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Chapter 5

ELEMENTS OF GROUP 5

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5.1 NITROGEN

5.1.1 Elemental Nitrogen

The possibility of separating the nitrogen isotopes by reverse phase liquid chromatography of their compounds has been investigated experimentally.[1] Thus the isotope effect on the dissociation of the anilinium ion is estimated to be 1.019. Although the separation factor obtainable by this method may be smaller than that in the conventional ion exchange process for NH_4^+, the authors suggest that the new approach may be attractive for the preparation of ^{15}N-enriched compounds in the laboratory. In spite of the low solubility of Li_3N in THF, it is sufficient to allow it to be used as a reducing agent with metal halides. The reduction process in this aprotic medium appears to be converting N^{3-} to $\frac{1}{2}N_2$.[2] The reductions, of $TiCl_4$ to $LiTiCl_4 \cdot 4(THF)$ and cp_2TiCl_2 to $[cp_2TiCl]_2$ and other polynuclear products, were reported as new synthetic uses of the technique. Protonated dinitrogen has been postulated by Olah et al.[3] as an intermediate in reactions (1) to (3). Naturally this intermediate decomposed under the reaction conditions according to (4).

$$^{14}NH_3 + {}^{15}NOBF_4 \xrightarrow{-80°C} [{}^{15}N{\equiv}{}^{14}NH]BF_4 + H_2O \qquad ...(1)$$

$$H^{14}N(SiMe_3)_2 + {}^{15}NOBF_4 \xrightarrow{0°C} [{}^{15}N{\equiv}{}^{14}NH]BF_4 + O(SiMe_3)_2 \qquad ...(2)$$

$$HN{=}C{=}O + {}^{15}NOBF_4 \xrightarrow{25°C} [{}^{15}N{\equiv}{}^{14}NH]BF_4 + CO_2 \qquad ...(3)$$

$$[{}^{15}N{\equiv}{}^{14}NH]BF_4 \rightarrow {}^{15}N{\equiv}{}^{14}N + HBF_4 \qquad ...(4)$$

Mason and collaborators[4] have discussed the n.m.r. relaxation mechanisms operating in dinitrogen complexes of Mo,W,Rh, and Os with tertiary phosphine co-ligands. Shilov et al.[5] have described a procedure for the catalytic reduction of N_2 at ambient temperature and pressure: it is based on the reaction with sodium amalgam/methanol/molybdenum(II) chloride/phospholipid/phosphine. Under favourable conditions the main N-containing product was hydrazine, although some NH_3 was also formed. More examples of transition metal complexes of dinitrogen have been described which are decomposed to NH_3 and/or N_2H_4 when treated with HCl or HBr; thus George and Tisdale[6] have investigated an extensive series of mono-N_2 complexes of Mo(O). In another paper the same group[7] have presented a detailed account of their evidence for the formation of a pair of intermediate, isomeric hydrazide(2-) complexes in the reaction of trans-$Mo(N_2)_2P_4$ complexes with HCl or HBr. They reported that the more labile intermediate appears analogous to nitrogenase.

5.1.2 Bonds to Hydrogen

The structure, association energies and vibrational frequencies of $(NH_3)_2$ and $(NH_3)_2H^+$ have been reinvestigated at a consistent, higher level of theory.[8] The reaction of lithium and aluminium with liquid NH_3 gives $LiAl(NH_2)_4$ over a period of days at 90± 10°C.[9] Formamide and N-methylformamides have been prepared from synthesis gas plus NH_3 via ruthenium "melt" catalysis.[10] Two reaction pathways were proposed, Schemes 1 and 2. Scheme 1 involves the formation of formamide which is then methylated by methyl ruthenium species, formed by hydrogenation of Ru-CO complexes. Scheme 2, which requires the formation of methanol and then methylamine which suffers carbonylation, was found to be supported by some of the experiments carried out by Knifton.

$$CO + NH_3 \longrightarrow H_2NC(O)H \xrightarrow{\text{'Me-Ru'}} MeNHC(O)H + Me_2NC(O)H$$

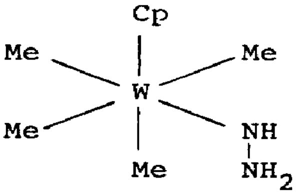
Scheme 1

$$\begin{tikzcd}
CO + H_2 \arrow[r] & MeOH \arrow[r] & Me_xNH_{3-x} \arrow[d, "CO"] \\
& & MeNHC(O)H + Me_2NC(O)H
\end{tikzcd}$$

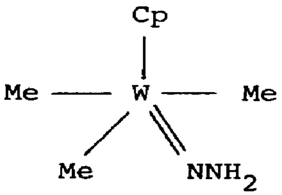
Scheme 2

Barley and coworkers[11] have reported that the water-soluble iron porphyrin $Na_3Fe^{(III)}(TPPS).12H_2O$ [H_2TPPS^{4-} = the tetraionic form of meso-tetrakis(p-sulphonatophenyl)porphine] acts as an effective electrocatalyst for the reduction of NO_2^- to NH_3. The advantage of this kind of iron porphyrin complex as a catalyst is that, once the reduction to NH_3 is complete, substitution at the relatively labile axial position allows for facile substitution by NO. The preparation of (1) by means of reaction (5) has been reported.[12] Although the structure of (1) has not yet been confirmed it was shown that (1) is converted to (2) in polar solvents, such as CH_2Cl_2. Reaction of (2) with $[CpWMe_4]PF_6$ produced a material which has been shown to be $[CpWMe_3]_2(\mu\text{-}N_2)$ by an X-ray study: the same product has also been made from $CpWMe_4$, $CpWCl_4$, N_2, and Na/Hg. The kinetics of the oxidation of NH_3 and NH_4^+ to N_2 by $S_2O_8^{2-}$ have been investigated and were found to have radical reaction pathways.[13]

$$[CpWMe_4]^+PF_6^- + 2N_2H_4 \rightarrow CpWMe_4(NHNH_2) + N_2H_5PF_6 \qquad \ldots(5)$$



(1)



(2)

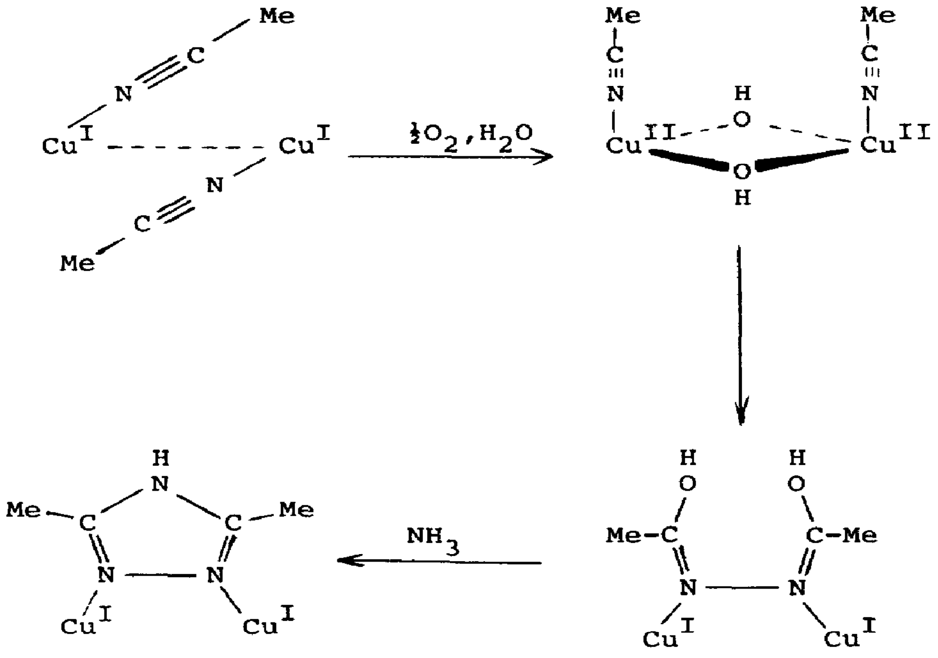
$Cp \equiv \eta^5\text{-}Me_5C_5$

5.1.3 Bonds to Boron

Photoelectron spectra of the aminodifluoroboranes NH_2BF_2, $NHMeBF_2$, and NMe_2BF_2 have been recorded.[14] Kroto and McNaughton discussed the results and compared them with theoretical calculations. Apart from the usual overestimation by the 4-31G calculations the agreement was pronounced excellent. The results imply that there is very little π-bond character for the N-B bond, although microwave studies indicate that the molecules are indeed planar.

5.1.4 Bonds to Carbon or Silicon

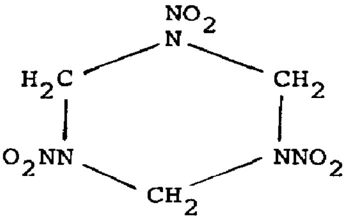
Reaction of a di-copper(II) complex of a macrocyclic ligand with MeCN in the presence of O_2 and H_2O has been shown to afford a pentanuclear complex containing two triply-bridging 3,5-dimethyl-1,2,4-triazolate groups.[15] A scheme outlining the probable steps in the formation of these bridging groups is shown in Scheme 3. Cyanogen reacts with $AgAsF_6$ in liquid SO_2 to form $[Ag(C_2N_2)_2]AsF_6$ as a colourless, water-sensitive solid which decomposes at 176°.[16] The ligand C_2N_2 acts as a bridging ligand between Ag ions, which are thus in square planar environments.



Scheme 3

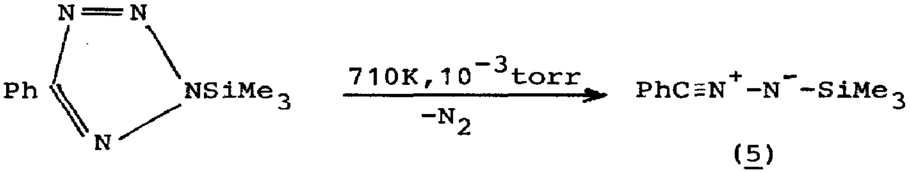
Nitrogen e.s.r. hyperfine splitting constants and π, π* optical absorption spectra maxima have been compared for 15 examples of $R_4N_2^{+\cdot}$ radicals.[17] M.o. calculations of these quantites were compared for $H_4N_2^+$ bent anti and syn at the nitrogens. The different symmetries for syn and anti σ,π mixing cause surprisingly large differences in spectral properties, depending on the type of bending at nitrogen for $R_4N_2^+$. Tetrakis(dimethylamino)ethylene, TMAE, is a pale yellow, involatile liquid which reacts rapidly with O_2 to give a strong chemiluminescence and is readily ionised. It has been reported[18] that excess electrons in TMAE have a mobility of $2.2 cm^2 (Vs)^{-1}$ at 20°C, a factor of 100 higher than that in other amines. The conduction band energy was estimated to be approximately -0.1eV.

Structure and dynamics studies of 4-, 6-, and 8-membered cyclic nitramines containing the $C(NO_2)_2$ fragment have been reported.[19] Thus the crystal structure of 1,3,3,5-tetranitrohexahydropyrimidine was determined by X-ray diffraction. The lattice dynamics and high-rate thermal decomposition of 1,2,3-triaminoguanidinium nitrate $[C(NHNH_2)_3]NO_3$ have been examined by rapid scan FTIR spectroscopy and d.t.a.[20] Cluster ions of the general formula $[(CH_2NNO_2)_nH]^+$, n = 4 to 15, have been observed in the "self" chemical ionisation mass spectrum of hexahydro-1,3,5-trinitro-1,3,5-triazine, RDX, (3).[21] These cluster ions are termed complex since they are composed of RDX molecules and methylenenitramine fragments of the parent molecule.



(3)

The first thermally generated nitrile imine (5) has been generated from the tetrazole (4) by vacuum flash pyrolysis, equation (6); it was characterised by mass spectrometry and i.r. spectroscopy and is stable at 77K.[22]



(4)

...(6)

Core binding energy data for CF_3NC, $CF_3NCCr(CO)_5$, and $CF_3NCW(CO)_5$ indicate that CF_3NC is a very strong π-acceptor ligand, practically as strong as CO.[23] The core data for CF_3NC and CF_3CN, when interpreted using the equivalent cores approximation, lead to an estimate for the isomerisation energy of -23 kcal mol^{-1}. Hydrogen halide, HX, addition to CF_3NC results in the formation of both isomers of each of $CF_3N{=}CHX$, X = Cl, Br, or F, with the E isomers predominating, as shown by electron diffraction.[24] All these methanimines dimerise slowly at room temperature forming the corresponding aminomethanimines, $CF_3N{=}CHN(CF_3)(CX_2H)$. The isocyanide also reacts with SF_5Br

yielding $CF_3N{=}CBr(SF_5)$. The pyrolysis of F_2HCN_3 at temperatures above 720K has shown to produce FCN by equation (7).[25] The reaction was controlled using a flow system under reduced pressure; it may prove to be a useful route to pure FCN. The pyrolysis of phenyltriazidosilane at above 700°C has been shown to

$$F_2HCN_3 \rightarrow N_2 + HF + FCN \qquad \text{...(7)}$$

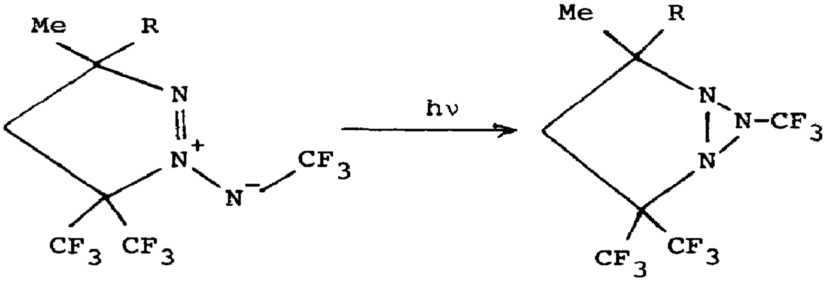
$$PhSi(N_3)_3 \rightarrow Ph{-}N{\equiv}Si + 4N_2 \qquad \text{...(8)}$$

(6)

form phenylsilaisocyanide, (6), which was characterised by He(I)-photoelectron spectroscopy.[26] The gas-phase molecular structures of two tertiary amines, $MeN(SiH_2Me)_2$ and $MeN(SiHMe_2)_2$ have been determined by electron diffraction;[27] both have planar $NCSi_2$ skeletons. Lukevics et al.[28] have pointed out that $J(^{15}N-^{29}Si)$ coupling constants are more readily obtained from the 100 times more sensitive technique of observing ^{15}N satellites on ^{29}Si resonances.

5.1.5 Bonds to Nitrogen

The synthesis of triaziridines, which are stable to at least 80°C, from suitable azimidine precursors has been achieved by reaction (9).[29] Hegarty and coworkers[30] have investigated the



...(9)

R = alkyl or aryl

pentazole (N_5^-) anion by ab initio calculations: the anion is predicted to lie 31 kcal mol^{-1} above the (N_3^- + N_2) system but the energy barrier for decomposition is 22 kcal mol^{-1}. They proposed that matrix isolation of the species is feasible as also would be the synthesis of $(\eta^5\text{-}N_5)Mn(CO)_3$ complexes. Ab initio m.o. theory has been used to study the hydrazinium radical cation, $NH_3NH_3^{+}\cdot$ and the dication $NH_3NH_3^{2+}$.[31] The radical cation is calculated to have a long N-N bond (2.164Å) but is nevertheless bound, by 134 kJ mol^{-1} with respect to NH_3 and $NH_3^{+}\cdot$: the N-N bond in the dication is shorter (1.442Å) however dissociation to $2NH_3^{+}\cdot$ is exothermic by 249 kJ mol^{-1} even if the activation energy barrier is large (194 kJ mol^{-1}). Nelsen and Blackstock[32] have reported the first measurement of hydrazine-hydrazine radical cation self-exchange electron-transfer rate, from a ^1H n.m.r. study.

The triplet and singlet excited state energies of N-nitrosodimethylamine and -piperidine have been determined spectroscopically:[33] the singlet state of nitrosamine-acid complexes dissociates rapidly to give aminium radicals and NO whereas the triplet shows no apparent chemical changes. Hydrazine is oxidised by hot nitric acid in a first order reaction in which the product proportions depend on the reaction time.[34] Thus for a reaction in 5.44M HNO_3 at 100°C that was 75% complete the outcome can be expressed by equation (10). The rate law is

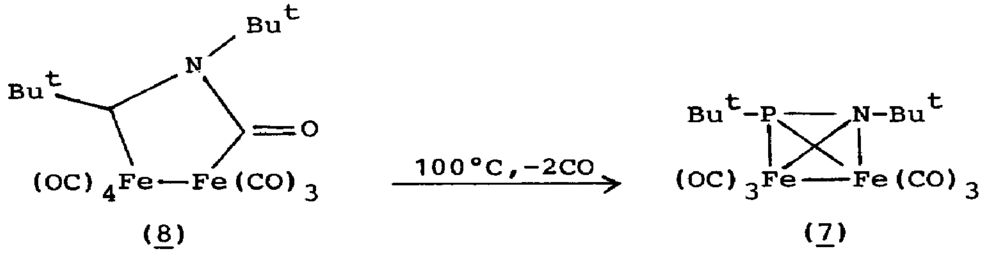
$$N_2H_4 + 0.8HNO_3 \rightarrow 0.19HN_3 + 0.17NH_4NO_3 + 0.7N_2 + 0.2N_2O + 1.8H_2O \qquad ...(10)$$

given by $-d(\ln[N_2H_4])/dt = k[NO_3^-][H^+]$. Gattow and Lotz[35] have characterised salts of 1,2-hydrazine-bis(dithioformate), $M_2[S_2CNHNHCS_2]$, M = Na or K. In the potassium salt the N-N distance is 1.388(6)Å at -85°C. Under similar conditions, N_2H_4, CS_2, and base, they also prepared the mixed dithiocarbamate-dithiocarbimate, $Na_3[S_2CNHN{=}CS_2].7H_2O$. The S-methyl ester of dithiocarbazic acid reacts with CS_2 in the presence of NaH or KH at -15°C to yield the unknown salts of the S-methyl ester of N-dithiomethylenedithiocarbazic acid, $M_2[S_2C{=}NNHCS(SMe)]$.

5.1.6 Bonds to Phosphorus

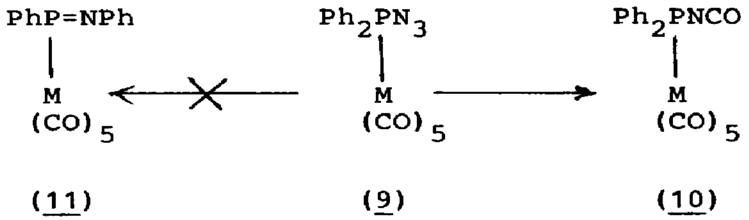
Cowley and coworkers[36] have reported the first example of a coordinated iminophosphine behaving as a 6-electron donor, see Figure 1. In (7), which was prepared from $Fe_2(CO)_9$ and $Bu^tN{=}PBu^t$, the P-N bond order is one whereas in the $Bu^tP{=}PBu^t$ analogue the central bond is of order two. In the same reaction, Scheme 4, (8) was also obtained in which interaction with a coordinated carbonyl group produces an unusual bridging ligand. Diphenylphosphineazide complexed to $M(CO)_5$, M = Cr or W, (9) reacts under thermolytic or

$$Fe_2(CO)_9 + Bu^tN{=}PBu^t \xrightarrow{25°C} (\underline{7}) + (\underline{8})$$



Scheme 4

photolytic conditions to give (10) rather than the expected iminophosphane (11).[37]



5.1.7 Bonds to Oxygen

The sonolysis of N_2O in water yields N_2, NO_2^- and NO_3^- as the principal products.[38] Nitrous oxide oxidises methane to formaldehyde over a Bi_2O_3-SnO_2 catalyst with a selectivity of approximately 90% at 550°C (1.7 to 2.7% conversion).[39] Catalytic reduction of NO_2^- to N_2O by formic acid in DMF occurs in the presence of either $MoO(S_2CNEt_2)_2$ or $MoO_2(S_2CNEt_2)_2$.[40]

A facile, pressure-induced disproportionation of NO occurs at 176K and 1.5GPa.[41] The reaction products are N_2O_4, N_2O and a small, variable, amount of N_2O_3 as identified by i.r., Raman, and visible spectroscopy. No free NO, N_2O_2 or NO_2 is observed after warming the sample to room temperature. The N_2O_4 produced subsequently undergoes photolysis to N_2O_3 and $NO_2^+NO_3^-$; there was also evidence for the nitrite form of N_2O_4. Nitrous oxide once

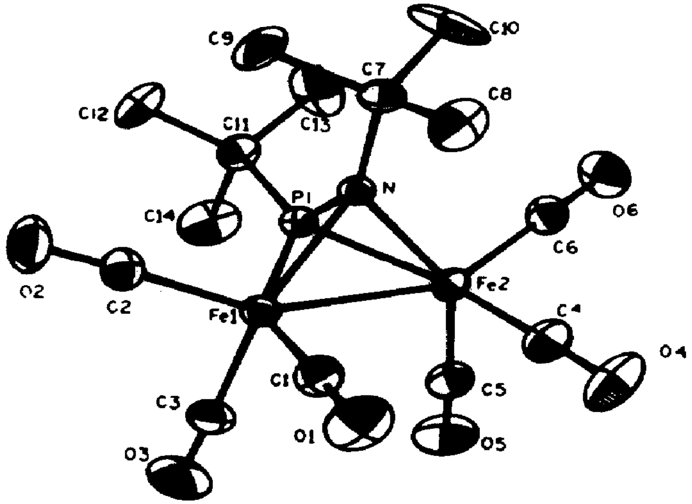


Figure 1. ORTEP view of (7) showing the atom numbering scheme for molecule I. Important parameters: P(1)-N = 1.687(7), P(1)-Fe(1) = 2.146(3), P(1)-Fe(2) = 2.147(3), N-Fe(1) = 2.001(7), N-Fe(2) = 2.011(6), Fe(1)-Fe(2) = 2.615(2)Å; C(11-P(1)-N = 130.4(4)°, C(7)-N-P(1) = 139.7(6)°. (Reproduced by permission from J. Am. Chem. Soc., 107(1985)2554).

formed is stable to 14GPa. The NO ligand in $HRu_3(CO)_{10}(NO)$ undergoes N-O bond cleavage in the presence of H_2 with the formation of $H_2Ru_3(NH)(CO)_9$, $H_2Ru_3(NH_2)(CO)_{10}$ and $H_4Ru_4(CO)_{12}$ as the principal metal-containing products.[42] Nitrogen-15 n.m.r. characterisation of $[RuCl(NO)_2(PPh_3)_2]BF_4$ in the solid state has been achieved by cross-polarisation, magic-angle spinning;[43] this compound shows a large chemical shift anisotropy for the bent NO as compared with the linear one.

Blough and Zafiriou[44] have shown that superoxide, O_2^- or possibly $HO_2\cdot$, reacts with NO in deaerated aqueous solutions at pH12 to 13 to form the peroxonitrite ion, $ONOO^-$. The diamagnetic product ion is stable in 0.1M base whereas at lower pH it is protonated and rearranges to NO_3^-. The role of NO in catalysing the decomposition of aqueous hyponitrite has been further investigated.[45] One mechanism proposed involves an initial hydrogen atom abstraction process; under chain-inhibited, e.g. with EtOH addition, conditions a substantial proportion of the $^{15}N_2O$ produced arises from reduced NO, equation (11). In the absence of such chain inhibitors significant quantities of N_2 are liberated; reaction (12) was postulated to rationalise this.

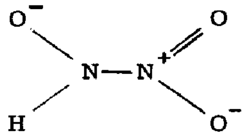
$$^{15}NO + HONNOH \rightarrow \begin{cases} ONNOH \rightarrow N_2O + {}^{\bullet}OH \\ + \\ H^{15}NO \rightarrow \tfrac{1}{2}\{^{15}N_2O + H_2O\} \end{cases} \qquad \ldots(11)$$

$$NO + {}^{\bullet}ONNOH \rightarrow ONONNOH \rightarrow NO_2 + N_2 + OH \qquad \ldots(12)$$

$$2NOCl + Hg(OTeF_5)_2 \rightarrow HgCl_2 + 2NO^+(OTeF_5)^- \qquad \ldots(13)$$

Nitrosonium pentafluorotellurate(VI) has been prepared by reaction (13) as a colourless ionic acid;[46] however, in the vapour phase it is clearly covalent.

In the oxidation of nitrite to nitrate by $S_2O_8^{2-}$ the rate law is $-d[S_2O_8^{2-}]/dt = k_1[S_2O_8^{2-}] + k_2[S_2O_8^{2-}][NO_2^-]$.[13] Since the rate is changed significantly on the addition of allyl alcohol the authors inferred the presence of free radicals to an extent greater than can be ascribed to the k_1 term alone. They went on to investigate the possible involvement of NO_2 as an intermediate. Ab initio m.o. calculations on HONO, extended to the MP4SDTQ level with a large basis set, have been published by Turner.[47] The energy difference between the cis and trans isomers, 3.5 kJ mol^{-1}, and activation energy, 53.6 kJ mol^{-1}, are in excellent accord with experiment. Methods have been reported for preparing salts of hyponitric (or oxyhyponitrous) acid with NH_4^+, $N_2H_6^{2+}$, $[C(NH_2)_3]^+$, and $[C(NH_2)_2NHNH_2]^+$ from either the lithium salt, $Li_2N_2O_3$, or from NH_2OH and ethyl nitrate.[48] Bazylinski and Hollocher[49] have attempted to resolve the question as to the rate determining step of the hyponitrate ion at pH7. The yields of the final products, N_2O and NO_2^-, and the isotopic distribution strongly favour (14) rather than (15) as the rate determining step. The reaction of NO_2/N_2O_4 with organic hydroperoxides in solution has been investigated.[50] Cumyl and tert-butyl hydroperoxides react rapidly in the presence of a base to form principally an organic nitrate along with minor amounts of nitrite, alcohol, and carbonyl



$\longrightarrow NO^- + NO_2^- + H^+$ ...(14)

$\not\longrightarrow NO + HONO^-$ ...(15)

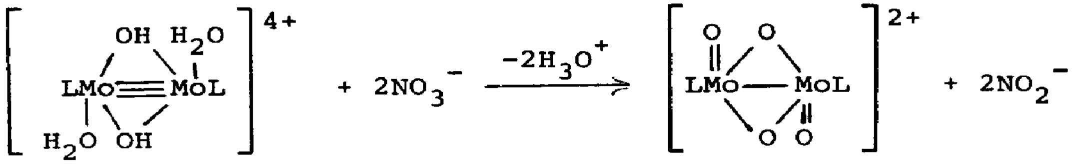
compounds. The authors suggest that this facile reaction may be significant in connection with the pulmonary toxicity of NO_2 in smoggy air. Stegmann and coworkers[51] have reported that the e.p.r. signals from spruce needles taken from healthy trees differ markedly from those from S3 (unhealthy) trees. Moreover the effect of treating healthy needles with NO_x or NO_x/SO_2 combinations, but not aqueous H_2SO_4 (pH 1), leads to comparable e.p.r. spectral changes. Matrix isolation FTIR and u.v. absorption spectroscopy have been used to study the products of the reaction between ClO and NO_2.[52] The techniques allowed both quantitative measurements of the major reactants and products as well as a simultaneous search for any minor products. The yield of chlorine nitrate (M = N_2 in equation (16) was found to be 0.9± 0.2 at 22 torr and 253K to 298K. The authors reported no evidence

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad ...(16)$$

for any other products, e.g. isomers of $ClONO_2$.

