u>) is related to that of the $Sb_2F_9Cl_2{}^-$ ion except that two atom positions <u>cis</u> to the bridge are statistically occupied by chlorine and fluorine atoms. Reaction between either UF_5 or UF_6 and antimony(V) fluoride in Freon 114 leads to the adduct $UF_5.2SbF_5$ which loses one mole of SbF_5 on heating to ca. 100°C.[509]

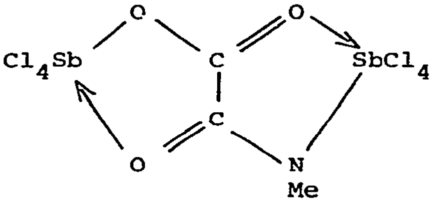


(<u>172</u>)

Reactions between $SbCl_5$ and dimethyl oxalate take place with methyl chloride elimination and formation of $(SbCl_4)_2(C_2O_4)$ while with the N-methyl amido derivatives $MeO_2C{\cdot}CONHMe$ and $MeO_2C{\cdot}CONMe_2$ the products are respectively compounds (<u>173</u>, R = H or Me).[510] Crystallographic analysis of the former points to octahedral coordination about antimony with Sb-Cl distances between 2.324 and 2.349Å and Sb-O bonds of 2.067 and 2.102Å. On treatment with the lithium derivative, $MeO_2C{\cdot}CONMeLi$, $SbCl_5$ gives the novel bicyclic heterocycle (<u>174</u>). Antimony pentachloride also reacts with the methoxy-dimethylaminophosphates $(MeO)_n(Me_2N)_{2-n}PO_2{}^-K^+$, where n = 1 or 2, eliminating potassium hexachloroantimonate to form $(MeO)_n(Me_2N)_{2-n}PO_2SbCl_4$.[511] X-ray structures are available for both



(<u>173</u>)

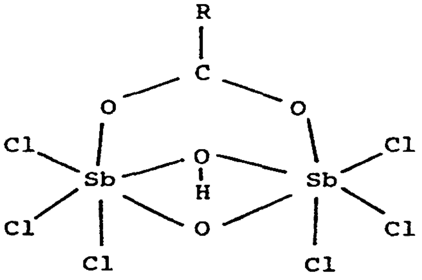


(<u>174</u>)

compounds showing C_{2h} molecular symmetry with octahedral coordination about antimony but with MeO/Me_2N disorder in the structure of the mixed compound.

Reactions between $SbCl_5$ and malondiamide[512] and the sodium derivatives of DMF[513] have been described, the latter giving compounds in the series $SbCl_{5-n}(CONMe_2)_n$ where n = 1, 2 and 3. Raman spectra for $SbCl_5.ReO_3Cl$ have been interpreted in terms of an Sb-O-Re bridged system.[514]

A new type of cyclic antimony compound is the product when the alkoxides $(Cl_4SbOR)_2$ react with either formic or acetic acids.[515] Elemental analysis leads to the formulation $2SbOCl_3.RCOOH$, but the unusual molecular structure shown in (175) is revealed by X-ray crystallography. The antimony atoms are in octahedral coordination (Sb-Cl 2.31, Sb-O 1.983 and 2.046 in Sb_2O_2 ring and 2.103Å to the carboxylate oxygen). The corresponding propionate bridged compound (175, R = C_2H_5) when treated with acetylacetone loses the acid and water to give the oxy-bridged species (176) for which an X-ray structure has been carried out.[516] 1:1 complexes have been isolated from reactions between $(SbCl_4OR)_2$ R = Me, Et or C_2H_4Cl and Ph_3AsO, naphthaldehyde and nicotinamide.[517]



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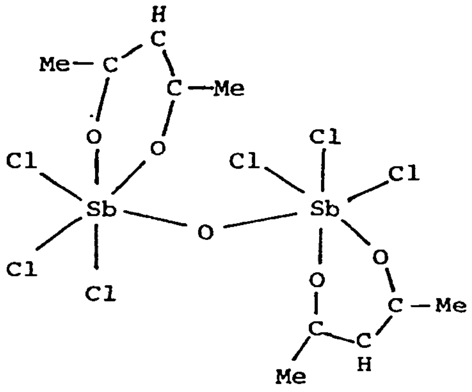

(176)

The interaction between acetyl bromide and antimony pentachloride[518] or $(SbCl_4OEt)_2$[519] and a number of related systems have been investigated using mainly Raman spectroscopy. With $SbCl_5$, products such as $MeCO^+SbBrCl_5^-$, $MeCO^+SbCl_6^-$ or $SbCl_3$ + Br_2 can be obtained depending on the mole ratio of the reactants. Evidence is presented for the formation of $SbBr_5.EtOAc$ from the Raman spectrum of a mixture of $SbBr_3$, Br_2 and ethylacetate.[519]

The hydrolysis product of $CsSbF_6$, i.e. $Cs(SbF_5OH)$, crystallises in the rhombohedral space group R3 and it is not possible to determine uniquely the OH group as the antimony is situated on a three-fold rotation axis.[520] Two groups of three atoms can be distinguished at distances of 1.83 and 1.92Å from antimony, implying that the oxygen position is not completely random.