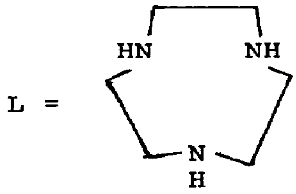
Nitrogen dioxide adds to the bridged binuclear Pt(II)-Pt(II) complex $Pt_2(P_2O_5H_2)_4^{4-}$ to give the Pt(III)-Pt(III) complex $Pt_2(P_2O_5H_2)_4(NO_2)_2^{4-}$.[53] The NO_2 ligands are N-bonded and occupy the axial positions on this product, as was shown by X-ray crystallography of the 8- anion. The thermal reaction between MeSH and NO_2 has been studied over the range 296-458K by monitoring the disappearance of NO_2 in a large excess of MeSH.[54]

Nitric acid is reduced catalytically by CO in the presence of $Pd_3(OAc)_6$ to form NO_2 then NO.[55] Wieghardt et al.[56] have reported the kinetics and mechanism of the reduction of NO_3^- to NO_2^- by bis(μ-hydroxo)bis[aqua(1,4,7-triazacyclononane)molybdenum-(III)](4+) (12) cation in aqueous acidic solution. Under anaerobic conditions reaction (17) was quantitative and it was shown, using ^{18}O-labelled nitrate, that the oxidised Mo(V) complex had aquired ^{18}O atoms in the terminally bound positions. In anhydrous MeCN silver(I) nitrate may be oxidised by electrolysis or by reaction (18) with N_2O_5.[57] From the e.s.r. spectrum at 77K



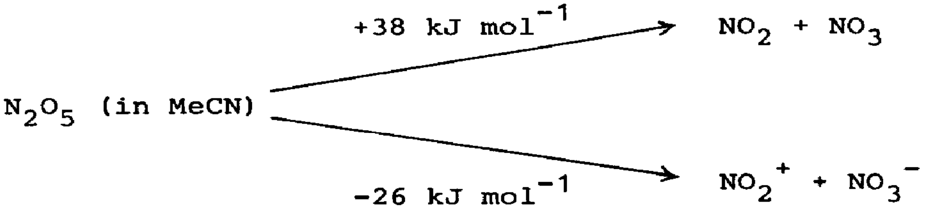
(12)

...(17)



$N_2O_5 + Ag^+ + 3NO_3^- \longrightarrow Ag(NO_3)_4^- + NO_2$ ...(18)

silver(II) is in an axially distorted square planar field and resonance Raman spectra confirm a square planar coordination by unidentate nitrate groups. Decomposition of $Ag(NO_3)_4^{2-}$ solutions in MeCN occurs to cyanomethyl nitrate and HNO_3 and they react with p-xylene to give $p\text{-}MeC_6H_4CH_2ONO_2$. From their equilibrium and electrochemical studies Tracey and Nash[57] deduced ΔG°_{298} values for the radical and ionic dissociation processes shown in Scheme 5. The kinetics of the gas-phase recombination of NO_2 and NO_3 at low



Scheme 5

$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$ ...(19)

$NO_3 + NO_2 \rightarrow N_2O_5$ ...(20)

$NO_3 + HCHO \rightarrow HONO_2 + HCO$ ...(21)

pressures have been measured by Smith and his colleagues.[58] Using published rate coefficients for the decomposition of N_2O_5 the quotient for equilibrium (19) and the $\Delta H_f^\circ(298)$ of NO_3 were calculated to be 2.5 x 10^{10} molecule cm^{-3} and 17.2 kcal mol^{-1} respectively. The absorption cross section of NO_3 at 622.3nm has been determined from spectra measured over the range 615 to 670nm in Cl_2-$ClONO_2$-N_2 and F_2-HNO_3-N_2 mixtures.[59] The rate coefficient for reaction (20) was determined to be (4.8±0.3) $x10^{-13}$ and (5.8±0.8) $x10^{-13}cm^3$ $molecule^{-1}s^{-1}$ at total pressures of 24 and 40 torr of N_2 respectively. The rate coefficient (2.7±1.0) $x10^{-11}cm^3$ $molecule^{-1}s^{-1}$ for the reaction between Cl and NO_3 at 298K was also deduced. The kinetics of reaction (21) have been studied by i.r. and visible spectroscopy of dilute gaseous mixtures of O_3, NO_2 and HCHO in N_2/O_2 at 700 torr.[60] The kinetic data were analysed using both product formation rates and reactant consumption rates and computer simulations of the complex reactions which follow reaction (21). The results show that reactions involving the HO and HO_2 radicals must also be considered when estimating the N_2O_5 decay rate in the presence of HCHO: the best estimate for k_{21} obtained in this way is (6.3±1.1) $x10^{-6}cm^3$ $molecule^{-1}s^{-1}$ at 25±2°C.

Electrochemical studies demonstrate that a rhodium wire can be used as a reference electrode in HNO_3-N_2O_4 mixtures.[61] Electrode reaction (22) occurs on the surface of the metal. Platinum can also be used as a reference electrode, although its performance is

$$NO_2^+ + e^- \rightarrow \tfrac{1}{2}N_2O_4 \qquad ...(22)$$

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \qquad ...(23)$$

slightly inferior to Rh. Electrochemical studies using this reference system indicate that stainless steels corrode in this medium by a mechanism involving transpassive breakdown. The breakdown is prevented by cathodic polarisation or by the addition of fluoride or PF_5. The i.r. and Raman spectra of solid and liquid HNO_3 have been reinvestigated in order to clarify the problem of self-dissociation in the liquid state. Potier et al.[62] provide evidence for the presence of H_2OH^+--ONO_2^-, H_2O--$HONO_2$, and H_3O^+ as well as the species shown in equation (23). An exploratory study of the Raman spectra of nitric acid solutions

(11m and 37m at 25°C) at temperatures up to 250°C has been carried out by Ratcliffe and Irish.[63] The decrease in the ν(N-OH) and δ(NO_2) bands of HNO_3 as temperature and concentration increase have been interpreted in terms of the reduced strength of hydrogen bonding. Approximate values of the degree of dissociation α have been determined and show that nitric acid is a very much weaker acid at high temperatures. Raman and u.v. spectroscopy of solutions of nitric acid in aqueous H_2SO_4 (1-98 wt%) and $HClO_4$ (1-70 wt%) have been carried out to determine the concentrations of HNO_3, NO_3^- and NO_2^+ as a function of composition of the medium.[64] The ground-state geometry of pernitric acid HO_2NO_2 has been investigated by SCF and perturbation theory calculations;[65] the equilibrium geometry has no symmetry. Vertical excitation energies were calculated and the results compared with the observed u.v. photolysis.

5.1.8 Bonds to Sulphur or Selenium

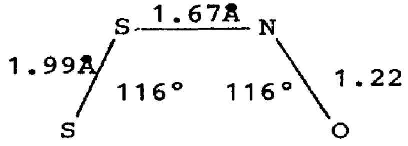
Coordinated NS and NO in their η^5-cpCr$(CO)_2$-complexes have been compared by gas-phase u.v. and X-ray photoelectron spectroscopy.[66] Most of the ionisation potentials are similar except for the N 1s binding energies which are almost 2eV lower for the NS analogues. A large number of new thionitrosyl transition metal complexes should be accessible via a very general route, see equation (24); this reaction is quantitative when M =

$$ML + NS^+AsF_6^- \rightarrow M(NS)^+AsF_6^- + L \qquad ...(24)$$

$$L = CO \text{ or } SO_2$$

cpFe$(CO)_2^+$.[67] As part of an attempt to understand structural and stability trends in sulphur-nitrogen compounds Gimarc et al.[68] have calculated topological resonance energies of some known and proposed rings and polycycles. Their results indicate that several species not yet reported should be stable. E.p.r. spectroscopy of the redox products from $NS^+SbF_6^-$ and $PNP^+S_3N_3^-$ showed signals only for the products of reduction of NS^+.[69] One species, $N_2S_3^+$, giving a triplet signal, has been detected previously but the other signal, a quintet of triplets, could not be assigned to a known radical.

The reaction of NO with blue polysulphide solutions in nonaqueous solvents generates the yellow colour of the perthionitrite ion, $SSNO^-$, which could be isolated as its stable PNP^+ salt.[70] The same compound was obtained from the reaction between $PNP(NO_2)$ and either sulphur or $PNPS_{12}$. The crystal structures of $PNP(S_2NO)$ and PNP(SNO) were solved; the dimensions of the two planar anions (13) and (14) are shown below.[71] The formation of the latter



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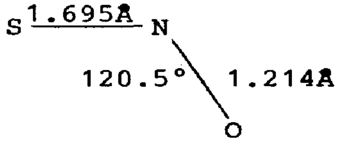


(14)

species from the perthionitrite can be rationalised as in equation (25).[70]

$$PNP(SSNO) + Ph_3P \rightarrow PNP(SNO) + Ph_3PS \qquad ...(25)$$

$$PNP = Ph_3PNPPh_3$$

Trithiazylchloride $(NSCl)_3$ reacts with metallic Cr or other Cr compounds to form as the major product, $S_4N_3^+[CrCl_4(N_2S_2)]^-$. This was converted by Ph_4AsCl to $(Ph_4As)_4[CrCl_4(\mu\text{-}N_2S_2)]_4.8CH_2Cl_2$: the structure of the novel anion is shown in Figure 2.[72] A series of vanadium and tungsten complexes containing the chelating ligand N_3S_2 have been prepared and characterised by X-ray crystallography. In the $[W(N_3S_2)O(N_3)_2]_2^{2-}$ binuclear anion (14) both the planar N_3S_2 ligands bridge the W atoms.[73] The reaction of $(NSCl)_3$ with VCl_4 generates the chlorine bridged dimer $[VCl_3(NSCl)_2]_2$, containing the N-bonded N≡SCl ligand.[74] Reaction of S_4N_4 with $ReNCl_4/Ph_4AsCl$ produces $(Ph_4As)_2[Cl_4Re(NS)(NSCl)].CH_2Cl_2$;[75] the dianion has both N-bonded NS and NSCl ligands in cis positions of a distorted octahedron. Tetrasulphur tetranitride reacts with $M(PPh_3)_4$, M = Pd or Pt, forming $[M(S_2N_2)(PPh_3)]_2.CH_2Cl_2$.[76] The X-ray structure of the Pt-compound shows the $Pt_2(S_2N_2)_2$ unit to be planar with bridging N atoms, see Figure 3.

From the reaction of NSF with $LiN(SiMe_3)R$, R = CMe_3 or $SiMe_3$, a range of compounds containing -N=S=N- fragments, e.g. $Me_3SiNSNR$ and $(Me_3CNSN)_2S$, have been isolated.[77] When the reaction with R = $SiMe_3$ was carried out without stirring a small yield of S_4N_5F (15)

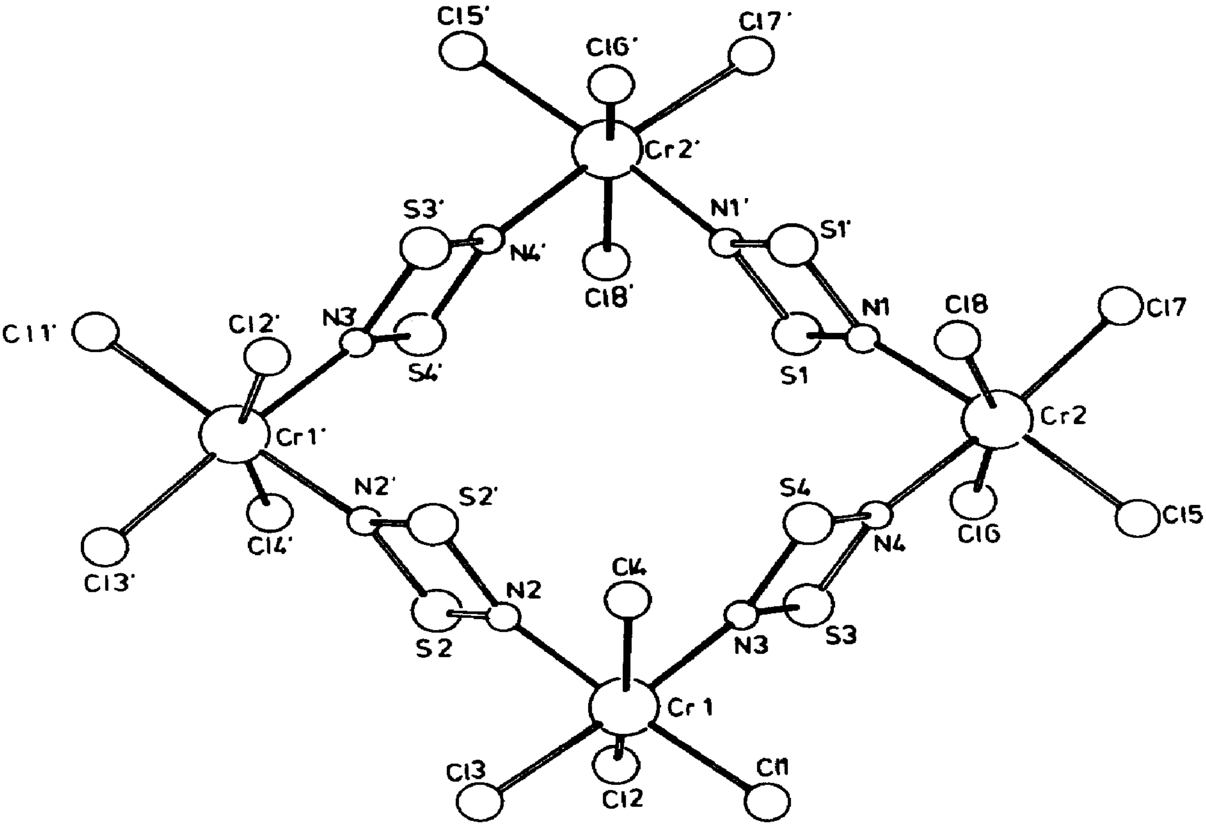


Figure 2. Structure of the $[CrCl_4(N_2S_2)]_4^{4-}$ ion (reproduced by permission from Z. Naturforsch., Teil B, 40(1985)1314)

was obtained. Sutcliffe and co-workers[78] have reported the reactions of NS_2AsF_6 with MeCN, MeC≡CH, and HC≡CH to yield respectively the AsF_6^- salts of (16), (17), and (18). The crystal structures of the first two of these salts were determined by X-ray methods. All three cations were reduced to the neutral radicals, which were then characterised by e.s.r. spectroscopy; solutions of these radicals were found to be stable at room temperature.

Solutions of the anion radical, $^{\bullet}ON(SO_3)_2^{2-}$, of Fremy's salt

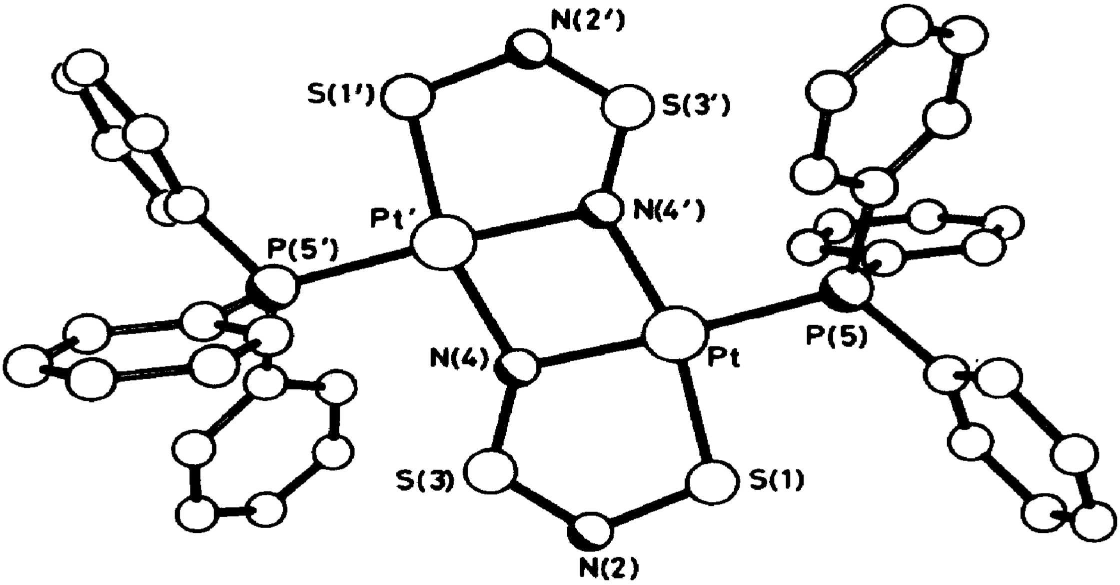
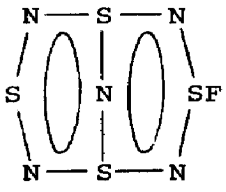


Figure 3. The molecular structure of $[Pt(S_2N_2)PPh_3]_2.CH_2Cl_2$; selected bond distances S(1)-N(2) 1.69, N(2)-S(3) 1.53, S(3)-N(4) 1.55Å, S(1)-N(2)-S(3) 120°, N(2)-S(3)-N(4) 113° (reproduced by permission from J. Chem. Soc., Chem. Commun., (1985)1325).



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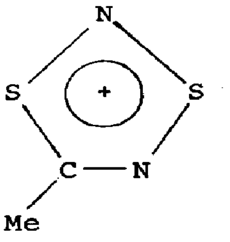

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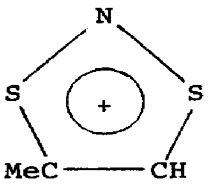

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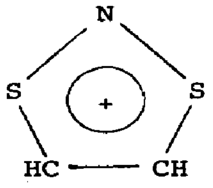


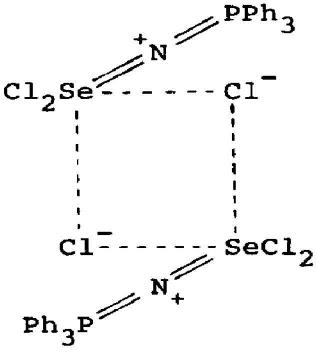
(18)

can be conveniently prepared for e.s.r. purposes by the aerial oxidation of an equimolar mixture of $NaNO_2$ and $NaHSO_3$ in aqueous alkali.[79] Sulphinyl (thionyl) fluoride, SOF_2, reacts with active NH groups, as in piperidine or morpholine, to give NS(O)F derivatives, whereas COF_2 fluorinates piperidine to the N-fluoro compound.[80] Trasher and co-workers[81] have found a new route, reaction (26), to a compound containing the $(SF_5)_2N$ group. Several new compounds containing N-Se single or (formally) double bonds have been prepared and characterised by X-ray methods. The N-Se bond lengths in (19) and (20) were shown to be 1.608(4) and 1.735(4)Å as represented by the resonance structures shown.[82] These bond lengths are significantly shorter than those found in other compounds which usually lie in the range 1.82-1.85Å.

$$SF_5NCl_2 + SF_5Cl \xrightarrow{h\nu} (SF_5)_2NCl + Cl_2 \qquad ...(26)$$

$$Ph_3P{=}N{-}SiMe_3 + SeCl_4 \rightarrow \underset{(\underline{19})}{Ph_3P{=}N{-}SeCl_3} + Me_3SiCl \qquad ...(27)$$

$$Ph_3P{=}N{-}SiMe_3 + (\underline{19}) \rightarrow \underset{(\underline{20})}{(Ph_3P{=}N)_2SeCl_2} + Me_3SiCl \qquad ...(28)$$



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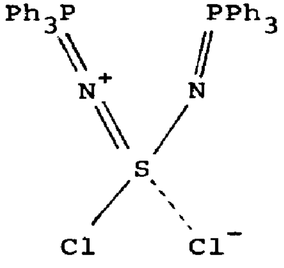


(20)

5.1.9 Bonds to Halogens

Aramaki et al.[83] have reported that high yields of NF_3 can be obtained from the oxidation of $(NH_4)_3AlF_6$ with F_2 over the temperature range 100° to 250°C. A new NF_4^+ salt, with the counterion CrF_6^-, has been prepared in 96% purity by the reaction of excess NF_4HF_2 with CrF_5 in HF solution.[84] It has been shown that strong Lewis acids, such as AsF_5 and SbF_5, strongly catalyse an intramolecular redox reaction of ZNF_2, where Z = CF_3, SF_5, Cl, CF_3O, or SF_5O.[85] When Z = Cl a 1:1 adduct with AsF_5 is formed at -78°C which has an F-bridged structure, according to Raman spectroscopic evidence. The decomposition products for Z = CF_3 and SF_5 were CF_4 and SF_6, respectively, along with trans-N_2F_2 and N_2FAsF_6. DesMarteau and co-workers[86] have prepared $(CF_3SO_2)_2NF$ and describe the new compound as a strong fluorinating agent.

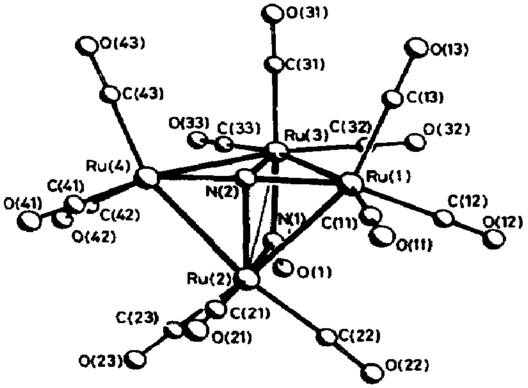
5.1.10 Bonds to Metals

The first example of a lithium methyleneamide ring species in which the ligand exclusively engages in μ_2-bridging between two Li atoms has been found in $[Bu^t_2C{=}NLi.OP(NMe_2)_2]_2$.[87] The Li_2N_2 ring is strictly planar with very short LiN bonds, 1.923 and 1.948Å. In dilute solution in benzene the monomeric form is however dominant.

$$2WCl_6 + N(SiMe_3)_3 \rightarrow W_2NCl_9 + 3Me_3SiCl \qquad ...(29)$$

The reaction, equation (29), of WCl_6 and $N(SiMe_3)_3$ produces the bright red W_2NCl_9 which appears to be dimeric through bridging chlorines.[88] Treatment of W_2NCl_9 with Ph_4PCl yields $Ph_4P[W_2NCl_{10}]$, containing the almost linear (173°) WNW unit with bond lengths 1.79 and 1.88Å. This new salt reacts slowly on the addition of CCl_4 in CH_2Cl_2 to give $(Ph_4P)_2[W_3N_2Cl_{14}].CCl_4.CH_2Cl_2$ in which the trinuclear anion has nearly linear, 176°, WNW bridges with bond lengths 1.84 and 2.07Å.[89] The reaction of either $GdCl_3$ and GdN or $GdCl_3$ and Gd/N_2 yields the new compound Gd_2NCl_3.[90] The crystal structure contains NGd_4 tetrahedra with Gd-N distances of about 2.27Å. Tetranuclear metal nitrido species of Ru have been characterised by Johnson et al.[91] using X-ray crystallography: the compounds were prepared by the reaction of $[Ru_3(CO)_{10}(\mu_2\text{-NO})_2]$ with CO. They both adopt 64-electron "butterfly" structures, Figures 4 and 5, in which the "hinge" metal-metal vector is long and supports either a μ_2-NO or a μ_2-NCO bridging group.

Near u.v. irradiation of Ni(tet-a)$(N_3)_2$ directly excites the $n\rightarrow\pi^*$ transition of the azido group, which yields a singlet nitrene intermediate;[92] this intermediate scavenges NH_3 to form N_2H_4. The ligand (tet-a) is a methyl substituted 1,4,8,11-tetraazacyclotetradecane. Reactions of various organic azides with $NbCl_3$ have



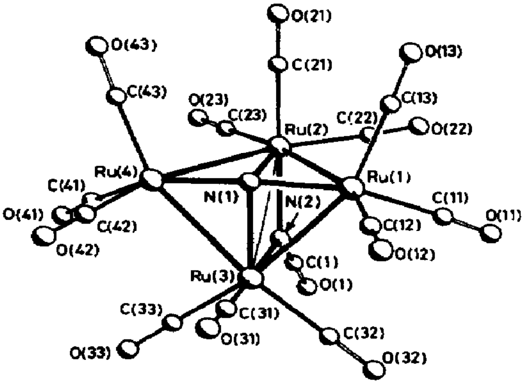


Figure 4. The molecular structure of $[Ru_4N(CO)_{12}(\mu_2\text{-NO})]$.

Figure 5. The molecular structure of $[Ru_4N(CO)_{12}(\mu_2\text{-NCO})]$.

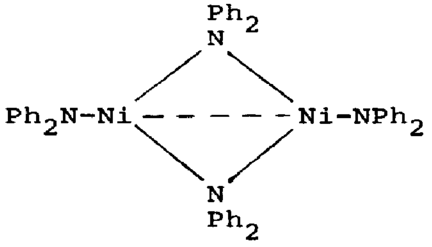
{both} Reproduced by permission from J. Chem. Soc., Chem. Commun., (1985)1526.

yielded a diverse range of products and provide access to azides, nitrenes, or nitrides.[93] Volatile crystals of $Me_3SiN(VCl_3)$, prepared from VCl_4 and Me_3SiN_3, have been characterised by X-ray crystallography.[94] The molecular lattice contains monomers with a linear (177.5°) skeleton and with V≡N 1.59Å. A careful study of the i.r. spectrum of $(\eta^5\text{-}Me_5C_5)_2VNPh$ has allowed Osborne and Trogler[95] to assign the ν(C-N) and ν(V-N) modes to bands at 1330 and 934 cm^{-1}. These bands shift on isotopic substitution with ^{15}N to 1307 and 923 cm^{-1}. These authors propose that the V-N-C oscillator is strongly coupled to the remainder of the molecule; if this also happens in the other known complexes then this rationalises the wide range of ν(M-N) values reported in the literature.

A progress report on the new class of halonitrenes, typified by $ReF_5(NF)$, has been published by Peacock et al.[96] The synthesis of $OsF_5(NCl)$ from OsF_6 by treatment successively with Me_3SiNCO and ClF_3 was described; the new compound was purified by recrystallisation from HF.[97] The product was characterised by mass spectrometry and i.r. spectroscopy.

Tuan and Hoffmann[98] have examined the linkage and mode of bonding of NCO^- and N_2O to ML_5 units by fragment analysis of m.o. calculations. Various features of the interaction between the fragments indicate that (a) N-linkage is more stable than O-linkage, and (b) σ bonding is the dominant factor in the metal ligand bond. Their results suggest that other transition metal complexes of N_2O, such as $[Os(NH_3)_5N_2O]^{2+}$ should be stable.

The structure of gaseous dimethylamidogallane, as determined by electron diffraction shows that the D_{2h} dimer, with a cyclic Ga_2N_2 skeleton, predominates.[99] The N-Ga bond length and the angle at N were found to be 2.027(4)Å and 90.6(0.8)°, respectively. The reaction of $[Me_2AuI]_2$ with KNH_2 in liquid NH_3 yields tetrameric and trimeric amidodimethylgold(III).[100] The tetramer converts spontaneously to the trimer at ambient temperature; the latter has a non-planar $(AuN)_3$ skeleton with Au-N 2.15Å. Well-defined, crystalline $[Me_2AuNHMe]_2$, along with other products, has been obtained by the reaction of Me_2AuI with LiNHMe.[101] The Au_2N_2 ring is symmetrical with Au-N 2.14Å. New diarylamido derivatives of the transition metals Ni and Co have been prepared.[102] They were characterised analytically, magnetically, and by single crystal X-ray studies: $Li(THF)_4[Ni(NPh_2)_3].0.5PhMe$ represents the first reported structure of three coordinate nickel(II). Neutral $[Ni(NPh_2)_2]_2$, (21) has a similar molecular structure to that of the Co(II) analogue, for which a revised structure is given in this paper. New imido/amino complexes of



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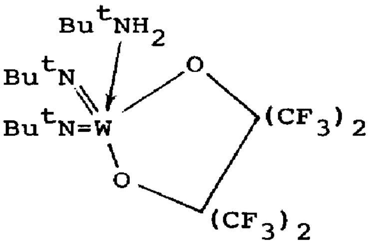
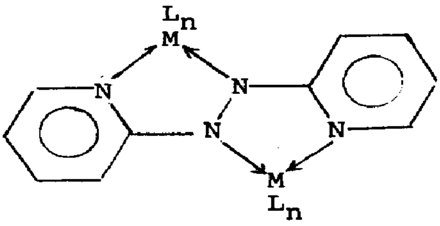


(22)

tungsten have been reported by Chan et al.[103] They were formed by the reaction of either perfluoropinacol or tetraphenylpinacol with $(Bu^tN)_2W(HNBu^t)_2$ and are typified by (22). These compounds were said to show great promise as ammoxidation catalysts.

The controlled synthesis of complexes with very long wavelength charge-transfer absorptions is of interest owing to their potential applications in the chemical use of solar energy. Kaim and co-workers[104] have synthesised two bis-chelate ligands, (23) and (24), and prepared binuclear compounds of each containing low-spin d^6 metals, e.g. ML_n = $Mo(CO)_4$. Thus the pale green $[Mo(CO)_4)_2$ complex (23) shows absorption in the u.v. and near-i.r. but none in the visible. The same group of workers[105] have compared the ligand behaviour of the bipyrimidines (25) to (28) by Huckel m.o. calculations and by experimental measurements of pK_a and spectroscopic and electrochemical properties of their complexes. They have reported that the hitherto neglected ligand (26) is the most π-electron deficient.



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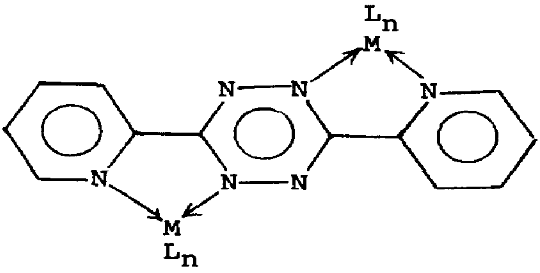

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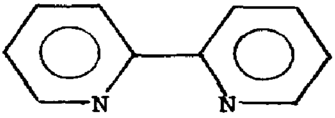

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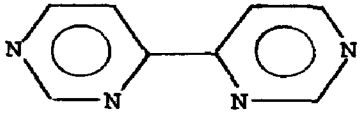

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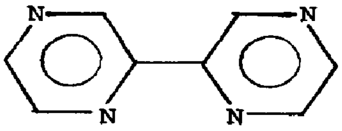

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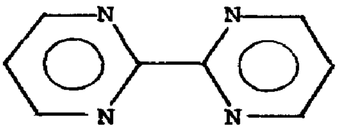


(28)

5.2 PHOSPHORUS

5.2.1 Phosphorus, Polyphosphines and Phosphides

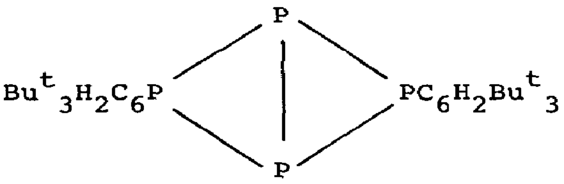
Three new ab initio calculations[106-8] indicate that P_8 is less stable than two P_4 molecules, in contrast to an earlier result. The results, however, point to greater stability for P_8 with a cubic structure than for P_2[106] and that, in the ground state, the $P_8 \rightarrow 2P_4$ transition is forbidden.[107] P_8 could then be a viable intermediate but preparation would not be possible from two tetrahedral P_4 molecules nor from four P_2 units. Preparation might be possible from two square planar P_4 units of electronically excited phosphorus. Factors influencing the stability of P_4 are considered to be the relatively low strain energy in the rings and multicentre bonding with increased 3d orbital participation.[108]

Theoretical studies are also reported for the phosphinidine unit, using PH as a model,[109] and phosphinophosphinidine, PPH_2,[110] which can be stabilised when bonded to transition metal fragments. With the latter, it is possible that in η^1-bonding both lone pairs of the terminal phosphorus can be donated with back coordination of metal electrons into an empty π^*(P-P) orbital.

There are two studies of the diphosphine radical cation, $P_2H_4^{+\cdot}$,[111,112] showing pyramidal geometry at the phosphorus atoms in contrast to the planarity of the related nitrogen species, $N_2H_4^{+\cdot}$. The barrier to torsion about P-P is lower than that about N-N in the hydrazine radical and the two phosphorus atoms are electronically non-equivalent;[111] the P-P bond length in the cation is predicted as being only 3% shorter than in the neutral molecule.[112] Ab initio calculations at the double-zeta level are available for the $P(PH_3)_2^+$ and $N(PH_3)_2^+$ cations.[113]

The major results from a series of ab initio calculations[114] on the $(PH)_n$ molecules with n taking values between two and six are: a) the trans-diphosphene is 2.5 kcal mol^{-1} more stable than the cis-isomer and there is a sizable barrier between the two forms, b) two of the hydrogen atoms are on one side of the ring for n = 3 and trans to the third hydrogen in the most stable form, c) hydrogen atoms are alternatively above and below a slightly distorted P_4 plane for n = 4, d) the P_5 ring is in a distorted envelope conformation, and e) for n = 6, the ring adopts the chair conformation. These results agree with information from X-ray diffraction already obtained on appropriate compounds.

A reaction between white phosphorus, 2,4,6-$Bu^t{}_3C_6H_2Li$ and 2,4,6-$Bu^t{}_3C_6H_2Br$ has led to a derivative of P_4H_2, the simplest possible bicyclic phosphine.[115] The compound (29) results from cleavage of only one of the P-P bonds in the P_4 tetrahedron; from X-ray diffraction the organic groups are in cis-positions, the central P-P bond is 2.166Å while the remaining P-P distances fall between 2.222 and 2.236Å. Also isolated from this reaction was $Bu^t{}_3C_6H_2P{=}PC_6H_2Bu^t{}_3$.



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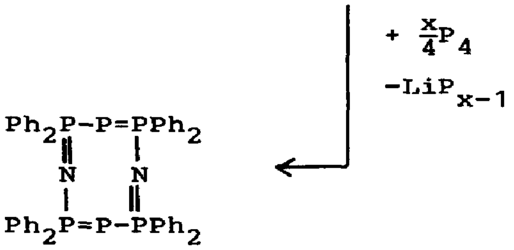
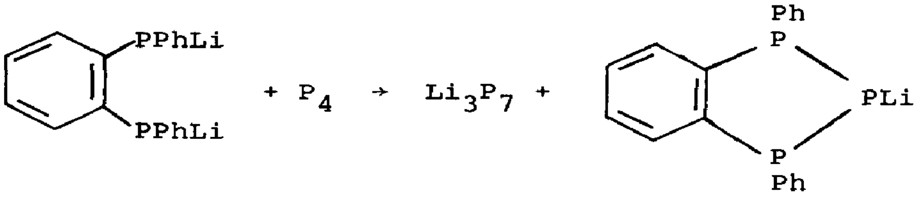
P_4 disproportionation continues to be investigated with a recent report on the formation of the dicyanophosphide anion, $P(CN)_2^-$, and a polyphosphide, usually P_{15}^-, from reactions of the element with cyanides as either alkali-crown ether or tetraalkylammonium salts.[116] (18-crown-6)$KP(CN)_2$ can also be obtained by treating $P(CN)_3$ with KF in the presence of the crown ether. The P-C distances in the anion, mean 1.68Å, are similar to those in phosphaalkenes with a C-P-C angle of 95.2°. Phosphorus also disproportionates with polyphosphide formation with the lithium aminophosphines, $Li[PhN{\cdot}PPh_2]$ and $Li[Ph_2P{\cdot}N{\cdot}PPh_2]$,[117] (equations 30 and 31) and with o-phenylene bis(lithium phosphide) (equation 32).[118]

$$Li[PhN{\cdot}PPh_2] + \tfrac{x}{4}P_4 \rightarrow LiP_{x-1} + Li[PhN{:}PPh_2{\cdot}P{:}PPh_2{\cdot}NPh] \qquad \ldots(30)$$

$$Li[Ph_2P{\cdot}N{\cdot}PPh_2] + \tfrac{x}{4}P_4 \rightarrow LiP_{x-1} + Li[Ph_2P{\cdot}N{:}PPh_2{\cdot}P{:}PPh_2{\cdot}N{\cdot}PPh_2]$$



(30) ...(31)



(31)

...(32)

The intermediate in equation 31 reacts with further phosphorus to give (30), an analogue of the cyclotetraphosphazene, $N_4P_4Ph_8$, in which two of the ring nitrogen atoms have been replaced by phosphorus.[117] An attempt to prepare the end member of this series, i.e. $P_4(PPh_2)_4$, by a similar disproportionation of P_4 with $LiPPh_2$ was unsuccessful probably because the compound is thermodynamically less stable than the P_2Ph_4 and P_4 decomposition products.

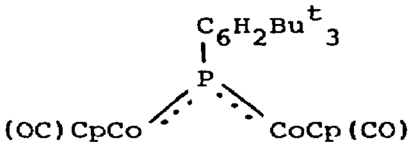
The benzotriphosphole product (31) from equation 31, which has been examined by single crystal X-ray diffraction, reacts readily with halides such as HX, MeX, $SiMe_3X$ and PPh_2X substituting the lithium atom.[118]

New phosphines, including $(CHF_2)_3P$, $(CHF_2)_2PI$ and CHF_2PI_2, have been synthesised from reactions at 190°C between white phosphorus and CHF_2I.[119] Treatment of $(CHF_2)_2PI$ with mercury gives the diphosphine $P_2(CHF_2)_4$, which can be converted to $(CHF_2)_2PH$ by hydrogen iodide, while reaction of $(CHF_2)_2PI$ with $HgCl_2$ at ca. 80°C gives $(CHF_2)_2PCl$. A new hybrid diphosphine $(CHF_2)_2P{\cdot}P(CF_3)_2$ can be obtained by equilibration of a $P_2(CHF_2)_4$-$P_2(CF_3)_4$ mixture at 25°C.

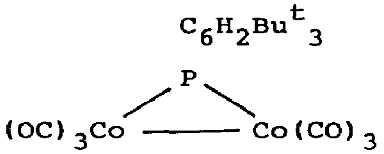
A short review covers the chemistry of compounds containing the λ^3-λ^5, λ^3-λ^4, and λ^3-λ^3 types of P-P bonds[120] and the ligand behaviour of multiply bonded species such as P_2, As_2, RC≡P, RC≡As, $R_2C{=}PR^1$, $R_2C{=}AsR^1$, RP=PR, RP=AsR etc. has been summarised.[121]

An open phosphinidene complex (32), i.e. one containing no M-M bond, has been prepared from 2,4,6-$Bu^t{}_3C_6H_2PCl_2$ and $Na[Co_2(CO)_2Cp_2]$ in THF,[122] while the three membered ring product (33) is obtained when $K[Co(CO)_4]$ is used.[123] $K[CpMo(CO)_3]$ gives a PMo_2 analogue and in each the phosphorus atom is trigonal planar.

t-Butyldichlorophosphine and $Na[Fe(CO)_2(C_2Me_5)]$ react in methyl-

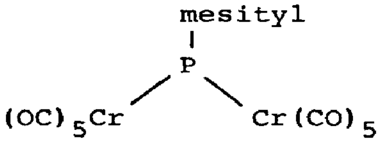


(32)



(33)

cyclohexane solution to give $(\mathrm{Me_5C_5})\mathrm{Fe(CO)PBu^tCl}$[124] but both phosphinidine, i.e. $[(\mathrm{OC})_5\mathrm{M}]_2\mathrm{PR}$, and diphosphene complexes, $[(\mathrm{OC})_5\mathrm{M}]_n.\mathrm{RP{=}PR}$ where n = 1 or 2, can be obtained from $\mathrm{Na_2[M_2(CO)_{10}]}$ (M = Cr, Mo or W), and $\mathrm{RPCl_2}$ (R = mesityl or $\mathrm{CH(SiMe_3)_2}$).[125] Of the compounds prepared, full X-ray structures have been carried out on compounds (34)-(36).



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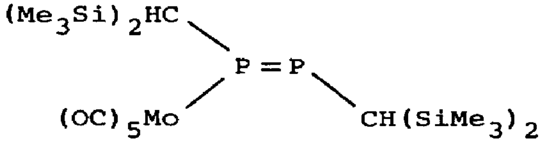

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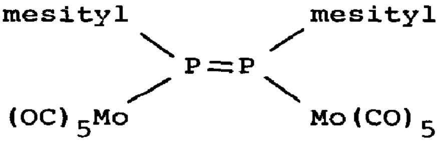
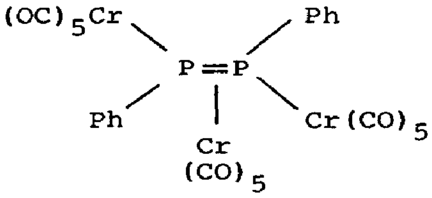


(36)

A recent theoretical study[126] of, in particular, the end-on bonding mode of diphosphene ligands has pointed to the inadequacy of its description as a simple two electron donation process.

The complexes $\mathrm{Bu^t{}_3C_6H_2P{=}P}$(mesityl)$.\mathrm{M(CO)_5}$, where M = Cr, Mo or W can be prepared either by reaction of the diphosphene with $\mathrm{M(CO)_5.THF}$ or by HCl abstraction between $\mathrm{Bu^t{}_3C_6H_2PH_2.M(CO)_5}$ and (mesityl)$\mathrm{PCl_2}$, but with the more heavily hindered compound $\mathrm{Bu^t{}_3C_6H_2P{=}PC_6H_2Bu^t{}_3}$, $\mathrm{Cr(CO)_6}$ reacts to give the mono- and bis-arene-$\mathrm{Cr(CO)_3}$ complexes.[127] Further work in this area shows that, as initially formed, the complexes $\mathrm{Bu^t{}_3C_6H_2P{=}PC_6H_2Me_3}$.-$\mathrm{M(CO)_5}$ are formed in the E configuration by donation from the phosphorus atom carrying the mesityl group but on irradiation at 0°C in hexane with a medium pressure lamp quantitative conversion occurs to the Z isomer.[128] The Z isomer for M = Cr has been examined by single crystal X-ray diffraction.

On heating to 70°C, the tri-chromium carbonyl complex (37) loses one $Cr(CO)_5$ unit to give (38) which can then react as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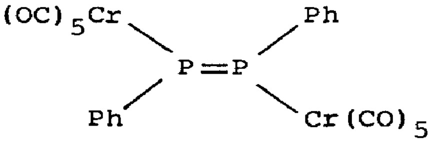
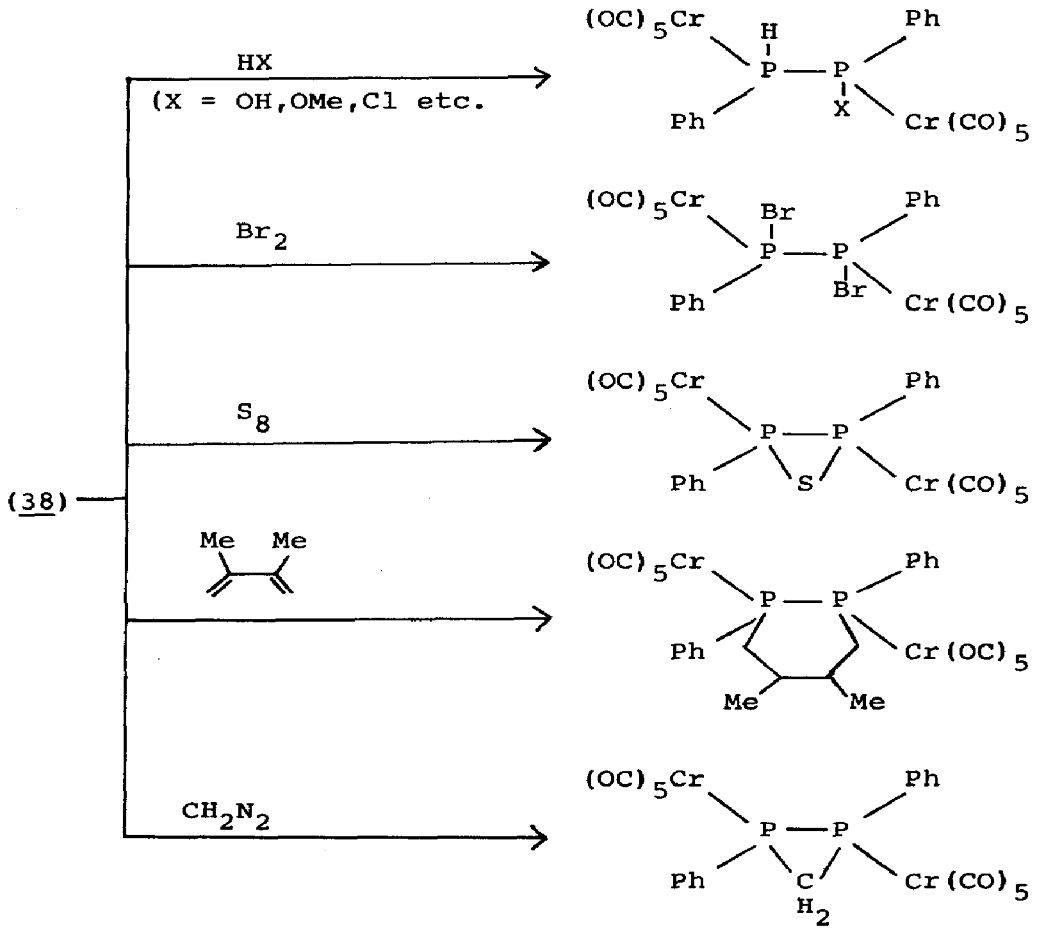
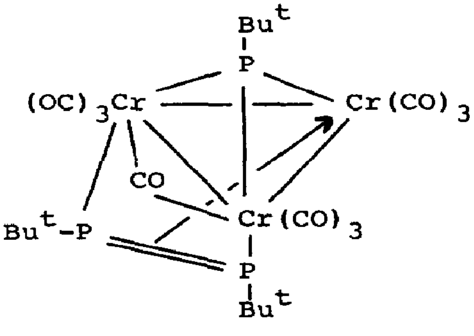

(38)

summarised in Scheme 6.[129] X-ray structures are available for a number of the products.



Scheme 6

Contrary perhaps to expectations, thermolysis of $Bu^tP[Cr(CO)_5]_2$ at 100°C does not yield the diphosphene complex $Bu^tP{=}PBu^t.\ Cr(CO)_5]_3$ but the product is a cluster compound (39) containing a $Bu^tP{=}PBu^t$ molecule both end and side bonded together with a μ_3-PBu^t group.[130] A novel diphosphene complex (40) is however obtained when 2,4,6-$Bu^t{}_3C_6H_2PCl_2$ and $(Me_5C_5)M(CO)_2[P(SiMe_3)_2]$ (M = Fe or Ru) react at room temperature in THF solution.[131] As in most complexes, the iron complex is in the E configuration with a P-P bond distance of 2.02Å. Isolation of a new diphosphene $(Me_5C_5)P{=}P)C_5Me_5)$ by magnesium promoted halogen abstraction from $(Me_5C_5)PBr_2$ has been announced;[132] among the by-products are the cyclic phosphines $(Me_5C_5)_3P_3$ and $(Me_5C_5)_2P_4$.



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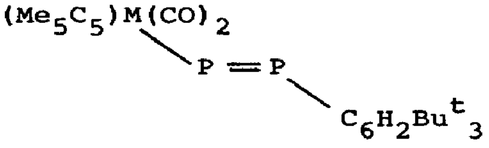
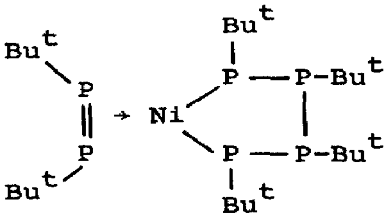


(40)

An unusual complex (41) containing both an η^2-bonded diphosphene and an NiP_4 ring has been isolated from reactions between $NiCl_2(PMe_3)_2$ and $Li_2[Bu^tP\text{-}PBu^t]$ in THF at -78°C.[133] The five-membered ring, which results from coupling between two $Bu^tP{=}PBu^t$ units, has t-butyl groups occupying positions alternately above and below the NiP_6 plane. A second diphosphene,



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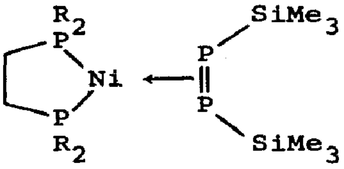
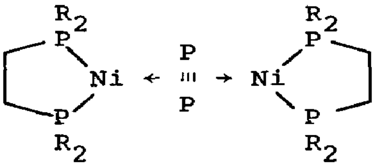


(42)

also not known in the free state, is stabilised in the nickel complex (42) obtained by treating $[R_2PCH_2CH_2PR_2]NiCl_2$ (R = Et or cyclohexyl) with $LiP(SiMe_3)_2$.[134] Similar products are obtained when the nickel chloride chelate reacts with either $R^1P(SiMe_3)_2$ or $[R^1(Me_3Si)P]_2$ for R^1 = Me, Bu^t or Ph but redox processes occur with $LiPR^1(SiMe_3)$, R = Me, Bu^t or Ph, and the products are diphosphines. Finally, reactions between the $NiCl_2$.chelate and either $P(SiMe_3)_3$, $[P(SiMe_3)_2]_2$ or $HP(SiMe_3)_2$, which might also have produced $Me_3SiP{=}PSiMe_3$ complexes (42), gave in fact (43) containing a coordinated P_2 group. The structure has been confirmed for (43, R = Et) by X-ray diffraction.

Reactions between CF_3PI_2 and a range of 1,3-dienes in the



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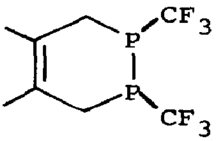

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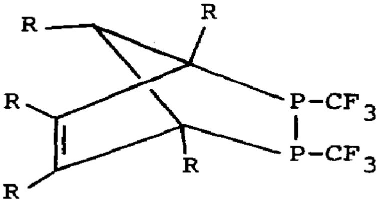

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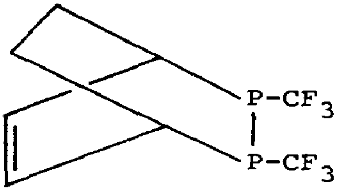


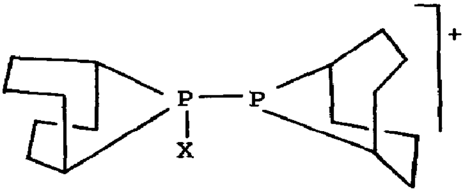
(46)

presence of tin(II) chloride yielded the new heterocycles (44)-(46) in one pot syntheses, probably proceeding via [2+4] cycloadditions with the diphosphene intermediate $CF_3P{=}PCF_3$.[135]

A range of radicals with the general formula $Ar(R_3Si)\dot{C}{\cdot}OP(O)Ph_2$ has been generated by irradiation of mixtures of Ph_4P_2 and aroyl silanes, $ArC(O)SiR_3$ where R = Me or Ph and Ar = Ph, $4\text{-}ClC_6H_4$, $4\text{-}MeOC_6H_4$, etc.[136]

Coordination chemistry of the ligands $Me_2E{-}P(CF_3)_2(\equiv L)$, where E = P or As, has been investigated to show the formation of complexes such as cis-$M(CO)_4L_2$, $[(OC)_4ML]_2$ and $[(OC)_5M]_2L$ where M = Cr, Mo or W.[137] P-P bond cleavage occurs when $Cp(CO)_3MH$ (M = Cr, Mo or W) reacts with diphosphines such as Ph_2PPPh_2, $(NC)_2PP(CN)_2$ and Ph(NC)PP(CN)Ph or $(PhP)_5$ giving products such as $Cp(CO)_3MPRR'$.[138] Iodine containing diphosphines, e.g. PhIPPIPh or P_2I_4, on the other hand show redox behaviour giving $Cp(CO)_3MI$ and unstable iododiphosphines.