5.4.4 Bonds to Oxygen

Catechol reacts with the antimony(III) halides in methanol to give products with the formula $C_6H_4O_2SbX$ where X = F, Cl or Br for which vibrational spectra and X-ray diffraction suggest a polymeric structure with halogen bridges.[521] Disorder along the a axis however prevented the determination of the complete structure. Antimony trichloride yields 1,3-diketonate complexes on reaction with the appropriate sodium salt and these complexes, in which the heavy atom is considered to be in six fold coordination to oxygen, may also be obtained from triethoxystibine and the diketone in benzene.[522]

The antimony(III) disulphate, $Sb_2(S_2O_7)_3$ obtained from a solution of the trioxide in oleum crystallises in the triclinic space group $P\bar{1}$ with two independent antimony atoms which are in pseudo-trigonal bipyramidal coordination.[523] One of the disulphate groups behaves as a chelate while the remaining two are bridging groups; Sb-O distances vary between 2.03 and 2.41Å. An X-ray diffraction and thermogravimetric investigation of the $PbO-Sb_2O_3$ system in the presence of oxygen shows the formation of $PbSb_2O_6$, $Pb_{3+x}Sb_2O_{8+x}$, $Pb_4Sb_2O_9$ and $Pb_6Sb_2O_{11}$.[524] Complete X-ray crystal studies have been carried out for $Sb_2Mo_{10}O_{31}$,[525] in which each antimony is coordinated to three oxygen atoms at 1.85 - 2.08Å and four further oxygens at 2.64 - 3.08Å in addition to the lone pair, and for the pyrochlore, $Tl_{0.51}Sb(III)_{0.71}Sb(V)_2O_{6.32}$.[526] A lead containing pyrochlore, $Pb(II)_2[Pb(IV)_{0.5}Sb(V)_{1.5}]O_{6.75}$, in addition to $PbSb_2O_6$ has been isolated from reactions between Sb_2O_3 and either PbO, PbO_2 or $Pb(OAc)_2.3H_2O$.[527]

A reexamination of the thermal behaviour of both Sb_2O_3 and Sb_2O_5 has removed a number of discrepancies in the published information. Both polymorphs of the trioxide show simultaneous volatilisation and oxidation on heating but while the weight loss for the cubic senarmonite between 500 and 660°C is 21-26%, there is a 0.8-2.4% gain in weight for the orthorhombic valentinite.[528] On heating antimonic acid, plateaux are observed at 650-850°C and 890-970°C corresponding respectively to conversion to Sb_6O_{13} and α-Sb_2O_4. X-ray crystallography on Sb_2O_5 (monoclinic, C2/c) shows the presence of distorted corner and edge sharing SbO_6 octahedra and the compound is isostructural with B-Nb_2O_5.[529] Ion exchange equilibria with the alkali[530] and alkaline earth[531] ions on crystalline antimonic acid, $Sb_2O_5.4H_2O$, have been reported.

5.4.5 Bonds to Sulphur, Selenium or Tellurium

^{121}Sb Mössbauer results for a number of dithiocarbamates including $Sb(S_2CNEt_2)_{3-n}X_n$, where X = Cl, Br or I and n = 0 - 3; $R_nSb(S_2CNEt_2)_{3-n}$ where R = Me or Ph and n = 1 or 2; $Me_4Sb(S_2CNEt_2)$ and $Me_3Sb(S_2CNMe_2)_2$ have been interpreted to give structural information including data on the effect of the antimony lone pair.[532] Spectroscopic data for the antimony(III) and bismuth(III) tris(dithiocarbamates) derived from piperidine, morpholine and thiomorpholine point to distortion of the octahedral coordination about the central atom by the lone pair of electrons.[533] Reaction of these products with a halogen displaces one ligand molecule leading to $M(S_2CNR_2)_2X$ species which are monomers for M = Sb but dimers for the corresponding bismuth compounds.