An interesting new diphosphine in the form of a mixture of the two salts (47 , X = H or I) is obtained on quaternisation of the secondary phosphine (48) with C_3F_7I.[139] The free diphosphine results on reduction of the salts with sodium hydride. A major product of the $AgAsF_6$-$PhPH_2$ reaction in dichloromethane is



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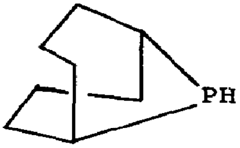

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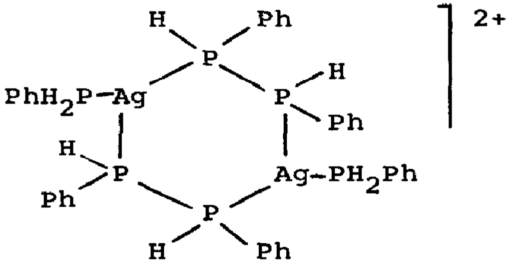

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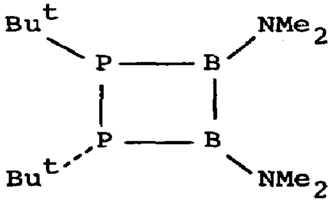
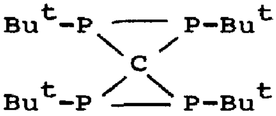


(50)

$[PhPH_2Ag(\mu\text{-}PhHP\text{-}PHPh)]_2[AsF_6]_2$ (49) shown to have a centrosymmetric cation;[140] a related Cu(I) complex can be produced using $Cu(AsF_6)_2$.

Cyclo-condensation of a substituted diboron dichloride, e.g. $Cl(Me_2N)B\text{-}B(NMe_2)Cl$, with $K_2(PBu^t\text{-}PBu^t)$ in pentane at −78°C gives (50) whose n.m.r. spectrum is interpreted in terms of a planar P_2B_2 ring.[141]

The spirocyclic molecule (51), for which full X-ray identification is now available, has ca. $\bar{4}$ symmetry with the t-butyl groups in an all trans arrangement,[142] and an air stable diphosphasilirane (52) is one of the products obtained by treating $Bu^t_2SiI_2$ with 2,4,6-$Bu^t_3C_6H_2PCl_2$ and an excess of lithium naphthalenide.[143] Among the other products is $Bu^t_3C_6H_2P{=}PC_6H_2Bu^t_3$. He(I) photoelectron spectra have been obtained for a series of three membered ring compounds containing from one to three phosphorus atoms and for the arsenic containing analogues, $(Bu^tAs)(Bu^tP)_2$ and $(Bu^tAs)_3$.[144]



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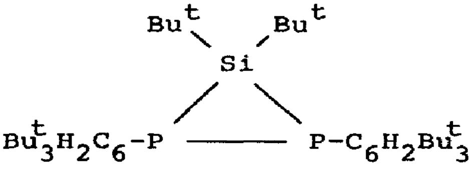
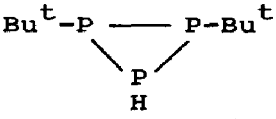


(52)

The new cyclotriphosphine (53), obtained by either hydrolysis of $KP(Bu^tP)_2$ or treatment of $(Bu^tP)_2SiMe_3$ with methanol, is unstable at room temperature and readily converted to the cyclotetraphosphine (54).[145] Reaction between $(Pr^iP)_3$ and $Ni(CO)_4$ in pentane solution gives a complex, $[Ni_2(\mu\text{-}P_3Pr^i_3)_2(CO)_4]$, as a mixture of two isomers differing in the relative arrangements of the P_3 rings.[146] The product is only slightly sensitive to air and moisture.



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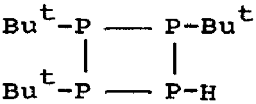
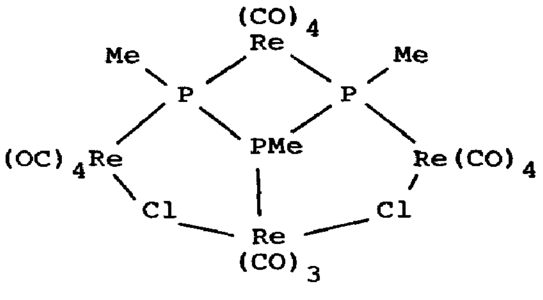


(54)

A triphosphine ligand, behaving as an 8 electron donor, occurs in the tetranuclear rhenium complex, $Re_4Cl_2(CO)_{15}[MeP{\cdot}PMe{\cdot}PMe]$ (55) obtained when $Re_2(CO)_{10}$ and $Ni(MePCl_2)_4$ are heated to 220°C.[147] The ligand is considered to arise via a nickel intermediate such as (56). Compound (55) will react with further $Re_2(CO)_5$ at between 230 and 250°C to give $Re_6(CO)_{18}(\mu_4\text{-}PMe)_3$ and $Re_5(CO)_{14}(\mu_4\text{-}PMe)(\mu\text{-}PMe_2)\{\mu_3\text{-}P[Re(CO)_5]\}$.[148] The former contains a trigonal prism of rhenium atoms with three μ_4-methylphosphinidene groups from the break up of the Me_3P_3 unit in (55). The latter



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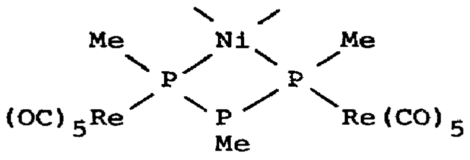


(56)

is based on a square pyramid of metal atoms base capped by one MeP group and bridged on one edge by a PMe_2 group; the structure is completed by one triangular face capped by a $PRe(CO)_5$ group.

Although neither Ph_3P nor $AlCl_3$ alone reacts with PCl_3, in combination they cause reductive cleavage of the trichloride (equation 33) with formation of a symmetrical phosphenium salt.[149] There are two independent molecules in the asymmetric unit with P–P distances (2.137, 2.128Å) falling between those for a single and double bond; the P–P–P angle (102.2, 103.0°) is low. In the presence of aluminium trichloride, hydrogen chloride or alkyl chlorides react with the triphosphenium salt (equation 34) and with a more basic phosphine, the salt can be converted into an unsymmetrical species (equation 35). A new cyclic cation (57)

$$PCl_3 + 2Ph_3P + 2AlCl_3 \rightarrow [Ph_3P{\cdot}P{\cdot}PPh_3]AlCl_4 + [Ph_3PCl]AlCl_4 \quad ...(33)$$

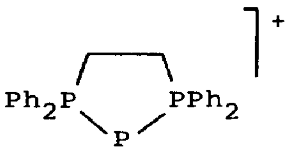
$$[Ph_3P{\cdot}P{\cdot}PPh_3]AlCl_4 + RCl + AlCl_3 \rightarrow [Ph_3P{\cdot}PR{\cdot}PPh_3][AlCl_4]_2 \quad ...(34)$$

R = H or alkyl.

$$[Ph_3P{\cdot}P{\cdot}PPh_3]AlCl_4 + Bu_3P \rightarrow [Bu_3P{\cdot}P{\cdot}PPh_3]AlCl_4 + Ph_3P \quad ...(35)$$

results on reaction with the chelating diphosphine, $Ph_2PCH_2CH_2PPh_2$, and (57) can be converted to a dipositive species (58) similar to that in equation 34 on treatment with t-butyl chloride and $AlCl_3$ in dichloromethane solution.[150] More complex species, i.e. (59)-(61), result from reaction with $PhP(CH_2CH_2PPh_2)_2$, $MeC(CH_2PPh_2)_3$ and $C(CH_2PPh_2)_4$ respectively.

Preparation of a dication was shown in equation 34 but such compounds can also be produced directly (see equation 36).[151] The X-ray structure of the product with R^1 = H shows pyramidal



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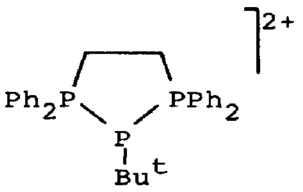

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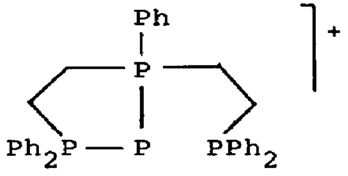

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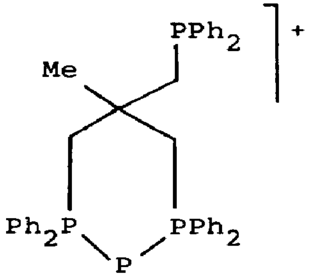

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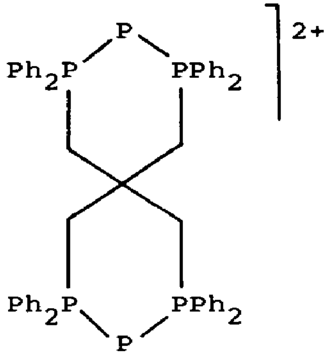


(61)

$$2R_3P + R^1PCl_2 + 2AlCl_3 \rightarrow [R^1P(PR_3)_2][AlCl_4]_2 \qquad ...(36)$$

R = Ph, Bu or Me/Ph
R^1 = H, Me, Et, CH_2Cl, etc.

geometry about the central phosphorus atom in contrast to planarity in the isoelectronic ylid $R_3P{\cdot}CR^1{\cdot}PR_3$ and it appears that two adjacent phosphonio groups are not sufficient to reduce the stereochemical activity of the phosphorus lone pair.

He(I) photoelectron spectra of the cage compounds (62, X = P, As or Sb) have been measured and the first five bands assigned using MINDO/3 model calculations.[152] It is probable that the cyclic P_6 molecule, obtained if all the CH groups in benzene were replaced by isoelectronic P atoms, would be unstable as an isolated molecule but the compound has been stabilised as part of the triple decker complex (see Figure 6) obtained as one of the products from heating white phosphorus and $[(Me_5C_5)Mo(CO)_2]_2$ in xylene at 140°C.[153] The compound is centrosymmetric with both

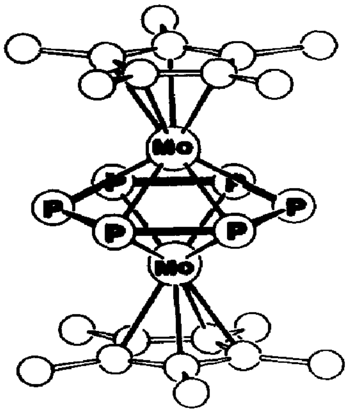
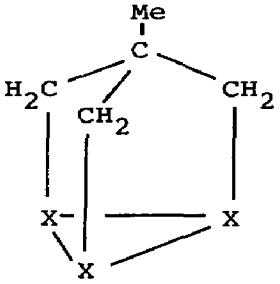


Figure 6. Structure of $[(Me_5C_5)Mo]_2P_6$ (reproduced by permission from Angew. Chem., Int. Ed. Engl., 24(1985)351).

the five- and six-membered rings being parallel. The mean P-P distance is 2.170Å, the P-Mo distance is 2.541Å. In addition to the P_6 compound, the initial reaction also produces compounds (63)-(65) containing other coordinated phosphorus groups.



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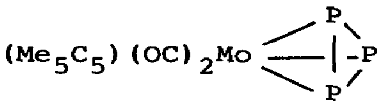

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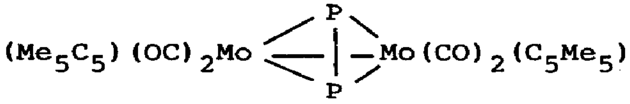
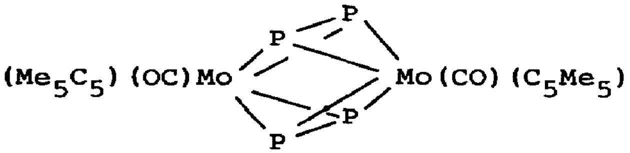
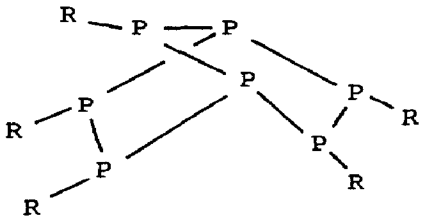


(64)



(65)

Reaction of methanol with $(Me_3Si)_3P_7$ gives the heptaphosphine P_7H_3 with a cage structure similar to that in P_4S_3;[154] two diastereoisomers are present according to an n.m.r. investigation which differ in the orientation of the three hydrogen atoms. Heptaphosphines P_7R_5, carrying small alkyl group substituents on the other hand have the bicyclo-[2.2.1] structure (66) but with R = Bu^t, the heptaphosphine structure (67) is based on the bicyclo-[3.2.0] form with an annelated four-membered ring.[155] Compound (67) can be isolated along with a range of other polyphosphines including $(Bu^tP)_{3,4}$, $Bu^t{}_4P_6$, $Bu^t{}_6P_8$ in the magnesium dehalogenation of Bu^tPCl_2-PCl_3 mixtures.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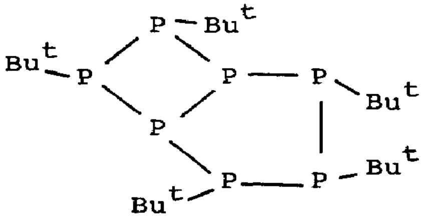
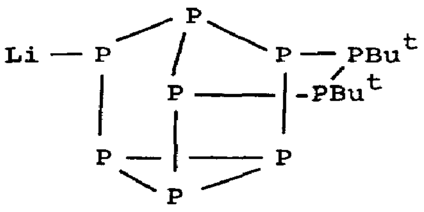

(67)

A specific synthesis for the tetracyclic P_9 skeleton (68) uses the reaction of Li_3P_7 with $ClBu^tP$-PBu^tCl in benzene at room temperature;[156] the remaining lithium atom can be replaced either by hydrogen or an alkyl group on reaction with, respectively, acetic acid and an alkyl bromide. The new polyphosphide $Li_2H_2P_{14}$ (69) can be isolated from a variety of reactions as an orange-red solid;[157] preparative methods include the following: P_2H_4-BuLi (-25°C), LiH_4P_5-P_2H_4 (-78°C), Li_3P_7-P_2H_4 (-25°C), the disproportionation of LiH_4P_7 (25°C). The structure, which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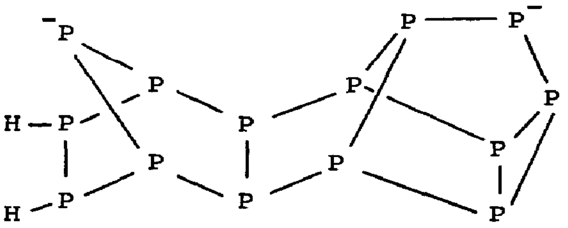

(69)

contains both P_7^{5-} and P_9^{3-} units, follows from a detailed two dimensional n.m.r. study. Methyl and ethyl hexadecaphosphines $P_{16}R_2$ can be prepared by treating Li_2P_{16} with the appropriate alkyl bromide in DMF.[158]

High temperature reactions of the elements give two isostructural ternary phosphides $Na_{10}Si_2P_6$ and $Na_{10}Ge_2P_6$, containing $M_2P_6^{10-}$ ions, based on edge sharing between two MP_4 tetrahedra,[159] with Si-P and Ge-P distances in the ranges 2.258-2.335 and 2.334-2.425Å respectively. The anions are analogues of the known $Ge_2S_6^{4-}$, $P_2S_6^{2-}$ and $Si_2S_2Br_4$ species. Among the other ternary phosphides reported during 1985 are:

Ni_2SnP with a structure related to the NiAs and MnP types;[160]

MCo_2P_2 (M = La, Ce, Pr, Nd, Sm, Th or U) MFe_2P_2 (M = La, Ce or U) and $ThCo_2As_2$;[161]

$LaCo_2P_2$, $CeCo_2P_2$, $PrCo_2P_2$, $LaFe_2P_2$, $CeFe_2P_2$ have the $ThCr_2Si_2$ structure;[161]

K_2CuP (Na_2CuAs structure), NaZnP (PbFCl structure) and K_4CdP_2 (a new structure type containing discrete $[P\text{-}Cd\text{-}P]^{4-}$ anions);[162]

ScCoP (TiNiSi structure), $ScCo_5P_3$ (isotype of YCo_5P_3), $Sc_2Co_{12}P_7$ and $Sc_5Co_{19}P_{12}$ (new structure but related to that of $Hf_2Co_4P_3$).[163] X-ray photoelectron spectra have been measured for a series of binary phosphides MP, where M = Sc, Ti, V, Mn or Fe.[164]

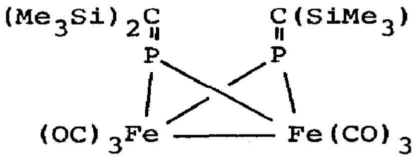
5.2.2 Bonds to Carbon or Silicon

As in previous reviews, carbon compounds are treated first, subdivided in terms of the phosphorus oxidation state. Compounds containing bonds to the heavier Group 4 elements then follow. Within each section multiply bonded compounds are considered first.

The +3 Oxidation State. Reaction of the η^2-phospha-alkyne complex, $Pt(PPh_3)_2(P{\equiv}CBu^t)$, with $Pd(PPh_3)_4$ gives a new five atom cluster compound, $Pd_2Pt_3(PPh_3)_5(P{\equiv}CBu^t)_3$, in which the phospha-alkyne groups act as bridging groups.[165] Although they remain η^2-bonded to one platinum atom (Pt-P 2.437Å) they also σ bond to a second (Pt-P 2.329Å).

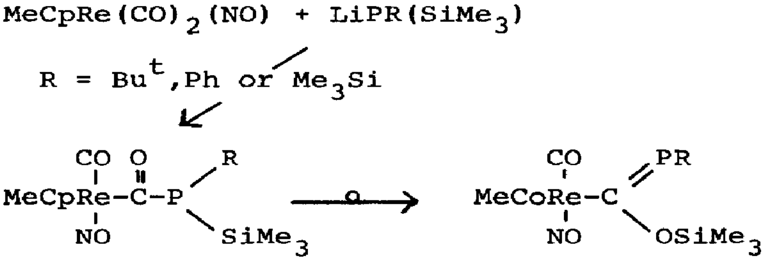
Bridging by phospha-alkene groups has been identified for the first time in complex (70) obtained from $(Me_3Si)_2C{=}PCl$ and $Na_2Fe(CO)_4$ in the presence of diazabicycloundec-5-ene in THF.[166]

The P-C separation, 1.650Å, corresponds to retention of the double bond. A novel approach to the formation of phospha-alkenyl complexes is shown in equation 37, where the initial step is



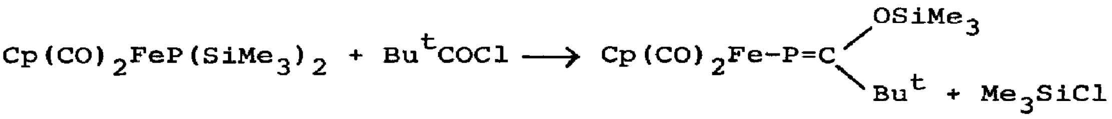
(70)

phosphide addition to a coordinated carbonyl in the starting material; a 1,3 Me_3Si shift then completes the phospha-alkene



...(37)

synthesis.[167] A second phospha-alkene metal compound in which there is a direct metal phosphorus bond is obtained via the method in equation 38.[168]

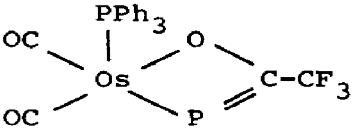


$$Cp(CO)_2FeP(SiMe_3)_2 + Bu^tCOCl \longrightarrow Cp(CO)_2Fe{-}P{=}C(OSiMe_3)(Bu^t) + Me_3SiCl$$

...(38)

An unexpected P-metallated phospha-alkene (71) has been obtained, rather than a phosphinidine complex, when $Co(PH_2)Cl(CO)_2(PPh_3)_2$ is treated successively with trifluoroacetic anhydride and sodium hydride;[169] and phospha-alkenyl complexes (72, M = Fe or Ru) are products when $[(Me_5C_5)M(CO)_3]BF_4$ reacts with the bulky silylphosphide $Li[P(C_6H_2Bu^t_3)SiMe_3]$.[170] The initial product, $(Me_5C_5)M(CO)_2{-}C(O)P(SiMe_3)(C_6H_2Bu^t_3)$, readily gives (72) via a 1,3-silylshift.

The nickel carbonyl complex, $Ni(CO)[ClP{=}C(SiMe_3)_2]_2$, which



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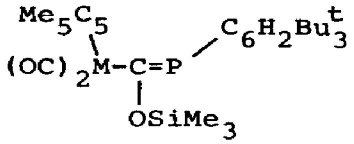
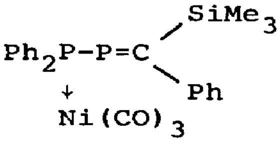


(72)

results when $Ni(CO)_4$ is treated with the chlorophospha-alkene, contains η^2-bonded ligands and in the solid state the two P=C groups and the Ni-CO moiety lie in a plane.[171] On the other hand, the initial product with $Ph_2P{\cdot}P{=}CPh(SiMe_3)$ is an η^1-complex (73) which loses further CO, dimerising to a novel complex (74) when the phosphine phosphorus and P=C groups behave respectively as η^1 and η^2 donors.



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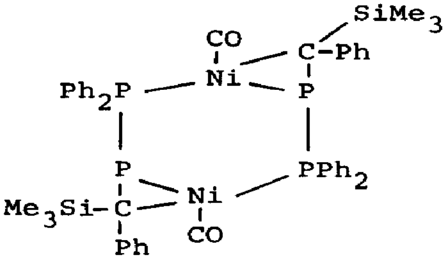
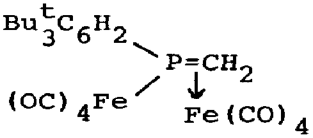


(74)

Structures have been reported for both the molybdenum and tungsten complexes $Cp(CO)_3M[P{=}C(SiMe_3)_2]$ formed in reactions of $ClP{=}C(SiMe_3)_2$ with $Na[CpM(CO)_3]$, the $MPCSi_2$ unit is planar with P-C distances of ca. 1.66Å.[172] There is increased nucleophilicity of the λ^2 phosphorus atom and the tungsten complex reacts with trifluoromethane sulphonic acid to produce a coordinated $HP{=}C(SiMe_3)_2$ ligand.

A new η^1-η^2 complex (75) can be obtained by treating $Bu^t_3C_6H_2P{=}CH_2$ with $Fe_2(CO)_9$ in hexane solution but two complexes in which the phospha-alkene behaves in respectively the η^1 and η^2 modes can also be isolated.[173] Bonding of the ligand in $Pt(PPh_3)_2[(mesityl)P{=}CPh_2]$ has been further investigated by a recent high resolution, solid state ^{31}P n.m.r. study.[174] This shows the pattern expected for η^1 coordination as shown by X-ray crystallography; the solution n.m.r. spectrum, on the other hand, indicates η^2 ligand behaviour.

(Mesityl)$P{=}C(SiMe_3)_2$, obtained by dehydrohalogenation of (mesityl)$PCl{-}CH(SiMe_3)_2$ with DBU, shows the characteristic reactions of a polar P=C double bond giving the ambident ion $[(mesityl)PMeC(SiMe_3)_2]^-$ on treatment with methyl iodide and the oxidation products (76) and (77) on treatment with respectively Me_3SiN_3 and S_8.[175] The latter can be desulphurised to (mesityl)$P(:S){=}C(SiMe_3)_2$ by tributylphosphine.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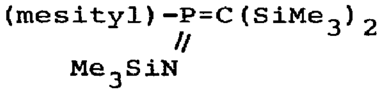
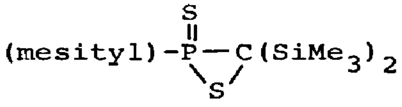
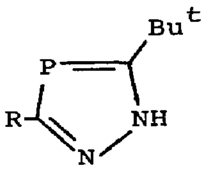

$$(mesityl){-}P({=}NSiMe_3){=}C(SiMe_3)_2$$
(76)


(77)

Different reactions occur between $Me_3SiP{=}C(OSiMe_3)Bu^t$ and aliphatic diazo-compounds with, for example, new phospha-alkenes $Me_3Si{\cdot}CHR{\cdot}P{=}C(OSiMe_3)Bu^t$ being produced with diazomethane, diazoethane and t-butyl diazoacetate following nitrogen elimination and CHR insertion into the Si-P bond.[176] With $RCHN_2$, on the other hand, where R = Bu^t or $SiMe_3$, the products are diaza phospholes (78) while azide dipoles such as MeN_3, PhN_3 or $NCCH_2N$ add to the phospha-alkene to produce triazaphospholes (79). A phosphorane (80) is the final product when a substituted o-quinone reacts with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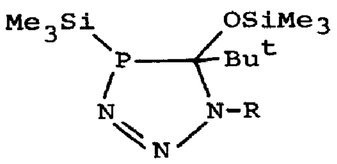
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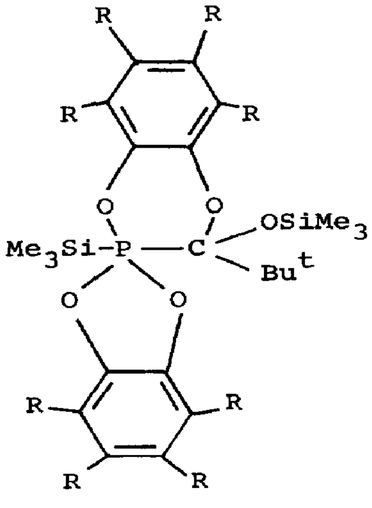
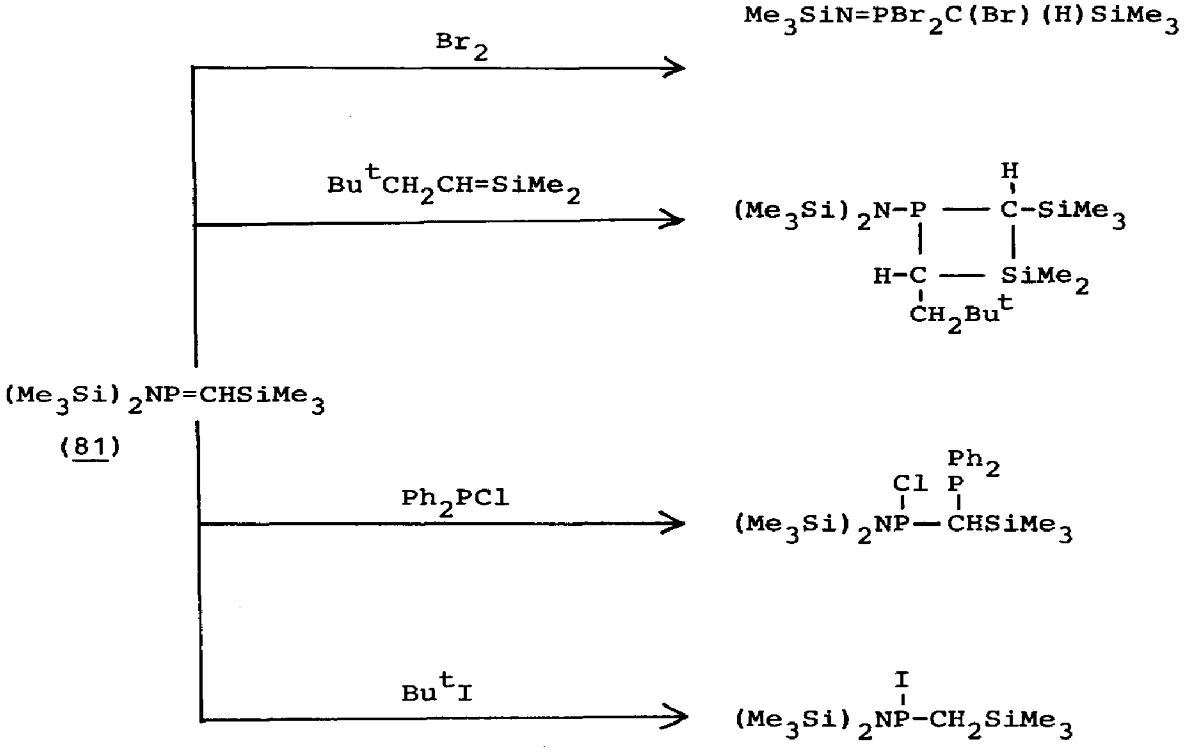

(80)

the phospha-alkene.

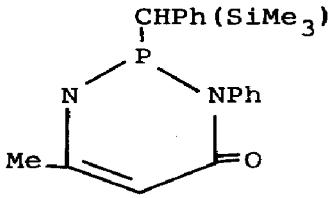
A series of reactions of the silylated alkene (81) are summarised in Scheme 7.[177]



Scheme 7

The chlorine atom in $ClP=CPh(SiMe_3)$ is readily replaced by alcohols, amines, phosphines and organo-lithium reagents; the products can be identified by n.m.r. spectroscopy and X-ray structures were carried out for $RP=CPh(SiMe_3)$ where R = Pr^i and PBu^t_2.[178] In the presence of triethylamine, the chlorine compound reacts with $PhNHCOCH_2COMe$ to produce (82) and after a Grignard reaction with 4-$Bu^tC_6H_4MgBr$, the product undergoes a [2+4] cycloaddition with cyclopentadiene to give (83).[179]

An extension of the use of solid KOH to eliminate HF and thus form phospha-alkenes has led to the formation of $CF_3P=CF_2$ from $(CF_3)_2PH$, identified by ^{31}P n.m.r. spectroscopy.[180] Among the by-products are CF_3H and CF_2H_2, which arise from base induced cleavage of P-C bonds; the precursor of the latter is probably $CF_3P(OH)CF_2H$ arising from the addition of water, present in the



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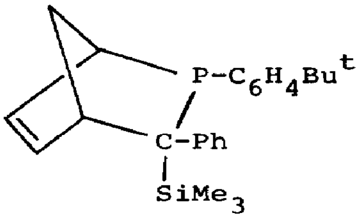
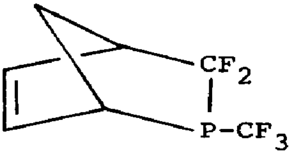


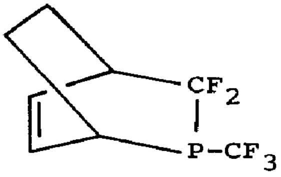
(83)

solid KOH, across the P=C double bond.

Close similarities in the behaviour of P=C and C=C systems are shown by the isolation of Diels-Alder adducts such as (84)-(86) from reactions of $CF_3P=CF_2$ with, respectively cyclopentadiene, 1,3-cyclohexadiene, and 2,3-dimethylbutadiene.[181] On pyrolysis, these adducts usually decompose to regenerate the starting materials but an alternative route for (85) also yields a new phosphetane (87).[182] Values of 330 and 157 kJ mol^{-1} have been estimated from mass spectrometric appearance potentials for the P-C σ and π bond energies respectively.



(84)



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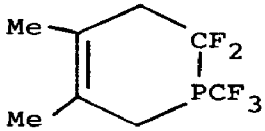
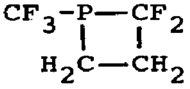


(86)

In a similar fashion to the formation of compound (86), a related Diels-Alder adduct can be obtained from RP=CPh(SiMe$_3$), where R = Bu, Ph$_2$C=N-, etc., and 2,3-dimethylbutadiene.[183] The product occurs in two diastereoisomeric forms which can be thermally interconverted; X-ray structures have been carried out on both of the P-sulphide isomers (88). Cycloaddition reactions



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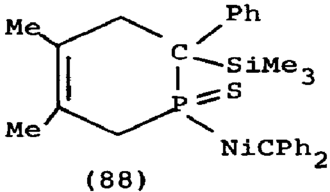
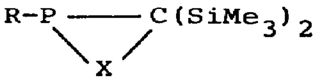
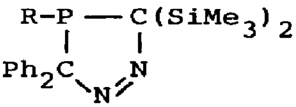


(88)

also have been reported for $Me_3SiC{\equiv}C-P{=}C(SiMe_3)_2$ with sulphur, selenium, 2,3-dimethylbutadiene, diazomethane and Me_3SiN_3, when products such as (89)-(91) (R = $Me_3SiC{\equiv}C-$) can be obtained.[184]



(89, X = S or Se)



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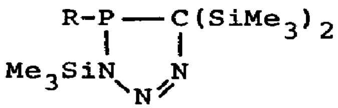
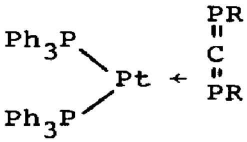


(91)

A stable diphospha-allene complex (92, R = 2,4,6-$Bu^t_3C_6H_2$) showing η^2 behaviour has been isolated[185] while in (93), obtained from RP=CHPClR (R = 2,4,6-$Bu^t_3C_6H_2$) and $Na[Co(CO)_4]$, the diphospha-allene generated in the reactions is an η^3 ligand.[186]



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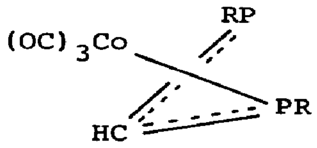
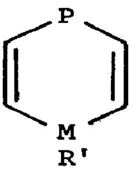


(93)

The $Mo(CO)_5$ fragment in the phosphabenzene (L) complex, $Mo(CO)_5L$, is coordinated symmetrically to phosphorus (Mo-P 2.464Å) and the dimensions of the ligand change little from those in the free state.[187] Proton affinities for both phosphabenzene and arsabenzene have been obtained from ion cyclotron resonance measurements.[188]

Cyclisation takes place on reaction of diethinylphosphine $RP(C{\equiv}CH)_2$, where R = Bu^t, CH_2Ph, etc., with for example $R'PH_2$ or $R'AsH_2$, for R = Ph, Bu^t or CH_2Ph;[189] the products are mixtures of the cis-trans isomers (94, M = P or As) and an X-ray structure has been performed on (94, M = P, R = Bu^t and R' = Ph).



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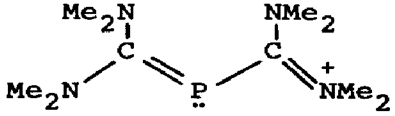

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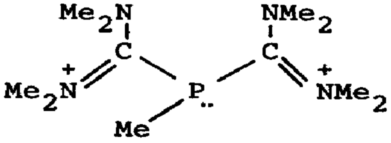
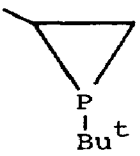


(96)

Non-empirical calculations on four possible conformers of the Cp_2P^+ cation point to the lowest energy with a C_s structure containing both η^1 and η^2 rings; the C_2 form with two η^2 bonded rings is some 9 kcal mol^{-1} higher in energy and two structures (C_{2v}) resembling a bent sandwich arrangement are ca. 25 kcal mol^{-1} more energetic.[190] In contrast recent MNDO calculations for this species and the silene Cp_2Si suggest the most stable form is that with two η^1 rings.[191]

Crystallographic determinations on the cationic phosphorus species, (95) and (96), point to substantial changes in electronic structure on P-methylation.[192] Normal allylic conjugation is present in (95) while the phosphorus lone pair becomes stereochemically active in (96), the conjugated system is broken and the cation becomes a simple phosphine substituted by two amidinium groups.

Two stable phosphiranes, (97) and (98), were reported in 1985. The former results when Li_2PBu^t is treated with 1,2-dichloropropane in a hexane-liquid ammonia mixture,[193] while the latter ($R = 2,4,6\text{-}Bu^t_3C_6H_2$) involves a five-step synthesis starting with RPH_2.[194] Hydrogen peroxide will oxidise the phosphorus atom in (98).



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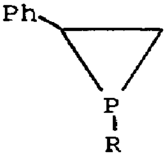
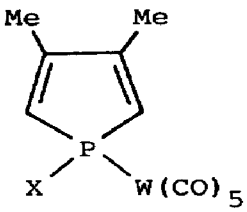


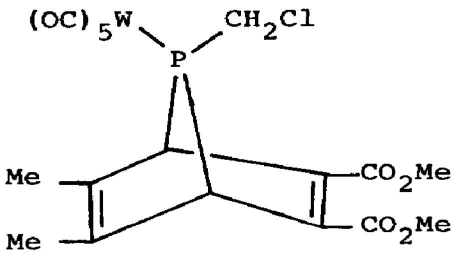
(98)

Ring cleavage is the initial reaction in the methoxide catalysed methanolysis of $(CF_3PCF_2)_2$ giving $MeO(CF_3)PCF_2P(CF_3)CHF_2$, but further P-C bond breaking occurs on subsequent reaction with formation of mixtures of $(MeO)_3P$, $MeOP(CHF_2)_2$, $(MeO)_2PCHF_2$ and $CF_3P(CHF_2)_2$.[195]

Reactions of the phosphole complexes (99a, X = CH_2Cl, b X = Ph) with the highly electrophilic reagent dimethylacetylene dicarboxylate, the latter in the presence of diphenylacetylene, give products (100)[196] and (101)[197] respectively. In a subsequent reaction, (100) was treated with copper(I) chloride at 55°C to study cleavage of the phosphorus bridge; in the presence



(99a X = CH_2Cl
b X = Ph)



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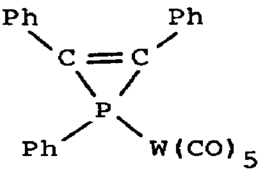
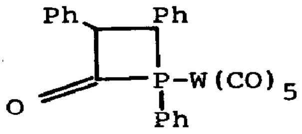


(101)

of methanol and 2,3-dimethylbutadiene as trapping agents, the products were $ClCH_2PH(OMe).W(CO)_5$ and (99a) respectively in agreement with the formation of $ClCH_2P{=}W(CO)_5$ as a transient.[196] Formation of the phosphirine complex (101) can be interpreted as resulting from the formation of an intermediate phosphinidine complex.[197] Phosphirine complexes such as (101) can be carbonylated with carbon monoxide at 160°C giving complexes such as (102).[198]



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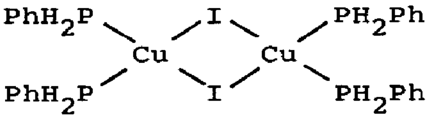


(103)

Reactions of a number of Group 5 trifluoromethyls with both trifluoronitrosomethane, CF_3NO,[199] and O-nitrosobis(trifluoromethyl)hydroxylamine, $(CF_3)_2NONO$,[200] have been reported. With the former, $(CF_3)_2PH$ gives $(CF_3)_2P(O)N(OH)CF_3$ as the major product, while $(CF_3)_2NOP(O)CF_3N(CF_3)_2$ and $(CF_3)_2NP(O)(CF_3)Cl$ are obtained with, respectively, $(CF_3)_3P$ and $(CF_3)_2PCl$.[199] The product when the hydroxylamine derivative reacts with $(CF_3)_3P$ is $(CF_3)_2NOP(O)(CF_3)_2$, with $(CF_3)_3As$ one obtains $(CF_3)_2NOAs(CF_3)_2$ but the antimony analogue gives a mixture of $[(CF_3)_2NO]_3Sb$ and $[(CF_3)_2NO]_2SbCF_3$.[200]

^{55}Mn n.m.r. spectra with chemical shifts varying over the range −415 to −1450 ppm relative to aqueous $KMnO_4$ have been obtained for a series of binuclear complexes $[(OC)_4Mn]\mu\text{-}E(CF_3)_2\mu\text{-}Y[Mn(CO)_4]$ where E = P or As and Y = Cl, Br, I, SR, SeR or TeR.[201]

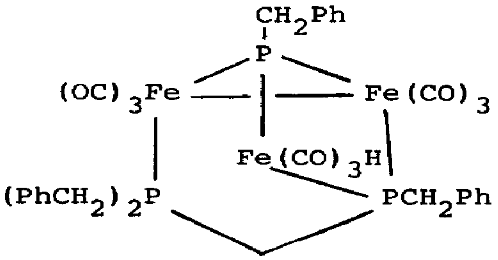
An X-ray crystallographic investigation on the copper(I) iodide complex with phenyl phosphine (103) shows an iodine bridged dimeric structure with tetrahedral coordination about copper.[202]

The phenylphosphine-perfluoro-n-octanonitrile reaction is complex giving tetraphenyldiphosphine and a range of 15 reduction and other products, among which are $C_7F_{15}CH{:}NH$, $C_7F_{15}CH_2NH_2$, $C_7F_{15}CH(NH_2)PPhH$, $C_7F_{15}CH(PPhH)N{:}CHC_7F_{15}$ and $C_7F_{15}C({:}NH)PPhC({:}NH)C_7F_{15}$.[203] The corresponding reaction with diphenylphosphine is simpler giving the adduct $C_7F_{15}C({:}NH)PPh_2$ and the reduction product $C_7F_{15}CH(NH_2)PPh_2$.[204]

Reactions in which there is a stepwise substitution of hydrogen atoms by halogen take place when $H_2P{\cdot}C(CF_3)_2{\cdot}OSiMe_3$ is treated with N-chloro or N-bromosuccinimide, and the monobromide, $HBrP{\cdot}C(CF_3)_2{\cdot}OSiMe_3$, can be dehydrobrominated by trimethylamine to give a new diphosphene, $Me_3SiO{\cdot}(CF_3)_2C{\cdot}P{:}P{\cdot}C(CF_3)_2{\cdot}OSiMe_3$, together with its cyclic, trimeric oligomer.[205]

The preparation of two 1-phosphino-thioformamides, $Ph_2PC(S)NMeR$ where R = Me or Ph, has been reported from Ph_2PLi and $RMeNC(S)Cl$ while linkage isomeric 1-phosphinothioformimidates, $Ph_2P(NR)SR'$ result by alkylation of secondary thioamides.[206] The allylphosphine derivatives, $Me_3E{\cdot}PH{\cdot}CH_2CH{:}CH_2$ for E = Si or Ge, can be obtained when Me_3SiCl and Me_3GeBr are treated with $CH_2{:}CHCH_2PH_2$ in dichloromethane.[207]

P-C-P bond cleavage occurs when diphosphines $Pr^iPH{\cdot}CH_2{\cdot}PH_2$ and $PhCH_2PH{\cdot}CH_2P(CH_2Ph)_2$ react with an excess of $Fe_2(CO)_9$ giving compounds such as (104)-(106);[208] full X-ray structures are



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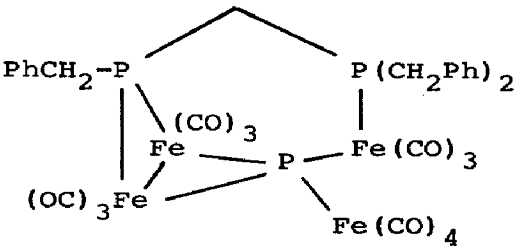

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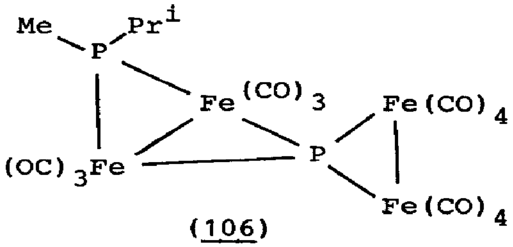


(106)

available for (<u>104</u>) and (<u>106</u>).

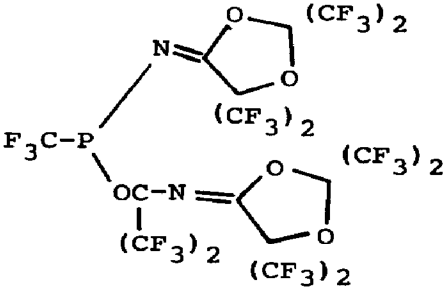
A new tin(II) ylid results when potassium di(t-butyl)phosphide reacts with $SnCl_2$ in toluene at -78°C;[209] in solution the compound, $Sn(PBu^t_2)_2$, is a dimer. Substituted phosphide anion formation by the action of lithium on tertiary phosphines, such as Ph_3P and $PhMe_2P$, in THF solution can be speeded up by irradiation with ultrasound.[210]

Addition of one or two atoms of sulphur or selenium to $[P(CN)_2]^-$ has been confirmed by n.m.r. spectroscopy giving species such as $P(CN)_2S^-$, $[P(CN)_2Se]^-$, $[P(CN)_2S_2]^-$, $[P(CN)_2Se_2]^-$ and $[P(CN)_2SSe]^-$.[211] A second mixed species, $[P(CN)_2SeO]^-$, has also been isolated. $[P(CN)_2]^-$ also reacts with Ph_2P^- giving successively $[Ph_2P\cdot PCN]^-$ and $[Ph_2P\cdot P\cdot PPh_2]^-$ as products; similar reactions with R_2PO^-, Ph_2PS^- and Ph_2PNPh^- give $[O{:}PR_2\cdot P{:}PR_2\cdot O]^-$, $[Ph_2P\cdot P{:}PPh_2\cdot S]^-$ and $[PhN{:}PPh_2\cdot P{:}PPh_2\cdot NPh]^-$, respectively as the products.

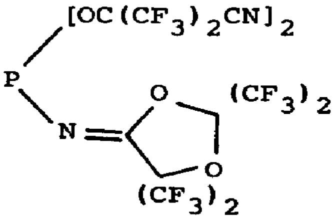
The $[P(CN)_4]^-$ ion, identified spectroscopically as an intermediate in the $P(CN)_3$-NaCN-crown ether reaction, disproportionates to give $[P(CN)_2]^-$ and an ion formulated as $[P_2C_{10}N_{10}]^{2-}$.[212] The latter consists of $P(CN)_2$ and $P(CN)_5$ groups bridged by an amino-malononitrile unit, i.e. $[(NC)_5P\cdot C(CN)_2\cdot NP(CN)_2]^{2-}$.

A Staudinger reaction between either phenyl or tosyl azide and $Et_4N[PhPCl(CN)_2]$ gives the previously unknown iminophosphoranide $Et_4N[PhPCl(CN)_2({:}NR)]$ as a highly moisture sensitive product.[213] Hydrolysis gives the four-membered ring compound $Ph\overline{P(O)\cdot NR\cdot P(O)Ph\cdot N}R$, via an isolable intermediate, $PhP(CN)({:}NR)$ where R = tosyl.

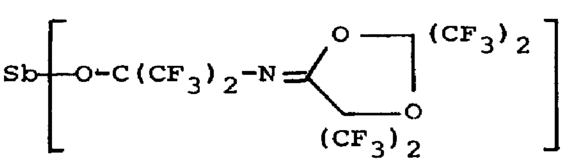
Reactions of hexafluoroacetone with Group 5 nitriles cause M-C bond cleavage to give the unusual compounds (<u>107</u>)-(<u>109</u>) from $CF_3P(CN)_2$, $P(CN)_3$ and $Sb(CN)_3$ respectively.[214] With arsenic



(<u>107</u>)



(<u>108</u>)



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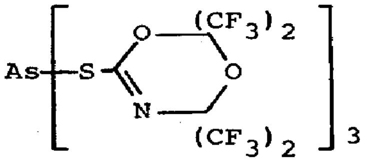
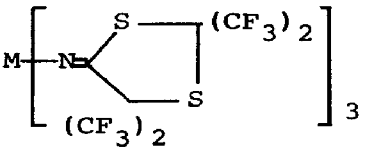


(110)

trithiocyanate, two mols of hexafluoroacetone add across each C-N bond to give the substituted trithioarsenite (110). The structures of (107) and (110) have been confirmed by X-ray crystallography. Related reactions of dimeric hexafluorothioacetone with the isomeric isonitriles, M(NC)$_3$ for M = P or As, PhP(NC)$_2$ and Bu^{t}As(NC)$_2$ lead to insertion into the C_2S_2 ring giving, for example, (111, M = P or As) with the tricyanaides.[215] Oxidation to a phosphorus(V) species (112) occurs with PhP(NC)$_2$ but the expected insertion product (113) is obtained from Bu^{t}As(NC)$_2$.



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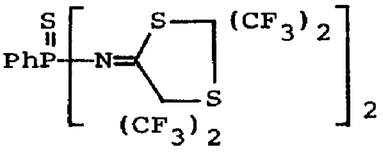

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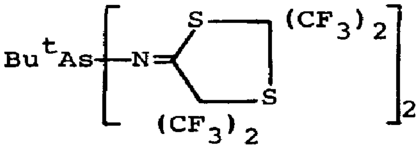


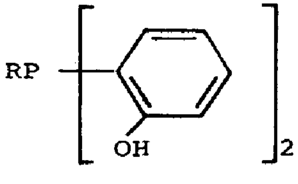
(113)

Neutron diffraction data at 95K for P(CH$_2$CN)$_3$ have been collected to probe further the inertness of this type of compound; the phosphorus, which lies on a three fold axis, is bonded to carbon at 1.865Å.[216]

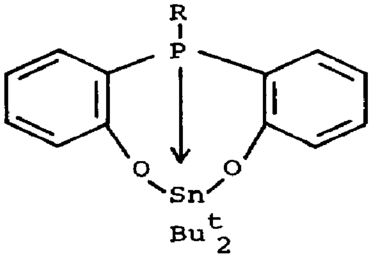
Tris(2-chlorophenyl)-Group 5 derivatives can now be formed in high yield from reactions of MCl$_3$ (M = P-Bi) with C_6H_4ClLi; tetramethylethylenediamine is added to hinder intramolecular LiCl loss and consequent benzyne formation.[217] Full preparative details are now available for the highly basic tris(2,4,6-trimethoxyphenyl)phosphine and a number of related species.[218]

The stereodynamics of a series of tertiary phosphines Bu$^t_2$PR, where R = H, Me, Et, Pr^i, Bu^t, Ph, etc., including prediction of the equilibrium conformation, have been probed in a variable temperature multinuclear n.m.r. study.[219]

Methanol is eliminated during reactions of Bu$^t_2$Sn(OMe)$_2$ and the bis(o-hydroxyphenyl)phosphine (114) giving a stannoline product (115).[220] Xenon difluoride oxidises Me_3E for E = P-Sb to the corresponding difluoride but requires $CFCl_3$ as solvent to moderate the reaction; oxidation of trimethylamine, on the other hand, leads to C-H bond cleavage and a complex mixture of products.[221] Peroxydisulphate oxidation of Ph_3E for E = P-Sb in an acetonitrile-water mixture is a process first order in both reactants but H^+ has a pronounced accelerating effect.[222] The products are oxides which are monomeric for E = P or As but polymeric for the antimony compound.



(114, R = Bu^t or Ph)



(115)

Additions of Br_2, I_2 or IBr to acetonitrile solutions of the tertiary phosphine, R_3P where R = Bu, octyl or cyclohexyl, in 1:2, 1:1 and 2:1 ratios give highly conducting solutions in agreement with the formation of $[(R_3P)_2X]X$, $[(R_3P)_2X]X_3$ and $[R_3PX]X_3$.[223]

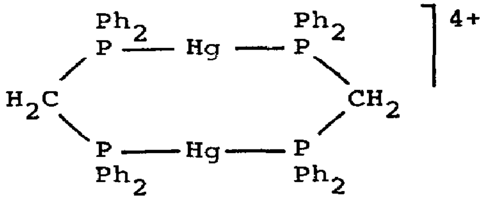
The donor properties of tertiary phosphines toward transition metals continue to be of interest. In $Mo_2(O_2CCF_3)_4$, two of the carboxylate groups become unidentate and the trans positions thus freed can take up two mols of R_3P where R = Me, Et or Bu.[224] A series of adducts, $M(CO)_4L$, for M = Fe, Ru or Os, L = Ph_3P, Ph_3As, Ph_3Sb and M = Ru or Os, L = Me_3Sb, can be obtained from the ligand and $M(CO)_5$;[225] in the ruthenium complexes, $[Ru(CO)_4.AsPh_3]$ and $[Ru(CO)_4.SbMe_3]$, the ligand is in an axial position while the equatorial position for Ph_3Sb in $Os(CO)_4.SbPh_3$ is rationalised on the basis of the weaker σ-bonding power of this ligand. Anhydrous nickel(II) chloride reacts with Ph_3P in dry ethanol in the presence of either tri(cyclohexyl)phosphonium chloride or triphenyl phosphonium chloride giving novel salts formulated as $[HPR_3][Ph_3PNiCl_3]$.[226]

Formation constants have been determined for the complexes $[Ag(PPh_3)_n]^+$ where n = 1-4 in both acetonitrile and ethanol solutions.[227] The P-Ge bond length in $Ph_3P.GeI_2$ has been evaluated as 2.503Å.[228]

Thionitrosyl complexes were previously thought to result from reactions of trithiazyl chloride with metal triphenylphosphine complexes but recent work has cast doubt on this.[229] A low yield of one such compound, $[RuCl_3(NS)(PPh_3)_2]$, has been obtained but the major products are $[Ph_3PNH_2]Cl.CH_2Cl_2$, whose identity was confirmed by an X-ray study, and $Ph_3P{:}NH$. The two compounds, can, in fact, be prepared from $S_3N_3Cl_3$ and Ph_3P in the absence of a transition metal compound.

Coloured solutions are formed when TCNE and the Group 5 triphenyls are mixed in CH_2Cl_2 solution, Ph_3P giving a 1:2 adduct while the heavier members produce 1:1 complexes.[230] Copper(I) bromide forms a monomeric 1:1 complex with trimesitylphosphine in contrast to the cubane type tetramers obtained with smaller phosphines; the two coordinate copper atom forms bonds to phosphorus and bromine at 2.193 and 2.225Å respectively.[231]

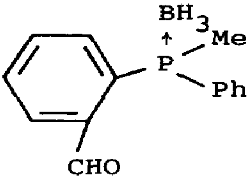
Diphosphines such as $(R_2P)_2CH_2$ (≡L) bridge between metal atoms in compounds such as $Pd_2Cl_2L_2$[232] and $[Re_2L_2(\mu\text{-}Cl)_2Cl_4].H_2PO_4.H_3PO_4.\text{-}4H_2O$,[233] while a metallocyclic cation (116) results from $(Ph_2P)_2CH_2$ and $[Hg(dmso)_6][O_3SCF_3]_2$ in dichloromethane solution.[234] Depending on reaction conditions, three different complexes, i.e.