The structure of NH_4SbS_2 contains pseudo trigonal bipyramidal SbS_4 units (Sb-S 2.395 - 2.928Å) connected in chains by a common edge, while the $NaSbS_2$ structure is based on edge sharing pseudo octahedral SbS_5 units.[534] The latter structure is similar to that previously observed for the potassium salt, but the two compounds are not isotypic. X-ray and neutron diffraction data for $Na_3SbS_4.9H_2O$, Schlippe's salt, have been used to elucidate the extent of hydrogen bonding.[535]

Mixtures of TlS and $TlSbS_2$ give the new phase Tl_3SbS_4 on heating to 200°C,[536] and a further new phase $Sn_5Sb_2S_9$ results when the elements in stoichiometric quantities are heated to 600°C.[537] The structure of the latter is based on a face centred cubic arrangement of $Sn(IV)S_6$ octahedra linked together by $(Sn,Sb)S_8$ dodecahedra, distorted by the antimony lone pair; Sb-S distances fall in two ranges 2.562 - 2.976 and 3.270 - 3.607Å.

SbS_3, pseudo-tetrahedral, and SbS_4, pseudo-trigonal bipyramidal units are the basic units found in the structures of the new thioantimonite species $RbSb_3S_5.H_2O$,[538] $K_2Sb_4S_7.H_2O$[539] and

$Cs_2Sb_8S_{13}$.[540] The general preparative route involves the treatment of antimony(III) sulphide with a mixture of either the required hydroxide and sulphide or the hydroxide and hydrogen sulphide. In the first compound two SbS_4 units and one SbS_3 unit combine to give $Sb_3S_5^-$ sheets, while in the second there are equal numbers of atoms in each type of coordination connected by common edges into a three-dimensional network. The final compound has a sheet structure based on corner sharing between seven SbS_3 units and one SbS_4 unit. Sb-S distances fall into the following ranges : SbS_3 2.43 - 2.55; SbS_4 equatorial 2.41 - 2.53, axial 2.56 - 2.94Å.

From single crystal data, $RbSbSe_2$ (triclinic, $P\bar{1}$) is isostructural with the corresponding sulphide,[541] while for $BaSb_2Se_4$, obtained from a stoichiometric mixture of Sb_2Se_3, selenium and barium metal at 980°C, the structure consists of sheets formed by edge sharing between $SbSe_3$ pseudo tetrahedral units (Sb-Se ca. 2.59Å) and $SbSe_4$ pseudo trigonal bipyramidal units (mean Sb-Se equatorial 2.63 and axial 2.85Å).[542]

In the Sb_2Te_3-MTe system where M = Eu or Yb the two compounds MSb_2Te_4 and MSb_4Te have been identified and compounds with the same stoichiometry are formed with bismuth telluride.[543] X-ray and thermal analysis in the Na-Sb-Te system shows formation of the new compound Na_3SbTe_3.[544]

5.5 BISMUTH

Reactions between $Co_2(CO)_8$ and metallic bismuth over an extended period or between the trichloride and $Co(CO)_4^-$ give the tris(cobalt carbonyl)bismuthane $Bi[Co(CO)_4]_3$, which is a discrete molecule with mean values of 2.77Å and 106.8° for the Bi-Co distance and the Co-Bi-Co angle respectively.[545] On reaction with Group 5 triphenyls carbon monoxide is displaced forming the compounds $Bi[Co(CO)_4]_n$-$[Co(CO)_3(Ph_3M)]_{3-n}$.

The ternaries $Ca_9Mn_4Bi_9$ and $Ca_9Zn_4Bi_9$ obtained at ca. 1500K from the elements contain chains formed by corner sharing between $Mn(Zn)Bi_4$ tetrahedra; Bi-Mn distances range between 2.827 and 2.974Å, the corresponding Zn distances between 2.815 and 3.059Å.[546]

Organo-bismuth chemistry for 1978 has been reviewed.[547] Vibrational data for Ph_2BiX, where X = Cl, Br, CN, SCN and N_3, together with molecular weight measurements point to monomeric structures in solution but association occurs in the solid state.[548] Reaction between triphenylarsine oxide and Ph_2BiClO_4 in acetone leads to the cationic complex $[Ph_2Bi(OAsPh_3)_2]^+$, which from an analysis of its vibrational spectrum has a pseudo trigonal bipyramidal structure;[549] data for the complex anions $Ph_2BiX_2^-$ where X = Cl, Br, CN, SCN and N_3 are similarly interpreted.

At -40°C, bismuth(III) chloride reacts with lithium monomethylcarbonate, $Li(O_2COMe)$, replacing two chlorine atoms and giving $BiCl(O_2COMe)_2$.[550] The compound is stable only at low temperatures, decomposing on warming with loss of CO_2 to form $BiCl(OMe)_2$. This compound, along with $Bi(OMe)_3$, can be prepared from the trichloride and lithium methoxide.[551]

Bismuth(III) halide complexes with 4-amino-benzophenone (=L) have the stoichiometries $BiCl_3.L$, $BiCl_3.2L$, $3BiBr_3.2L$, $BiBr_3.2L$ and $2BiI_3.3L$.[552] The formation of halide ion complexes in solution[553] and the nature of the species extracted from such solutions by tributylphosphate, cyclohexanone, etc.,[554] have been investigated by Raman spectroscopy.