(116)

$\alpha\text{-}Mo_2Br_4L_2$, $\beta\text{-}Mo_2Br_4L_2$ and $MoBr_2L_2$, can be isolated from reactions of $Mo_2Br_8^{4-}$ with $(Ph_2PCH_2)_2$.[235] The extended ligands $Ph_2P(CH_2)_nPPh_2$ for n = 8, 10 or 16 also bridge in complexes with Co(II), Ni(II), Rh(I) and Ir(I).[236]

A novel synthetic route to phosphinoborines, $PhR^1R^2P{\rightarrow}BH_3$, begins with a phosphine oxide which is treated with a $LiAlH_4\text{-}NaBH_4\text{-}CeCl_3$ mixture; compounds containing one P-H bond, i.e. $Ph_2PH.BH_3$, can be alkylated at phosphorus by alkyl halides in the presence of KOH.[237] Stereospecific removal of BH_3 by diethylamine from (117) is also possible and a method has been developed to give optically pure samples of the chelate (118). $Me_3P{\cdot}BH_2{\cdot}PMe_2(:X)$ for X = O or S



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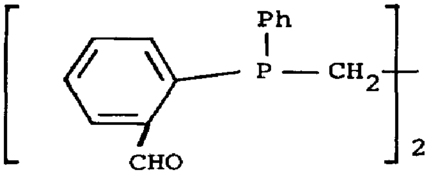
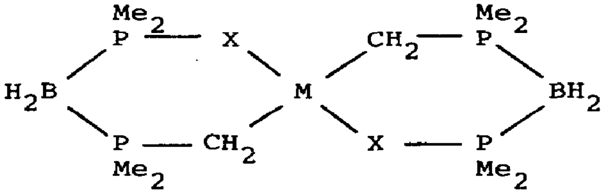


(118)

can be synthesised from Me_3PBH_2Br and $K[PMe_2X]$ and, in the presence of butyl lithium, they behave as ligands giving spirocyclic compounds such as (119, M = Be, Zn or Cd).[238]

Among the new phosphorus(III) ligands prepared during 1985 are (120),[239] (121)-(124),[240] and the linear species (125)[241] and (126).[242] Compound (125) is produced as a mixture of racemic and meso forms when o-$C_6H_4(PPh_2)(NH_2)$ is treated with lithium and 1,3-dichloropropane[241] and on reaction with $PtCl_2(dmso)_2$ gives two distinct products. That from the racemic form contains the ligand as a tridentate unit while the stereochemistry of the meso form allows the ligand to be tetradentate. Ligands (126) are optically active and tetradentate in their Co(III) complexes; the structure and absolute configuration of $(+)_{589}$-Λ-cis β-[Co(acac)-



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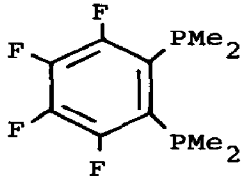

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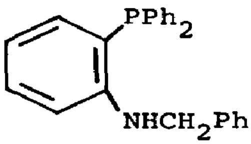

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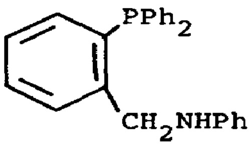

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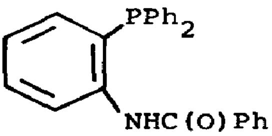

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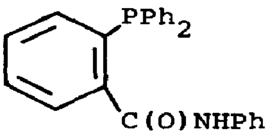

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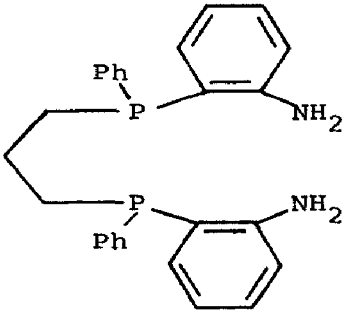
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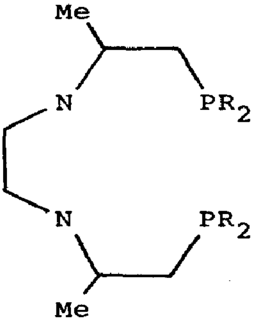
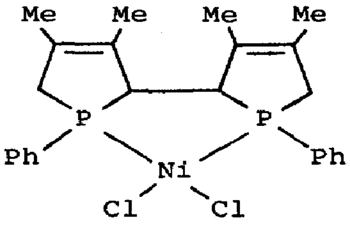

(126, R = Me or Ph)

(126,R = Me)][ClO_4]$_2$.H_2O, have been determined by X-ray crystallography.[242]

A new biphosphole ligand has been identified in the nickel complex (127) obtained when 1-phenyl-3,4-dimethylphosphole (128) is heated with nickel(II) chloride to 140-170°C in, for example, cyclo-hexanol.[243] The reaction is stereoselective, none of the meso-diastereomer being detectable in solution, and gives an almost planar nickel atom with short Ni-Cl (2.201Å) and Ni-P (2.126Å) bonds. The ligand is very air sensitive and can be displaced from the complex by CN^- and converted to a stable dioxide or disulphide by air and sulphur respectively.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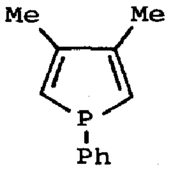
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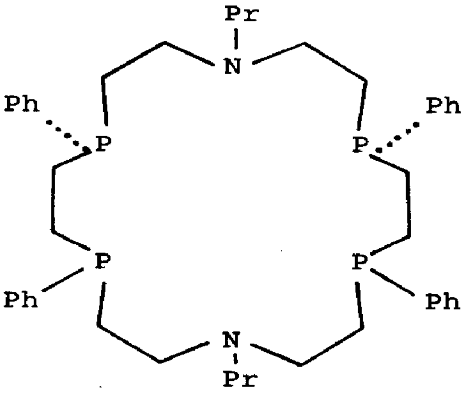
The synthesis of the potentially tridentate ligand, $LiN(SiMe_2CH_2PR_2)_2$ where R = Me, Pr^i or Bu^t, has been reported and structures reported for the complexes $MCl_3[N(SiMe_2CH_2PR_2)_2]$ where M = Hf, R = Me and M = Zr, R = Pr^i.[244] In both the monoclinic and orthorhombic forms of the former the ligand bonds in the tridentate facial mode while the zirconium complex is meriodionally coordinated. The hexaphosphine, $(Et_2PCH_2CH_2)_2PCH_2P$-

$(CH_2CH_2PEt_2)_2$ (≡L) recently synthesised is capable of both bridging and tris chelating two metal centres.[245] The initial product on reaction with cobalt(II) chloride is the red-brown Co_2Cl_4L, which on standing is converted to green $[Co_2Cl_2L]^{2+}$; further treatment with H_2/CO gives the binuclear carbonyl cation $[Co_2(CO)_4L]^{2+}$.

Continuing research into the ligating properties of tetraphosphine macrocycles, X-ray data are now available for the Fe(II), Co(II) and Ni(II) complexes of the β isomeric form of (129),[246] the Co(II) complex of the δ form of (130, n = 3),[247] and the Co(II) and Ni(II) complexes of the ε form of (130, n = 2).[248] A new 11-membered P_3 macrocycle (131, X = PH) has been prepared



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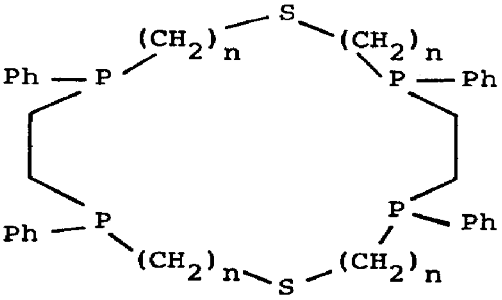

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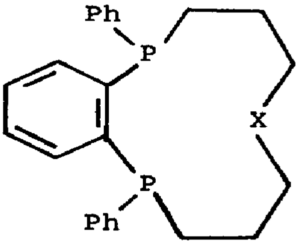
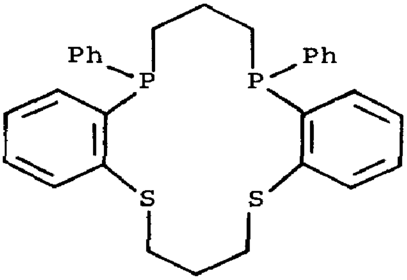


(131)

in two isomeric forms depending on the orientation of the hydrogen atom with respect to the phenyl groups;[249] it forms complexes-with Rh(1) and Mo(0) via the three phosphorus atoms. X-ray structure determinations have been carried out for a series of metal complexes containing (131), i.e. M = $Mo(CO)_3$, X = NMe; M = $W(CO)_3$, X = PPh; M = $NiCl_2$, X = NH; M = CuCl, X = S.[250]

Three new 14-membered macrocycles containing P_2S_2 and P_3S donor sets (132)-(134) have been synthesised as mixtures of two isomeric forms which can be separated on alumina.[251] The most abundant



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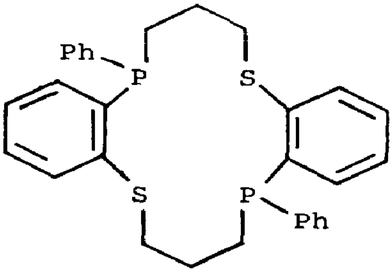

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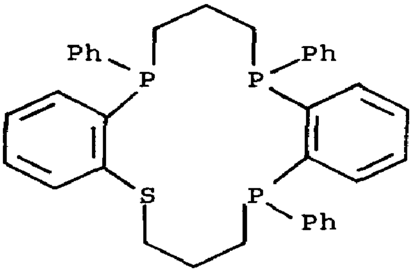
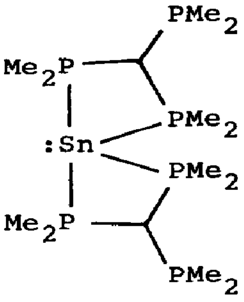


(134)

form of (132) is the chiral trans isomer and the cis form of (133) has been identified in its platinum(II) complex.

A range of reactions have been reported using $Li[C(PMe_2)_3]$, $Li[C(PMe_2)_2(SiMe_3)]$ and $LiCH_2PMe_2$. Tin(II) chloride and the first compound give the room temperature stable homoleptic tetraphosphine complex (135), with pseudo-trigonal bipyramidal coordination about tin and planar geometry about the central carbon atoms.[252] Aluminium trichloride yields $Al[C(PMe_2)_3]_3$ and $Al[C(PMe_2)_2SiMe_3]_3$ which have ^{27}Al n.m.r. signals in the range expected for octahedral coordination.[253] With $LiCH_2PMe_2$, the chlorines in aluminium trichloride can be substituted in a stepwise fashion to give $[Cl_2AlCH_2PMe_2]_2$, $[ClAl(CH_2PMe_2)_2]_2$, $[Al(CH_2PMe_2)_3]_2$ and $Li[Al(CH_2PMe_2)_4]$.[254] The monochloride (136) shows a chair conformation with P-Al distances of 2.425Å. In a



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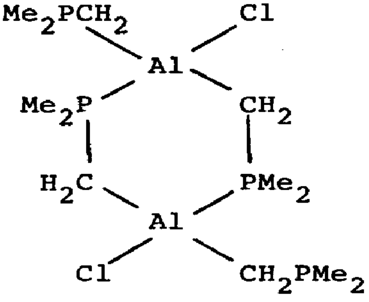
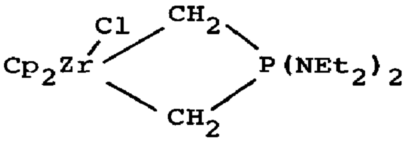


(136)

similar fashion, $[Me_2AlCH_2PMe_2]_2$ has been prepared from Me_2AlCl and $LiCH_2PMe_2$. If tetramethylethylenediamine is also included in the reacting system, complexes of the type $[(TMEDA)(THF)Li(Me_2PCH_2)AlMe_3]$ and $[(TMEDA)Li(Me_2PCH_2)_2AlMe_2]_2$ can be isolated when $AlMe_3$, $[Me_2Al(CH_2PMe_2)]_2$ and $[Al(CH_2PMe_2)_3]_2$ react with either LiMe or $LiCH_2PMe_2$.[255] X-ray structures have been obtained for the two lithium compounds.

The +5 Oxidation State. New ylids formulated, as $Me_n(Et_2N)_{3-n}P{=}CH_2$ where n = 0-2, have been isolated as reactive distillate liquids from reactions of $Me_n(Et_2N)_{3-n}PI$ and potassium hydride in pentane.[256] Two isomeric products (137) and (138) in which the ylid is respectively chelating and unidentate have been isolated from Cp_2ZrCl_2 and the ylid with n = 1;[256] when n = 2 the zirconium complex is dinuclear (139). Carbon diselenide and Bu_3P



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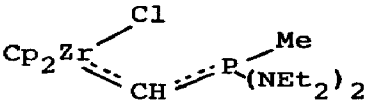

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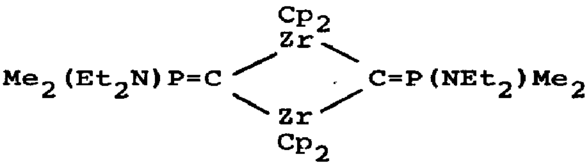

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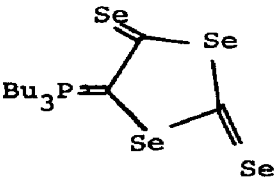
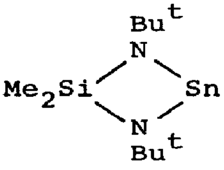


(140)

in ether solution give the tetraselenium ylid (140) as dark red prisms; the C_3Se_2 ring is planar and the selenium atom arrangement is similar to that in tetraselenabisfulvalenes leading to the possibility of derivatives of this compound showing similar unusual conductivities.[257]

An isocyano substituted methylene ylid, $Ph_3P{:}CHNC$, was surprisingly readily formed from Me_3SiCH_2NC in THF solution with either Ph_3PCl_2 or a mixture of Ph_3P and C_2Cl_6.[258] The initial product, $[Ph_3PCH_2NC]Cl$, is readily deprotonated by $NaNH_2$ in THF, but the ylid is highly reactive and isomerises to the normal cyanide on heating in toluene. Two new ylids, $Ph_3P{=}CHCOOR$ with R = Pr or Bu, have been synthesised[259] and transylidation of $Ph_3P{=}CHR$ with bis(thioesters), $(CH_2)_n(COSEt)_2$, gives new derivatives of the type $Ph_3P{=}CR{-}C(O)(CH_2)_nC(O)CR{=}PPh_3$.[260]

A structure determination for $Ph_3P{=}CH_2.B_3H_7$ shows a zwitterion with positive and negative charges on phosphorus and the borane group, respectively.[261] Reaction of $Ph_3P{=}CH_2$ with η^4-butadiene metallocenes gives σ-crotylmetallocenyl substituted ylids, $Cp_2M(CH{=}PPh_3)(CH_2CH{=}CHMe)$ where M = Zr or Hg, via a sigmatropic hydrogen shift.[262] Crystalline 1:1 adducts result from treating phosphorus ylids, such as $Me_3P{=}CH_2$ and $Ph_3P{=}CH_2$ or Me_3PO with the cyclic tin(II) compound (141); with $Ph_3P{=}NH$, on the other hand, tin(II) is displaced as $Sn(NPPh_3)_4$.[263] A highly active ethylene polymerisation catalyst (142) results when $Ni(cod)_2$ is treated with benzoylmethylenetriphenylphosphorane, $Ph_3PCHC(O)Ph$, and $Me_3P{=}CH_2$; the compound arises following oxidative addition of the Ph_3P group of the benzoyl ylid and nucleophilic attack of both the C=O group and Me_3PCH_2 on nickel.[264]



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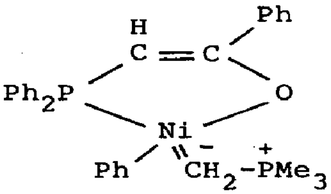

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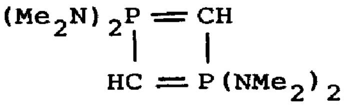
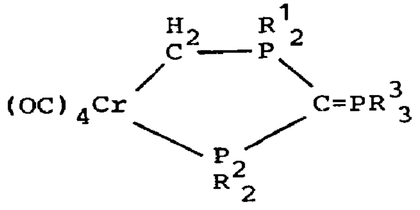


(143)

At low temperatures, $Me(Me_2N)_2PF_2$ reacts with BuLi in pentane to give the centrosymmetric diphosphete (143),[265] probably via formation of $(Me_2N)_2PF{=}CH_2$ and $(Me_2N)_2PF{=}CHLi$ and followed by further LiF loss.

The carbo-diphosphorane $Ph_3P{=}C{=}PPh_3$ reacts with sulphur, selenium or tellurium giving unstable 1:1 addition compounds, which decompose at or below room temperature.[266] Crystallography confirmed formation of $(Ph_3P)_2CSe$ with selenium and with iodine, the diphosphorane gives $(Ph_3P)_2CI^+$ with either I^- or I_3^- as the counter ion. A novel double ylid coordinated to a transition metal (144) is formed when, for example, $Cr(CO)_5[CH_2S(O)Me_2]$ reacts with $R^1_2P{-}C{=}PR^3_3(PR^2_2)$ (R^1, R^2, R^3 = Me or Ph).[267]



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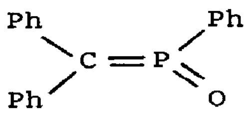
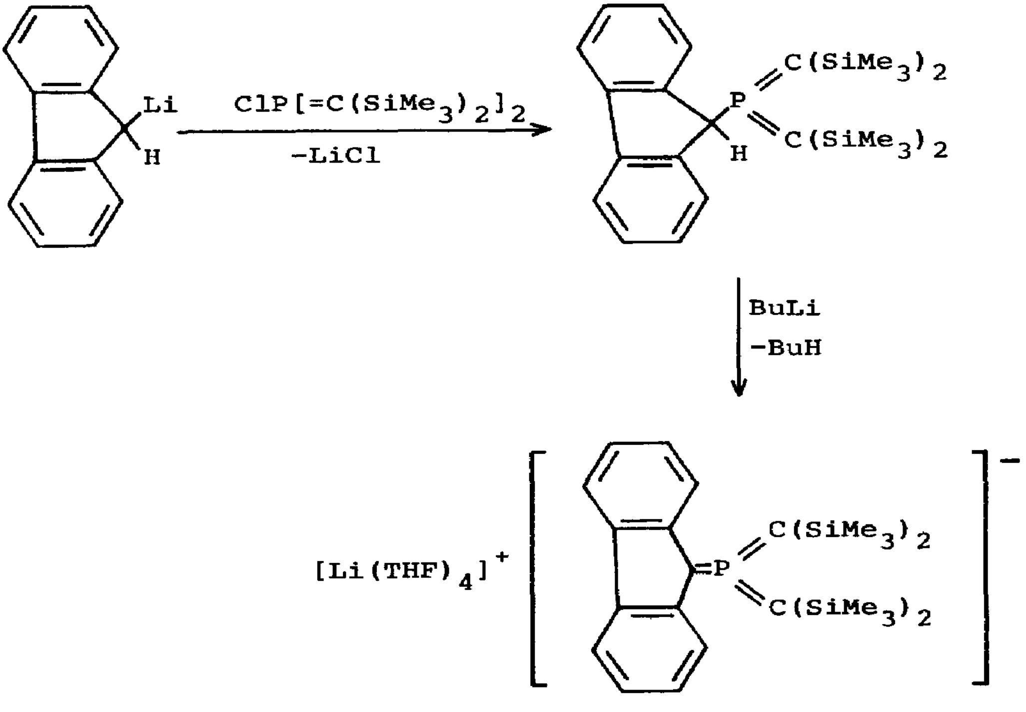


(145)

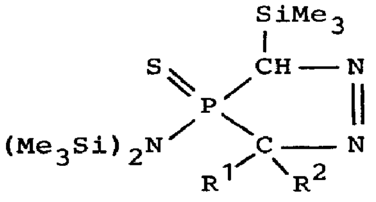
The first synthesis of an anion containing three P=C double bonds is outlined in equation 39; X-ray diffraction confirmed the



...(39)

structure and showed P=C distances of 1.67Å to the fluorenyl group and 1.69Å to the CSi_2 group.[268] The phosphene derivative (145) results from either thermal or photochemical loss of nitrogen and phenyl group migration from (diazobenzyl)diphenylphosphine oxide, $PhCN_2 \cdot P(O)Ph_2$.[269]

Low coordination number phosphorus(V) compounds, such as $(Me_3Si)_2NP(:S)(:CHSiMe_3)$, react with diazoalkanes $R^1R^2CN_2$ to give initially diazaphospholines (146) which, depending on the nature of R^1 and R^2, stabilise either by a 1,3 $SiMe_3$ migration to produce (147) or by a cyclo-reversion to the azine $(Me_3Si)HC{=}N{-}N{=}CR^1R^2$ and the unstable $(Me_3Si)_2NP{=}S$. The latter is trapped by diazoalkane as $(Me_3Si)_2NP(:S)(:CR^1R^2)$.[270] Similarly with t-butyl azide, the initial product is a triazaphospholine (148) which also undergoes a 1,3 $SiMe_3$ migration.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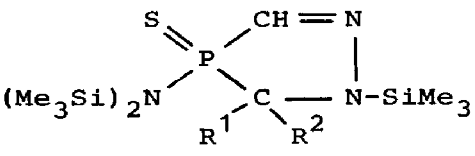
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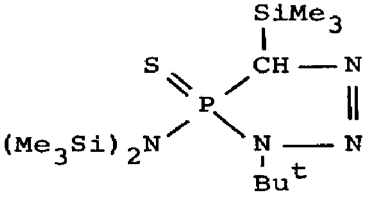

(148)

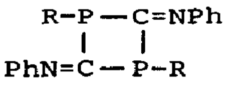
From X-ray crystallography Ph_4PBr has an ionic structure with $\bar{4}$ symmetry for the cation and a P-C distance of 1.800Å.[271] The P-O and P-N distances in $Bu^t_3P{=}O$ and $Bu^t_3P{=}NH$, according to recent electron diffraction results, are long (P-O 1.590(12), P-N 1.652(11)Å) and almost equivalent to single bonds.[272] In both cases the t-butyl groups are tilted away from each other, minimising steric interactions and providing good protection for the oxy and imide groups thus accounting for their high chemical and thermal stabilities.

The bis(phosphine), $H_2C{=}C(PPh_2)_2$, can be quaternised by methyl iodide to $[H_2C{=}C(PPh_2Me)_2]I_2$ and because the double bond is activated by the P^+ centre methanol, for example, can add to give $[(MePh_2P)_2CH(CH_2OMe)]I_2$.[273]

In the presence of HBF_4, the zwitterion $Et_3\overset{+}{P}.CS_2^-$ reacts with $Mo_2(OAc)_4$ producing dimeric $[Mo_2(OAc)_3(S_2CPEt_3)(OPEt_3)]BF_4$ where one of the bridging acetates has been replaced by the two sulphurs of the zwitterion; the X-ray structure also shows the phosphine oxide ligand occupying one of the axial positions at molybdenum.[274]

The Heavier Group 4 Elements. Ab initio calculations on $HP{=}SiH_2$ show substantially greater stability for this phosphasilene form than for other closed shell valence isomers such as $H_2P{-}SiH$, $H_3Si{-}P$, $H_3P{-}Si$;[275] a second series of ab initio calculation has been reported for P-Si compounds based on single and multiply bonded structures together with an ylid-like form.[276]

Insertion of phenyl isothiocyanate into a P-Si bond of $RP(SiMe_3)_2$, where R = Me, Ph Bu^t or mesityl, gives initially $RP(SiMe_3)[C(:S)NPh(SiMe_3)]$,[277] confirmed for R = Me by a full X-ray structure.[278] With the exception of this methyl compound, the insertion products lose $(Me_3Si)_2S$ to give unstable bis(phenylimino)methylidene phosphine $RP{=}C{=}NPh$, which rapidly dimerises to a mixture of the E and Z isomers of the diphosphetane (149). These compounds also result in the sodium hydroxide catalysed loss of $(Me_3Si)_2O$ from the phenyl isocyanate adducts of $RP(SiMe_3)_2$.



(149)

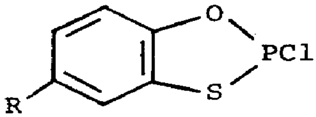
Stable compounds containing double bonds between phosphorus and both germanium[279] and tin[280] have now been isolated. The former, $(mesityl)_2Ge{=}P(C_6H_2Bu^t_3)$, is an orange, air sensitive solid with high reactivity toward hydrogen compounds such as H_2O, MeOH, HCl and $Me_3P{=}CH_2$, which add across the double bond. The tin compound $[(Me_3Si)_2CH]_2Sn{=}P(C_6H_2Bu^t_3)$ results from dehydrofluorination of $[(Me_3Si)_2CH]_2SnF{-}PH(C_6H_2Bu^t_3)$.

5.2.3 Bonds to Halogens

The +3 Oxidation State. Full details are now available on the structures of five complexes between zero valent metals and the ligand $MeN(PF_2)_2$ ($\equiv$L).[281] In FeL_4, the overall geometry is trigonal bipyramidal with three monodentate ligands and one which is bidentate, spanning axial and equatorial positions. Complexes $Co_2L_3L^{1}{}_2$, where L^1 = CO, $MeNHPF_2$ or Me_2NPF_2, contain three bridging bis(phosphines) and a metal-metal bond with unidentate L^1 groups occupying the vacant axial positions. The bis(phosphine) is chelating in $CrL(Me_2NPF_2)_4$.

Halogen exchange between PCl_3 and SiF_4 at temperatures between 500 and 600°C give PF_3 and $PClF_2$ while only mono- and di-fluorinated derivatives can be obtained with $POCl_3$ and SiF_4.[282]

Benzooxathiaphospholenes (150) are the products when 2-mercaptophenols react with PCl_3, the remaining halogen being readily substituted by a variety of protonic reagents.[283] The paper also reports stepwise substitution of the chlorine atoms in PCl_5 giving (151, n = 1 or 2) and (152).



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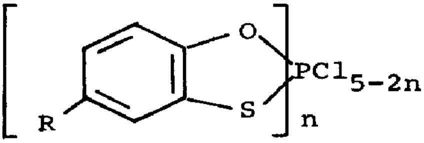

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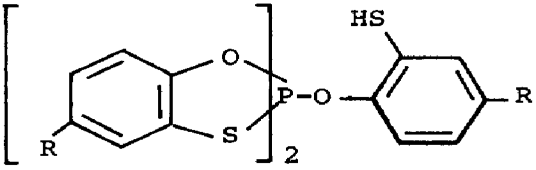
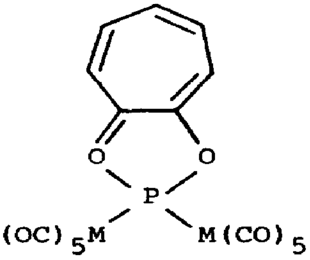


(152)

Substitution of either one or two chlorines in PCl_3, PCl_5, $POCl_3$ or $PSCl_3$ is observed on reaction with urethane in the presence of pyridine[284] and PCl_3 reacts with Schiff bases in acetone to give compounds where the azomethine hydrogen is replaced by a PCl_2 group.[285]

Phosphinidine complexes $[(OC)_5M]_2PX$ (X = Cl, Br or I) can be isolated when phosphorus trihalides are treated with $Na_2[M_2(CO)_{10}]$ for M = Cr, Mo or W and conversion to the chelates (153) and (154) occurs on further treatment with, respectively tropolone and 8-hydroxyquinoline.[286] The structure has been determined of the chromium tropolone compound.



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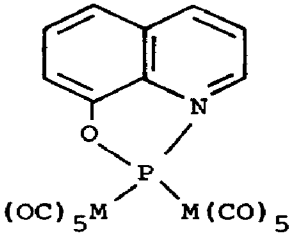
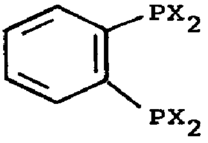


(154)

Reaction of anhydrous LiI in benzene with o-phenylenebis(dichlorophosphine) (155, X = Cl) gives the corresponding tetraiodide but in the presence of water the product is bicyclic (156, X = I).[287] The chlorine analogue of the latter can also be obtained by electrochemical reduction of (155, X = Cl) while reduction of (156, X = I) either electrochemically or by magnesium in THF gives a product formulated on the basis of mass spectrometry and solid state n.m.r. as the pentamer $[C_6H_4P_2]_5$.



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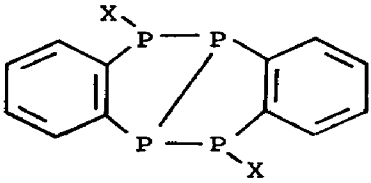

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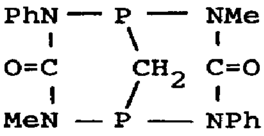


(157)

Methylenebis(dichlorophosphine) reacts in ether solution with $(Me_3Si)MeN{\cdot}CO{\cdot}NPh(SiMe_3)$ to give the bicyclic compound (157) which, as expected, can be oxidised at the phosphorus(III) centres with either hydrogen peroxide or elemental sulphur.[288] A by-product in the synthesis of $CH_2(PCl_2)_2$ from CH_2Cl_2, $AlCl_3$ and PCl_3 is the triphospha-alkane $Cl_2PCH_2PClCH_2PCl_2$, whose methylated or methoxylated products serve as versatile ligands in reactions with $Ni(CO)_4$ or $Fe_2(CO)_9$.[289]

The +5 Oxidation State. A theoretical study of apically and axially substituted trigonal bipyramidal phosphoranes PH_4X points to an apicophilicity order: Cl > CN > F > CCH > H > Me > OH > O^- > S^- > NH_2 > BH_2.[290] Apicophilicity, which is enhanced by ligand electronegativity, is reduced by π donation and these analyses are interpreted as showing the importance of d orbitals in bonding at the apical positions.

Primary, secondary and tertiary amine salts are easily prepared by reacting the appropriate amine with an aqueous solution of $pyH[PF_6]$.[291]

Electron diffraction of PCl_2F_3 at 22-24°C shows the chlorine atoms in equatorial positions in a trigonal bipyramidal arrangement of atoms about phosphorus.[292] There is no evidence for isomers with axial chlorines although it is known that fluorine-chlorine exchange takes place at the experimental temperature. Major molecular parameters are:

$r_g(P-F_e)$	1.546(9)Å	F_a-P-F_e	89.3(3)°
$r_g(P-F_a)$	1.593(4)Å	Cl-P-Cl	122.0(5)°
$r_g(P-Cl)$	2.004(2)Å		

New ^{35}Cl n.q.r. data for $C_6F_5PCl_4$, differing from earlier results, have been interpreted as showing trigonal bipyramidal geometry with the C_6F_5 group axial.[293] It is possible that two different structures are present, one in which the equatorial chlorines are equivalent, the second where these are differentiated.

The solvates, $[PCl_4][SbCl_6].\frac{1}{2}POCl_3$ and $[PCl_4][NbCl_6].SOCl_2$, have been prepared from PCl_5 and the appropriate pentahalide and solvent.[294] Vibration data are available and a structure determination for the antimony derivative shows the compound is ionic. Other salts containing the PCl_4^+ cation are $[PCl_4]_2[SnCl_6]$, $[PCl_4]_3[SnCl_6][PCl_6]$, $[PCl_4]_2[Sn_2Cl_{10}]$, and $[PCl_4][SnCl_5]$.[295] In $PCl_4[(Pr^iN)_2CCl]$, obtained in the reaction of PCl_5 with di-i-propylcarbodiimide, $Pr^iN:C:NPr^i$, the phosphorus atom is octahedrally coordinated to four chlorines at distances between 2.096 and 2.160Å and two cis nitrogen atoms at 1.82Å.[296] The N-P-N angle is 70.9°.

A correlation has been established between Δ_1 - the ^{31}P chemical shift difference between a phosphonium ion A^+ and the corresponding phosphorane AX - and Δ_2 - the ^{31}P shift difference between A^+ and AX_2^-, which is useful in predicting shifts expected for currently unknown compounds.[297]

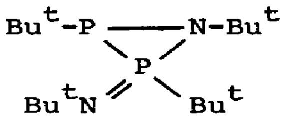
Low temperature reactions have allowed isolation of the addition compound $P_2O_3Cl_4.2SbCl_5$, in which the donors are the two P=O groups.[298] $POCl_3.SbCl_5$ is liberated if the compound is heated in dichloromethane giving the dichlorophosphate $[SbCl_4(O_2PCl_2)]_2$. From X-ray diffraction the latter is dimeric, containing an eight-membered centrosymmetric ring in a chair conformation; mean Sb-O and P-O distances are respectively 2.06 and 1.50Å.

5.2.4 Bonds to Nitrogen

Sub-division in this section in terms of oxidation state and bond order follows the system used in section 5.2.2.

The +3 Oxidation State. Ab initio calculations of the barrier to interconversion of H_2PN and HP=NH in both singlet and triplet states is large enough to support the existence of H_2PN confirming the possibility of isolating R_2PN during photolysis of R_2PN_3.[299] A related study included, in addition to calculations on various geometries for PNH_2, calculations on $(H_2N)_2PN$ and various dimeric forms.[300]

On thermal decomposition, compound (158) gives monomeric $Bu^tP{=}NBu^t$, characterised by field emission mass spectrometry and u.v. photo-electron spectroscopy.[301] The monomer rather unusually behaves as a six-electron donor in (159), one of the products obtained from a reaction with $Fe_2(CO)_9$ in hexane at 25°C.[302] Coordination occurs in the cis conformation with a P-N distance of 1.687Å, equivalent to a single bond. A second product from the reaction (160) has a novel bicyclic structure, resulting from iminophosphine attack on a bonded carbonyl group.



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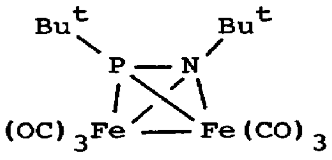

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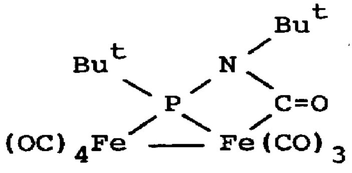
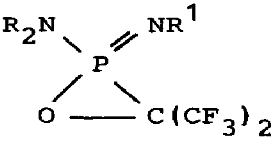


(160)

Amino-iminophosphines, $R_2NP{=}NR^1$, on reaction with hexafluoroacetone give three- (161) or four-membered ring products (162) depending on the nature or R and R^1.[303] The reaction course can be correlated with the changes in the p.e.s. determined ionisation energies of the two lowest lying levels and the positions of two absorption bands below 50,000 cm^{-1}.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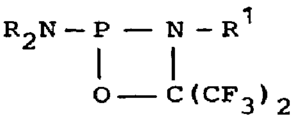
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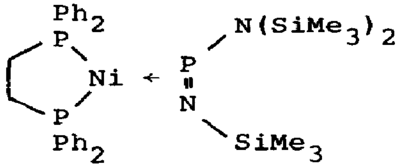
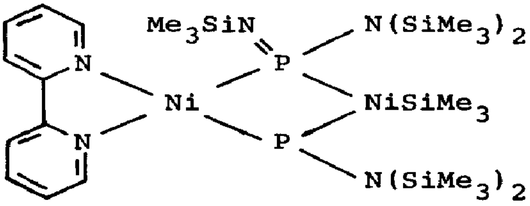

(163)

$(Me_3Si)_2NP{=}NSiMe_3$ (≡L) is η^1-bonded via the phosphorus arom in the complex NiL_3, obtained with $Ni(cod)_2$.[304] Further reaction with dppe displaces two ligand molecules giving (163) in which the final amino-iminophosphine is η^2-bonded, but reaction with bipyridine gives a nickel substituted azadiphosphetidine (164). The ligand L behaves as a bridging group in $Pt_3(\mu\text{-}CNBu^t)(\mu\text{-}L)_2\text{-}(CNBu^t)_3$ and $Pt_3(\mu\text{-}L)_3(CO)_3$[305] and face bonding has been identified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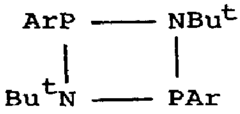
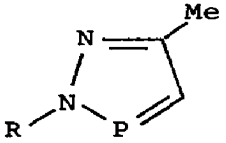

(165)

when two of the μ_3-η^2-isocyanide groups in $Ni_4(CNBu^t)_7$ are displaced by L.[306]

A monomeric amino-iminophosphine could not be isolated from $Bu^t_3C_6H_2PCl_2$ and t-butylamine in the presence of Et_3N and only $ArP(O)H(NHBu^t)$ was isolated; in the presence of DMU the product was the dimer (165).[307] Reaction of $ArP(Li)SiMe_2Bu^t$ and RNSO (where R = 2,4-Bu^t_2-6-Me-C_6H_2), however, gives ArP(S)=NR in addition to ArP=PAr, $ArP\overset{S}{-}PAr$ and RN=S=NR and the first product can be desulphurised to the monomer ArP=NR, identified by its ^{31}P n.m.r. shift of 420 ppm. Rather than oligomerisation, the unstable product hydrolyses readily to ArP(O)H(NHR).

Diazaphospholes such as (166, R = Me, Ph) are not oxidised by bromine but are converted via 1,2-additions and subsequent elimination of HBr to the monobromide (167).[308] Diphospha-1,3-dienes (168, R = Me or Ph)[309] and 1,3,4-thiazaphospholes (169)[310] have been synthesised for the first time. Preparation of the former involves HCl loss from a mixture of $CH_2(PCl_2)_2$ and $RNHNH_2$ while the starting material for (169) synthesis is either a thiocarboxamide or an N,N-disubstituted thiourea.



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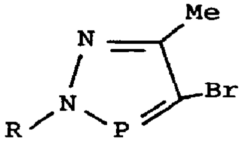

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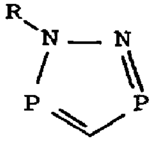

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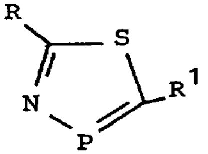


(169)

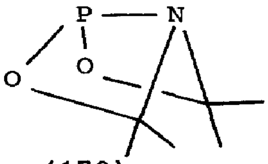
Following the successful syntheses of bis(dialkylamino)-phosphines, $(R_2N)_2PH$, preparations for the related primary phosphines R_2NPH_2 have now been reported.[311] The reaction involves $LiAlH_4$ reduction of the appropriate aminodichlorophosphine and although $Pr^i_2NPH_2$ appears to be unstable, the cyclohexyl and 2,2,6,6-tetramethylpiperidino derivatives can be isolated as air sensitive liquids. Stable metal carbonyl complexes containing these compounds as ligand can also be obtained.

In the presence of triethylamine, HCl is eliminated on treating $(Me_3Si)_2NPH_2$ with carbon tetrachloride to give initially $(Me_3Si)_2NPH(CCl_3)$ but, on refluxing, further HCl loss occurs and $(Me_3Si)_2NP{=}CCl_2$ can be isolated as a viscous liquid.[312] Initially reaction with $SiCl_4$ in place of CCl_4 is similar giving $(Me_3Si)_2NPHSiCl_3$ but in the following step $HSiCl_3$ is eliminated to give a biphosphine $(Me_3Si)_2NPH{\cdot}P(SiCl_3)N(SiMe_3)_2$.

Although previous attempts to prepare $(Me_2N)_2PH$ were unsuccessful, the compound has recently been isolated by reduction of $(Me_2N)_2PCl$ with the hindered borohydride, lithium tri(sec-butyl)borohydride,[313] and the same approach has allowed preparation of $Me\overline{NCH_2CH_2N(Me)P}H$. A second report indicates that thermally stable phosphines of the type $RPH(NR^1_2)$ ($R = Bu^t$, NPr^i_2 or NEt_2) can be isolated by $LiAlH_4$ reduction of the corresponding chloride when $R^1 = SiMe_3$, but with related alkyl substituents, the phosphines are unstable, losing amine to give diphosphines such as

$Pr^i{}_2NPH-P(NPr^i{}_2)_2$.[314]

Isolation and X-ray crystal structure of a bis(borane) adduct of the bicyclic aminophosphine (170) has confirmed basic character at both the phosphorus and nitrogen atoms.[315] The B-P and B-N distances are 1.873 and 1.655Å respectively and the P-N bond length (1.757Å) indicates the absence of π-bonding.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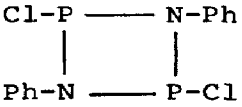
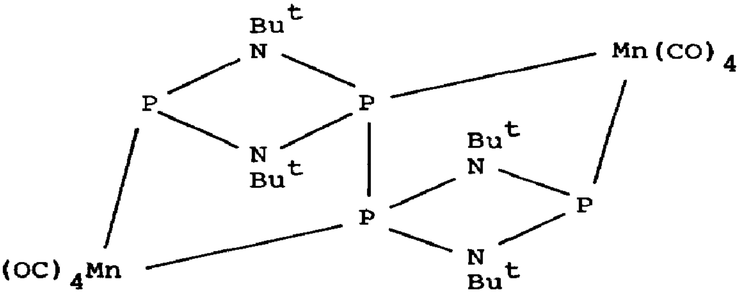


(171)

The new diphosphinoamine, meso-$Pr^iN(PPhNHPr^i)_2$, is diastereomerically formed in the presence of Et_3N from $PhPCl_2$ and Pr^iNH_2 at 0°C in toluene solution; the reaction also gives the expected disubstitution product, $PhP(NHPr^i)_2$.[316] A diazadiphosphetidine (171), confirmed by X-ray diffraction as the cis isomer, is obtained in a variety of reactions and is considered to be the thermodynamically stable form as it remains unchanged after boiling in toluene for 24 hours.[317]

Equimolar quantities of $(ClPNBu^t)_2$ and $NaMn(CO)_5$ in THF initially at -78°C but subsequently refluxed for 10 hours precipitate sodium chloride and evolve CO giving the green complex (172).[318] An S_4N_4 type cage molecule $P_4(NBu^t)_4$ can be isolated when $(ClPNBu^t)_2$ is reduced and the P-N unit in (172) may represent an intermediate in this process, trapped and stabilised here by two $Mn(CO)_4$ units.



(172)

Among the complexes reported recently containing the cyclophospha(III)azane, $(MeNPMe)_4$, (≡L) are $[LCoCl]_2[CoCl_4]$, $LM(CO)_3$ where M = Cr, Mo, W or Mn^+, and $LNi_2(CO)_3$.[319] The neutral $LM(CO)_3$ compounds can be quaternised giving $[LM(CO)_3R]I$, where R = Me, CH_2CN or $CH_2C(O)NH_2$, and then deprotonated by butyl lithium to ylidic species such as $[LMo(CO)_3CH_2]$. Related compounds result with the ethylated phosphazene, $(MeNPEt)_4$, and a new member of the series $(MeNPPh)_4$ has been synthesised.

Reaction of $(Pr^i_2N)_2PCl$ with the lithium salt of trimethylsilyldiazomethane, $Li[Me_3SiCN_2]$ at 0°C in THF solution gives $(Pr^i_2N)_2P{\cdot}C(N_2)SiMe_3$ which, on irradiation in the presence of trapping agents such as Me_3SiCl or Me_2NH, gives respectively $(Pr^i_2N)_2PCl{=}C(SiMe_3)_2$ and $(Pr^i_2N)_2P(NMe_2){=}CH_2$.[320] The products do not show typical carbene reactivity probably as a consequence of the presence of an electron rich phosphorus atom.

The preliminary report in last year's review on the photolysis of $(Pr^i_2N)_2PN_3$ has been supplemented in the full paper to include data on the related oxo, thio and phenylimino systems, $(Pr^i_2N)_2P(X)N_3$.[321] In the oxygen case, irradiation gives $Pr^i_2NP(:O)(:NNPr^i_2)$ as a transient via a Curtius-type rearrangement, which on trapping with methanol is isolated as $Pr^i_2NP(O)(OMe)(NHNPr^i_2)$. The thio derivative gives a much more complex reaction whose products include $(Pr^i_2N)_2P(S)NH_2$, $(Pr^i_2N)(MeO)P(S)(NHNPr^i_2)$ and $(Pr^i_2N)_2P(O)NH_2$.

Irradiation of $Ph_2PN_3{\cdot}M(CO)_5$, for M = Cr or W, does not lead to a Curtius-type rearrangement but nitrogen is released producing isocyanate complexes, $Ph_2PNCO{\cdot}M(CO)_5$.[322] The mechanism is probably one involving reaction of CO with an intermediate nitrene.

The +5 Oxidation State. Ab initio calculations have been carried out for $H_3P{=}NH$, in which the multiple bond shows similarities with the P=C bond in ylids, the cations $[H_3PNH_2]^+$, $[H_2PNH_3]^+$ and the $[H_2PNH]^-$ and $[HPNH_2]^-$ anions.[323]

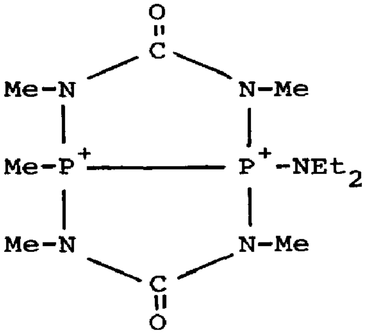
The N-isocyanide, Ph_3PNNC, can be isolated as an unexpectedly thermally stable solid by treating formyl hydrazine as shown in equation 40.[324] Its use as a ligand has been explored by isolating $M(CO)_5(CNNPPh_3)$ (M = Cr, Mo orW), $PdX_2(CNNPPh_3)_2$ (X = Cl or I) and $Cr(CO)_4(CNNPPh_3)_2$.

A series of aminophosphonium chlorides, $[R_3PNMeR^1]Cl$ for R = Me,

$$H_2NNHCHO + 2PPh_3 + 2CCl_4 + 2NEt_3 \rightarrow Ph_3PNNC + 2CHCl_3 + Ph_3PO + 2Et_3NHCl \quad ...(40)$$

Et, Pr or Ph and R^1 = H or Me, has been produced by treating R_3P with either methyl or dimethylchloramine.[325] Methylchloramine prepared by a gas phase reaction of $MeNH_2$ and chlorine gives optically active solutions and the resulting phosphonium salts are chiral; on the other hand MeNHCl prepared via the Raschig process showed no optical activity.

The dimethylurea bridged compound (173) has been synthesised to test the effect of the presence of positive charges on both phosphorus atoms, but at 2.189Å the P-P distance is not significantly different from that in a range of other P-P systems.[326] The bis(borane)-cyclenphosphorane (174) structure



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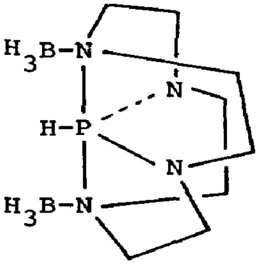


(174)

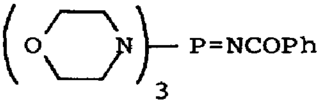
shows no evidence for the open form tautomer and both BH_3 groups are attached to nitrogen atoms.[327] The phosphorus stereochemistry is basically trigonal bipyramidal, displaced ca. 10% toward the square pyramid alternative, with donor nitrogens in axial positions. The axial distances, 1.872 and 1.864Å are the longest reported and are likely to be single P(V)-N(III) bonds; the equatorial P-N distances (1.645, 1.654Å) on the other hand are very short.

On heating in methanol solution, $P(NH_2)_4Cl$ loses ammonia to give mixtures of NH_4Cl, $[(H_2N)_3P{=}N{-}P(NH_2)_3]Cl$ and amidophosphoric esters of the type $(H_2N)_{3-n}P(O)(OMe)_n$.[328]

A series of short chain phosphazenes including: $OPCl_2{\cdot}NPCl_3$,

$\mathrm{OPCl_2{\cdot}N{:}PCl_2{\cdot}N{:}PCl_3}$, $\mathrm{[Cl_3P{\cdot}N{:}PCl_2{\cdot}N{:}PCl_2{\cdot}N{:}PCl_3]PCl_6}$, $\mathrm{O{:}P(OPh)_2{\cdot}N{:}P(OPh)_3}$, $\mathrm{O{:}P(NHPh)_2{\cdot}N{:}P(NHPh)_3}$ and $\mathrm{O{:}P(NHPh)_2{\cdot}N{:}P(NHPh)_2{\cdot}N{:}P(NHPh)_3}$, has been synthesised as models for the highly polymeric poly(phosphazenes).[329] Extensive crystallographic studies point to the preference for cis-trans planar P-N conformations in these compounds and show that although stability results from electron delocalisation the molecular conformation is determined by non-bonding intramolecular forces.

Further details on the conformation of phosphorus-morpholine derivatives are now available following crystal structure studies of (175)-(177).[330,331] In all three compounds the lone pair on



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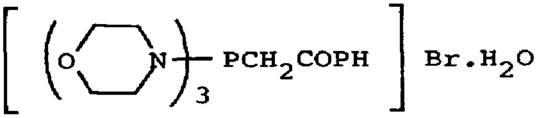

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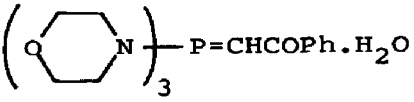
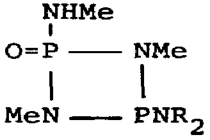


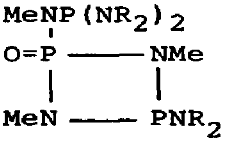
(177)

one of the morpholine nitrogen atoms is antiperiplanar to either the P=N or P-C bond; the lone pairs on the other nitrogens are approximately orthogonal to this bond. It is curious but the P-N(morpholine) distances vary over the range 1.608-1.668Å.

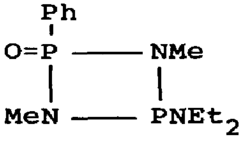
New cyclic compounds (178)-(180) have been prepared by treating $\mathrm{P(NR_2)_3}$ with either $\mathrm{PO(NHMe)_3}$[332] or $\mathrm{PhPO(NHMe)_2}$.[333] Complete substitution occurs when $\mathrm{Cl_3\overline{P{\cdot}NR{\cdot}PCl_3{\cdot}N}R}$ is aminated but the products isolated are imido-oxo partial hydrolysis products.[334,335]



(178, R = Me or Et)



(179, R = Me or Et)



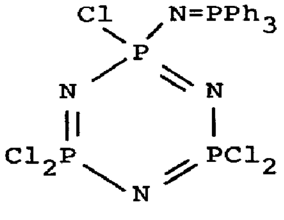
(180)

Two to five of the fluorine atoms in the cyclotriphosphazene, $N_3P_3F_6$, are replaced following a non-geminal reaction path on treatment with $LiOCH=CH_2$, the salt of the acetaldehyde enolate.[336] The ligand is ambidentate but in all cases bonding is via the oxygen atom. One phenyl group can be introduced in a geminal position by Friedel-Crafts reaction of $N_3P_3F_5(NMe_2)$ and $N_3P_3F_5Bu^t$; the reaction course has been confirmed in the latter case by X-ray crystallography confirming that π-donation from an exocyclic substituent is not a necessary condition.[337]

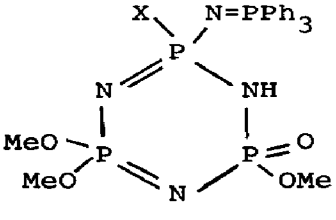
An unusual reaction, in which there is migration of an amido group from a geminal to a non-geminal position, has been identified when the chlorine atoms in $N_3P_3Cl_4(NH_2)_2$, known to have a gem structure, are substituted by NaOR (R = Et, Pr or Bu) in the appropriate alcohol as solvent.[338]

A detailed investigation of the kinetics of chlorine substitution in $N_3P_3Cl_6$ by dimethylamine in acetonitrile solvent points to an S_N2 type mechanism for the first step, while replacement of the second and third chlorines is considered to involve a one-step concerted process on account of the reduced $\Delta H^{\ddagger}$ values.[339] There is then a sharp changeover to an S_N1 mechanism when the fourth chlorine is released; ionisation of a chlorine from $N_3P_3Cl_3(NMe_2)_3$ being promoted by release of electrons to the ring by the NMe_2 groups. The first step in the related $N_3P_3F_6$–Me_2NH reaction is also an S_N2 process, but the much slower rate of reaction is attributed to the greater difficulty in forming the five coordinate intermediate as phosphorus d orbitals in the fluoride are more strongly involved in ring π-bonding.

Chlorine atoms in the phosphazotriphosphazene (<u>181</u>) can be substituted by a variety of primary and secondary amines[340,341] and by methoxide in methanol solution.[342] Among the amine products isolated and characterised are $N_3P_3Cl_{5-n}R_n(NPPh_3)$ for



(<u>181</u>)



(<u>182</u>)

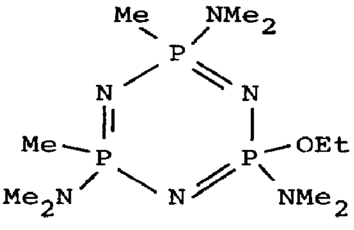
n = 1, R = NHMe, $NHBu^t$, NMe_2, NC_5H_{10}, NEt_2; n = 2, R = NMe_2, NC_5H_{10}, NEt_2; n = 3, R = NMe_2, $NHBu^t$; n = 5, R = NMe_2.[340] The variation in reaction course with change in solvent from ether to acetonitrile was also investigated. A complete series of aziridine derivatives, $N_3P_3Cl_{5-n}(NC_2H_4)_n(NPPh_3)$ with n = 1-5, can be isolated and both geminal and non-geminal isomers are formed for n = 1.[341] The major reaction pathway involves the successive replacement of the chlorine atoms at a PCl_2 group followed by substitution of that at the $PCl(NPPh_3)$ phosphorus. The fully substituted compound has been examined by X-ray crystallography.