Two bismuth fluorosulphates, $Bi(SO_3F)_3$ and $BiCl(SO_3F)_2$, have been prepared as hygroscopic white solids insoluble in common solvents from the triacetate, trichloride or oxide chloride BiOCl.[555]

Three papers deal with aspects of the rather complicated chemistry of basic bismuth nitrates. One product obtained when $Bi(NO_3)_3.5H_2O$ is treated with 0.05M nitric acid has the formula $Bi_6O_4(OH)_4(NO_3)_6.H_2O$ and contains the $Bi_6O_4(OH)_4^{6+}$ cation (see Figure 5) similar to that observed already in a basic perchlorate.[556]

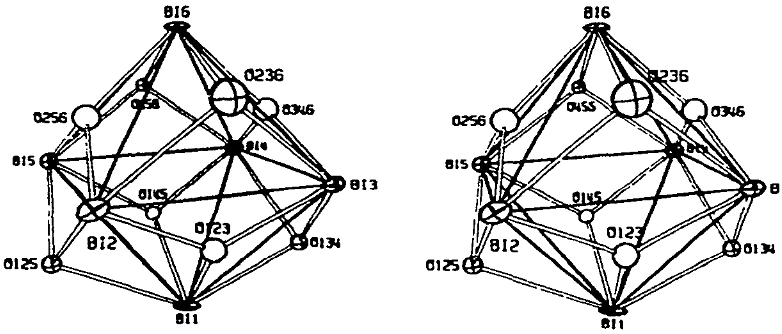

Figure 5. A stereoview of the complex $Bi_6O_4(OH)_4^{6+}$. The solid lines between bismuth atoms do not indicate bonding. (Reproduced by permission from Acta Chem. Scand., A33(1979)221).

Each bismuth atom is in pseudo-trigonal bipyramidal coordination with the lone pair in an equatorial position. A second compound, obtained by hydrolysis of the nitrate at pH below 1.2, is a tetrahydrate with a related structure.[557] Heating this compound for days at 323K yields a new phase which still contains the Bi_6 octahedral unit but is formulated from X-ray crystallographic results as $[Bi_6O_4(OH)_4(H_2O)(NO_3)](NO_3)_5$.[558]

Four oxysulphates, $9Bi_2O_3.Bi_2(SO_4)_3$, $4Bi_2O_3.Bi_2(SO_4)_3$, $2Bi_2O_3.Bi_2(SO_4)_3$ and $Bi_2O_3.3Bi_2(SO_4)_3$, have been identified in the oxide-sulphate system,[559] and the oxide reacts with CuO and PdO to give the 1:1 compounds Bi_2CuO_4 and Bi_2PdO_4.[560]

Metathesis reactions between R^1BiBr_2, where R^1 = Me or Ph, and the appropriate sodium dithiocarbamate lead to $R^1Bi(S_2CNR^2_2)_2$, where R^2 = Me or Et and R^2_2 = $(CH_2)_5$,[561] and an X-ray structure for $MeBi(S_2NEt_2)_2$, which is dimeric in the solid, shows the bismuth atom in the unusual pentagonal pyramidal coordination.[562] The methyl group occupies the axial position while four sulphur atoms from the two chelating ligands (Bi-S ca. 2.70Å) and a fifth sulphur from the neighbouring molecule (Bi-S ca. 3.30Å) fill the equatorial positions.

Only $Bi_4S_5Cl_2$ has been identified in the sulphur rich section of the Bi_2S_3-$BiCl_3$ system.[563] The structure is noteworthy in showing statistical occupancy of the anion sites by sulphur and chlorine and by the fact that there is nine fold coordination about one bismuth atom in the form of a distorted tricapped trigonal prism, while the remaining three are surrounded irregularly by eight atoms. More conventional six fold coordination is found for bismuth in the structure of $Tl_4Bi_2S_5$.[564]

Although $Ge_3Bi_2S_6$ has been reported as resulting from heat on a stoichiometric mixture of GeS and Bi_2S_3 attempts to repeat this led to multiphase products that were probably mixtures of elemental bismuth and GeS_2.[565] The bismuth sulphide-cadmium sulphide system shows new compounds at the ratios 2:5, 3:5 and 1:1, but in the corresponding selenide system evidence was obtained for only the 1:1 compound.[566] Two incongruently melting compounds $Mn_3Bi_2Se_6$ and $MnBi_2Se_4$ have been identified in the Bi_2Se_3-MnSe system.[567]

Structures have been determined for the bismuth tellurides BiTe and Bi_4Te_3,[568] and there is evidence for the ternary $CeBiTe_3$ in the Bi_2Te_3-Ce_2Te_3 equilibrium diagram.[569]

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