Reaction of both $N_3P_3Cl_5(NPPh_3)$ and $N_3P_3Cl_4(NMe_2)(NPPh_3)$ with methoxide give mixed methoxy-hydroxy compounds, such as $N_3P_3(NPPh_3)(OMe)_4(OH)$, $N_3P_3(NPPh_3)(OMe)_3(OH)_2$, $N_3P_3(NPPh_3)(NMe_2)(OMe)_3OH$, in addition to the fully substituted compounds $N_3P_3(NPPh_3)(OMe)_5$ and $N_3P_3(NPPh_3)(NMe_2)(OMe)_4$.[342] N.m.r. data for the monohydroxy compounds indicate formulation as a cis-trans mixture of the tautomeric oxophosphazadiene (182, X = OMe or NMe_2).

A series of spiro-cyclic triphosphazenes can be prepared by treating the spermidine-$(N_3P_3Cl_4)_2$ derivative with 1,3-diaminopropane[343] and i.r. spectroscopy of aminophosphazenes, particularly in the N-H stretching region, has been investigated in relation to antitumor activity.[344]

Reaction of RCOCl (R = Me or Ph) with $N_3P_3(OMe)_5(OH)$ in the presence of an HCl acceptor gives carboxylates $N_3P_3(OMe)_5(OCOR)$ whose spectroscopic properties are compatible with a triphosphazene rather than the tautomeric diphosphazene structure.[345] Fluorination of cis-$N_3P_3Cl_4(NEt_2)_2$ with, respectively, SbF_3 and KSO_2F leads to the 1,3- and 5,5-difluorides; with either reagent further fluorination gives the tetrafluoride.[346]

Reaction between Grignard reagents and non-geminally substituted $N_3P_3Cl_3(NMe_2)_3$ depends markedly on reagent concentrations, solvent and the product isolation method.[347] In ether solution, MeMgI gives the expected $N_3P_3Me_3(NMe_2)_3$ after treatment with triethylamine but a second product (183) is also formed by reaction with the solvent. The corresponding ethyl analogues were also prepared but with THF, the products were compounds with 4-chlorobutoxy groups attached to phosphorus. The mixed phosphazene-siloxane (184) is currently of interest as a



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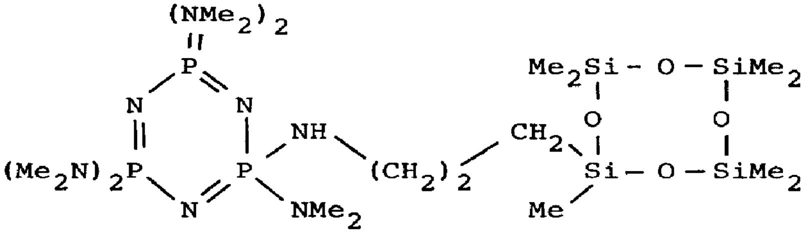
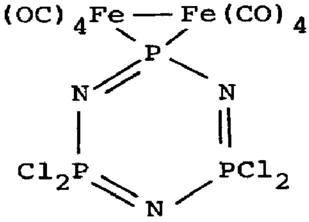


(184)

cocatalyst in the polymerisation of $(Me_2SiO)_3$; its structure has been determined showing a dihedral angle of 100.1° between the mean planes of the two rings.[348] The N_3P_3 ring is effectively planar in three monospiro substituted triphosphazenes, $N_3P_3[O(CH_2)_nO]Cl_4$ where n = 1,2 or 3, according to recent X-ray studies but the phosphate ring parameters vary greatly (O-P-O 98.3-106.1, P-O-C 111.2-121.9).[349]

Although thermal polymerisation of substituted cyclophosphazenes such as $N_3P_3(OPh)_6$ does not appear to be possible, recent mass spectrometric data show that the higher oligomers $[NP(OPh)_2]_{6,9 \text{ and } 12}$ are formed in the ion source at 200°C.[350] Phosphazenes are fire retardants and a new route has been described to $N_3P_3(C_6H_4\text{-}4\text{-}NO_2)_6$, which can be obtained in distinct forms melting at 249-250° and 262-263°C; the nitro group can be reduced readily.[351]

The phosphazene ring in (185) can serve as a template giving new spiro-metallic and cluster compounds such as (186) and (187, M = Co) obtained by reaction with $CpCo(CO)_2$.[352] With $CpRh(CO)_2$ the



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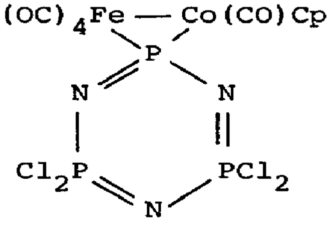

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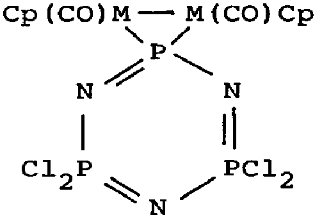
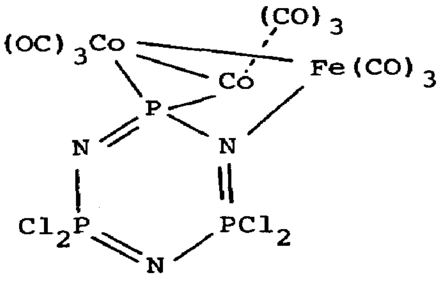


(187)

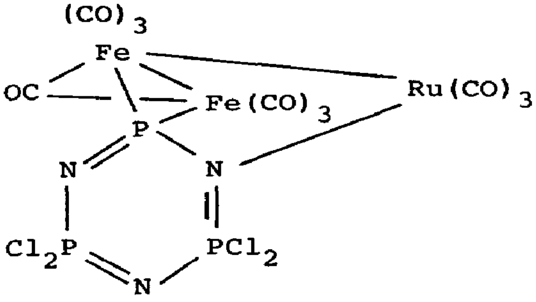
product is (187, M = Rh) while the cluster compounds (188) and (189) involving additional metal-nitrogen interaction are obtained with, respectively, $Co_2(CO)_8$ and $Ru_3(CO)_{12}$.

The pressure dependence of the ^{35}Cl n.q.r. spectra for $N_3P_3Cl_6$

and $N_4P_4Cl_8$ has been evaluated.[353] The possibility of injecting electron density from a spiro substituent into a cyclophosphazene ring via (p-d)π delocalisation has been examined theoretically and shown to be possible in compound (<u>190</u>, R = OCH_2CF_3).[354] The synthesis from $N_3P_3Cl_6$ and (<u>191</u>) requires $EtPr^i_2N$ in dioxan and the four remaining chlorines are substituted using CF_3CH_2ONa in THF. Compound (<u>190</u>) can be methylated with $[Me_3O][BF_4]$ at the exocyclic imide nitrogen and isolated as the tetrafluoroborate salt; the structure was confirmed by X-ray diffraction. Both (<u>190</u>) and the methyl derivative are electroactive and e.s.r. data are given for the first reduction steps.



(<u>188</u>)



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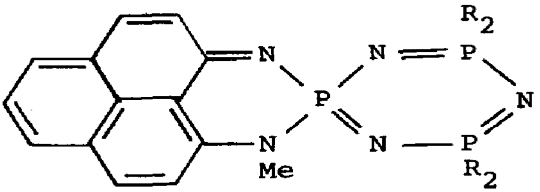

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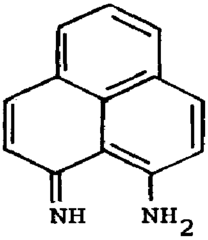
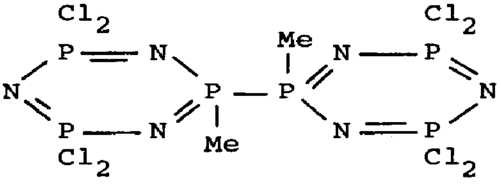


(<u>191</u>)

Mössbauer spectroscopy and d.c. polarography have been used to investigate oxygen interaction with hemin and related molecules attached to the backbone of a water soluble poly(aminophosphazene) such as $\{NP(NHMe)_x(NMe[CH_2]_3NH_2)_y\}_n$.[355] The results show formation of both stable oxygen adducts and irreversible oxidation depending on the system. As a model for such polymeric species, $N_3P_3(OPh)_5[NMe(CH_2)_3NH_2]$ has been synthesised and converted to a picket fence hemin derivative.

The P-P bonded bis(phosphazene) (192) obtained from $(NPCl_2)_3$ and methylmagnesium chloride lies on a centre of symmetry with a P-P bond length of 2.200Å.[356] The methyl groups are thus trans to each other; the N_3P_3 rings are puckered with the methyl substituted phosphorus lying 0.21Å above the plane of the other ring atoms.

Non-geminally substituted mixed halogenotetraphosphazenes, $N_4P_4F_4X_4$ and $N_4P_4F_6X_2$ (X = Cl or Br), can be obtained via room temperature reactions of either anhydrous hydrogen chloride or bromide with the appropriately substituted $N_4P_4F_n(NMe_2)_{8-n}$.[357]



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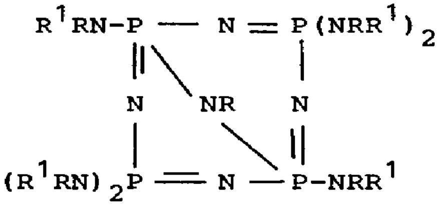
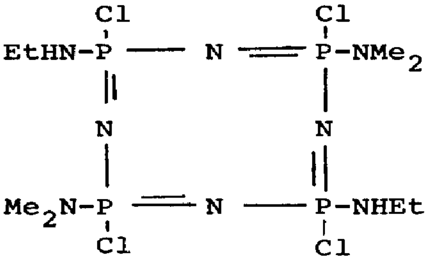


(193)

Monospirocyclic tetraphosphazenes, $N_4P_4Cl_6(X(CH_2)_nX)$ result by treating $N_4P_4Cl_8$ with difunctional reagents such as $H_2N(CH_2)_nNH_2$ (n = 2 or 3), $HO(CH_2)_nOH$ (n = 2 or 3) and $HO(CH_2)NHMe$, but the products are unstable to hydrolysis and/or intermolecular condensation.[358]

Transannular bridged tetraphosphazenes (193) are well known but recent work has shown that the bridge is incorporated only after the tetrakis stage of chlorine replacement in $N_4P_4Cl_8$.[359] Compound (194) with a non-geminal arrangement of substituents is converted by one mole of dimethylamine into (195) while five mols of ethylamine produce a second new bridged compound (196).



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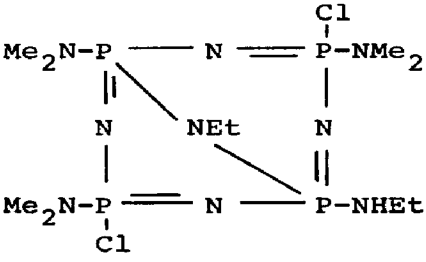

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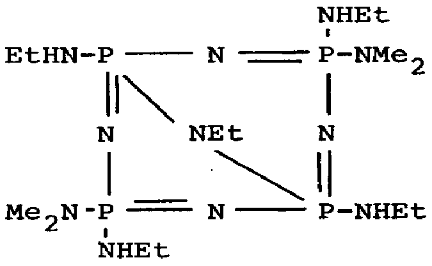


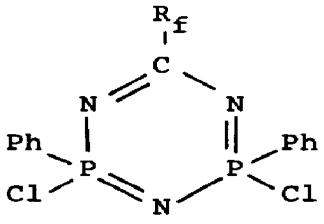
(196)

Crystallographic data for the higher members of the methylphosphazene series $(NPMe_2)_{9-12}$, obtained by Grignard reactions on the separated fluorides, show a mean P-N distance of 1.595Å, somewhat longer than that in the corresponding chlorides and fluorides as a result of the lower methyl group electronegativity.[360] The endocyclic angle at phosphorus decreases from 119.8° in the tetramer to 116.3° in $(NPMe_2)_{12}$, but the P-N-P angles vary as the nitrogen lone pair can be delocalised into phosphorus d orbitals. The molecular structures are compact, with ring atoms folded into the centre and the conformations adopted are controlled primarily by methyl group interactions. In this respect there are similarities with the cycloalkane structures of similar degrees of polymerisation.

A geminal pathway is followed in the reaction of $N_5P_5Cl_{10}$ with NaOR (R = Et or Ph) in either benzene or ether as solvent.[361] In general, up to four chlorines can be substituted but attempts to produce higher degrees of substitution by more forcing conditions lead to decomposition. Small amounts of more highly substituted products, i.e. $N_5P_5Cl_{10-n}(SEt)_n$ for n = 5, 6 and 10, have been observed in a related thioalkoxy series.

Chlorine substituted diphospha-s-triazine[362] (197) and phospha-s-triazines[363] (198) have recently been isolated following the reactions in equations 41 and 42; the halogen atoms can be

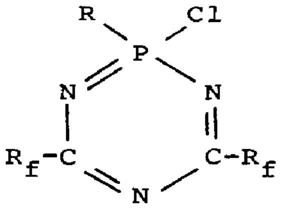
$PhPCl_4{\cdot}N{:}PPhCl_2 + R_fC(:NH)NH_2 \rightarrow$



(197) ...(41)

$R_f = C_3F_7OCF(CF_3)CF_2OCF(CH_3)$
or C_7F_{15}

$$RPCl_4 + R_fC(:NH)\cdot N:C(NH_2)R_f \rightarrow \qquad \ldots(42)$$



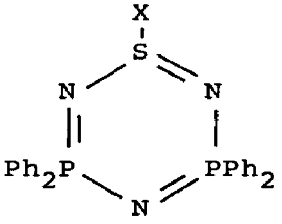
(198)

R = Cl or Ph

R_f = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$
or C_7F_{15}

substituted for a variety of other groups including SPh, giving products which are anticorrosive and antioxidation agents.[364]

X-ray structures for four derivatives of the mixed P-N-S ring system (199, X = Cl, I, NMe_2 and Ph)[365] show effective planarity when X = Ph but substantial deviations for the sulphur atom in the other three derivatives. As well as long S-halogen bond lengths there are marked inequalities in the P-N distances. Hartree-Fock-Slater SCF calculations on the model compound (200),



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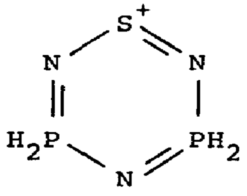
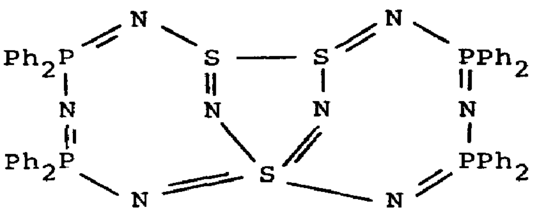


(200)

to compare this with the homomorphic N_3P_3 and N_3S_3 systems point to the presence of 6π electrons in the ring but the localisation of π bonding in the P_2N and N_2S segments. In addition there is strong N_2S antibonding character in the LUMO. Electrochemical reduction potentials in the series of ring compounds ranging from N_3P_3 (resistant to oxidation) through $N_3P_2S^+$ and N_3PS_2 to $N_3S_3^-$ (easily oxidised) correlate with πLUMO-πLOMO energy differences.

Thermolysis of a wide range of P-N-S heterocycles, including (199, X=Cl,Br,I,N_3 or NR_2) and (201), gives a new 6,6-spirocyclic compound (202), which was fully characterised by X-rays.[366] This paper reports that, in addition to (202), the reaction of sodium azide with (199, X=Cl) also yields smaller quantities of the 12-membered heterocycle (203) and a new compound tentatively identified as (204).



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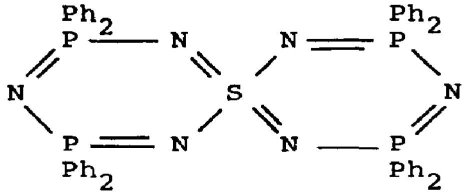

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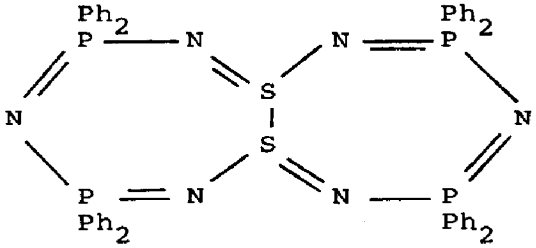

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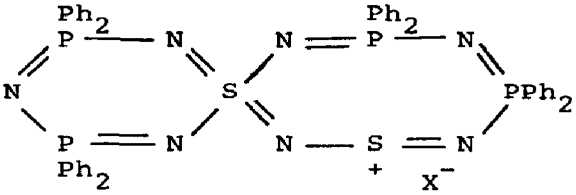


(204)

The crystal structure of a monohydrated aziridine substituted mixed ring compound $N_3P_2S(O)(NC_2H_4)_5$, already known in monoclinic and orthorhombic forms,[367] and low temperature electronic spectra and preresonance Raman spectra of $N_3S_2PPh_2$ and $N_4S_2(PPh_2)_2$[368] have been reported.

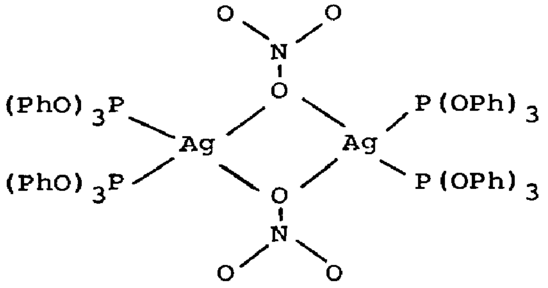
5.2.5 Bonds to Oxygen

Lower Oxidation States. Vanadyl(IV) hypophosphite, $VO(PO_2H_2)_2.H_2O$, which can be prepared either by reducing the pentoxide with hypophosphorous acid or from $VOSO_4$ and the acid, has been fully characterised spectroscopically and shown to undergo complex thermal decomposition yielding finally polymeric vanadium(III) phosphite.[369]

Co-condensation of chromium vapour and $P(OMe)_3$ gives $Cr[P(OMe)_3]_6$ in good yield but the corresponding ethyl derivative which can be prepared similarly is unstable, probably for steric reasons.[370] The related molybdenum and tungsten compounds $M[P(OR)_3]_6$ were also prepared as were low yields of the mixed complex, $Cr(arene)[P(OR)_3]_3$. A silver nitrate-triphenylphosphite addition compound $(AgNO_3)_2.[P(OPh)_3]_4$ with structure (205) has asymmetric Ag-O-Ag bridges with O-Ag-O and P-Ag-P angles of respectively 71.9 and 147.9°.[371]

The phosphorus triester, $P(OPh)(OC_6H_4\text{-}4\text{-}Cl)(OC_6H_4\text{-}4\text{-}Me)$, can be prepared from $P(OPh)Cl_2$ and the two phenols in the presence of triethylamine in ca. 51% yield and can be resolved.[372]

A monomeric, tetrahedral complex (<u>206</u>) incorporating the open form of the bicyclic aminophosphine ligand (<u>207</u>) has been isolated in a reaction with $[Co(NO)_2Cl]_2$.[373] The product is



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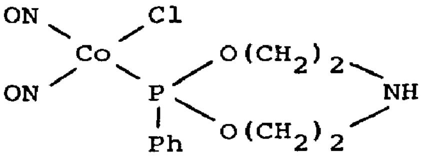

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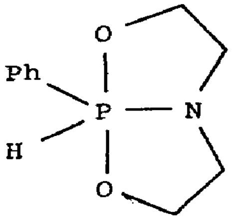

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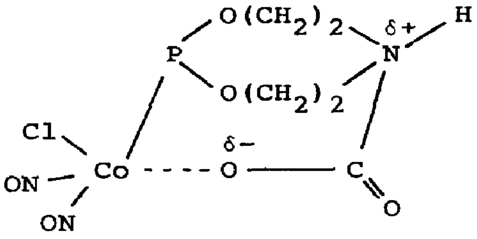
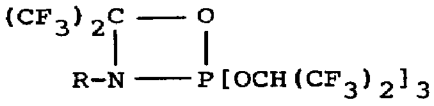


(<u>208</u>)

unusual in that it can reversibly coordinate carbon dioxide in THF solution at -30°C to give a dark brown solid where the CO_2 is probably held as a carbamate group (<u>208</u>).

The lithium salt $Li[OCH(CF_3)_2]$ converts amidodifluorophosphines $RNHPF_2$ (R = H, Me or Bu^t) to the expected amidophosphites, $RNHP[OCH(CF_3)_2]_2$, which with hexafluoroacetone yield oxazaphosphetanes (<u>209</u>).[374] In (<u>209</u>, R = H) the phosphorus atom is in



(<u>209</u>)

distorted trigonal bipyramidal coordination with the ring oxygen and an oxygen of one of the $OCH(CF_3)_2$ groups in axial positions.

The procedure for preparing diphosphite complexes such as $M_4[Pt_2(P_2O_5H_2)_4].2H_2O$ (M = K, Na, ½Ba, Bu_4N or Ph_4As) has been modified so that the products are free from oxidised platinum species.[375] The compounds can be oxidised to the d^7-d^7 compounds $[Pt_2(P_2O_5H_2)_4X_2]^{4-}$ (X = Cl, Br, I, NO_2 or SCN) and $[Pt_2(P_2O_5H_2)L_2]^{2-}$ (L = H_2O, pyridine or nicotinamide), and recent X-ray studies for the former with X = Br or I show structures containing four P-bonded bridging diphosphite groups with halogen atoms in axial positions (see Figure 7).[376] In agreement with their σ-donating strength, the Pt-Pt distance decreases from 2.754Å for X = I to 2.695Å for X = Cl. The Pt(II) anion is also oxidised by NO_2 giving $[Pt_2(P_2O_5H_2)_4(NO_2)_2]^{4-}$ with axial NO_2 groups, and addition of halide ions can displace the nitrite groups to give mixed species.[377]

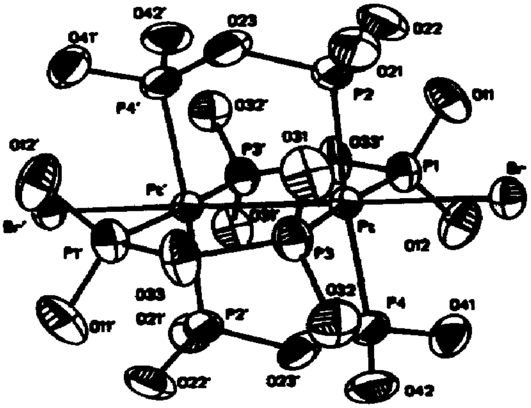


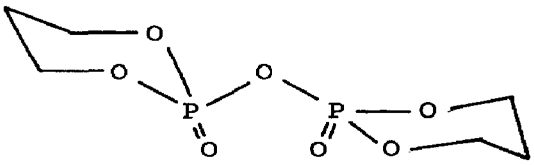
Figure 7. Structure of $[Pt_2(P_2O_5H_2)_4Br_2]^{4-}$ (reproduced by permission from Inorg. Chem., 24(1985)2803).

The +5 Oxidation State. Monomeric metaphosphate continues to command attention with recent plasma studies pointing to its thermodynamic stability (ΔH_f −190±8 kcal mol^{-1}) in the gas phase.[378] The species thus shows greater stability than the nitrogen analogue and the acid strength is estimated to be comparable to that of sulphuric acid.

According to recent theoretical studies, the traditional $\geqslant P=O$ structure for the phosphoryl bond is unreasonable on symmetry grounds and a model involving resonance between singly and triply bonded structures should be substituted.[379] Although electronegative substituents at phosphorus generally strengthen the P-O bond, fluorine is anomalous with a lower strengthening effect than a hydroxy group. In the related $\geqslant P=S$ system, the bond is substantially weaker and triply bonded structures are relatively of lower importance. The stable conformations of phosphoric, phosphonic and phosphinic acids have been investigated by ab initio studies on H_3PO_4, H_3PO_3 and H_3PO_2 and the forces giving rise to specific molecular arrangements have been analysed.[380] These are almost entirely electrostatic in nature (dipole-dipole) with relatively small effects from internal hydrogen bonding and steric effects. In all three acids, the acidic protons are oriented toward the phosphoryl oxygen at distances of 2.7 to 2.8Å.

The protonated base and $H_2PO_4^-$ anions, which constitute the units in the 1:1 adduct of phosphoric acid and 1,2,3-benzotriazole, are linked together by very short N-H-O and O-H-O hydrogen bonds.[381] Of the former, one distance (2.611Å) is comparable with the shortest yet recorded and the latter which occur in chains of the anions are 2.451 and 2.484Å. A second "complex" of phosphoric acid, $(H_3PO_4.H_2O)_2.$(18-crown-6) can be prepared from the components in THF solution.[382]

2-Amino-3-phosphonopropionic acid is present as a zwitterion, $^{-}HPO_3CH_2CH(\overset{+}{N}H_3)COOH$, in the solid state[383] and in the tetraalkyl diphosphate (210) both rings are in the chair conformation with the P-OP bonds in axial positions.[384] The P-O-P bridge angle is 129.2° with bridge P-O distances of 1.597 and 1.606Å. An unusual trigonal bipyramidal structure (211) with an axial hydrogen atom has been confirmed by X-ray crystallography on the product obtained by treating Ph_2PCl with triethylammonium per-



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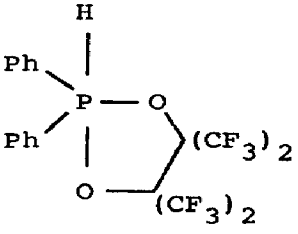

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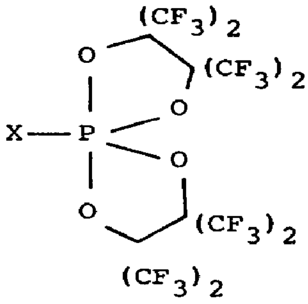

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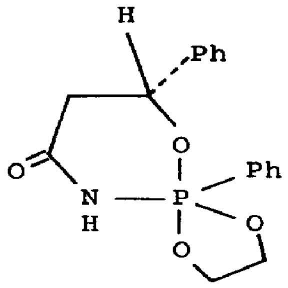
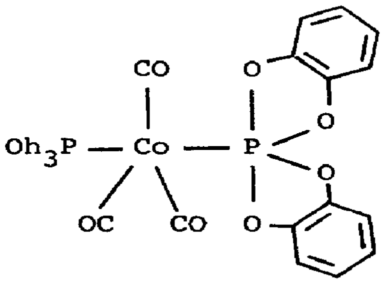


(213)

fluoropinacolate,[385] P-O distances to the axial and equatorial atoms are respectively 1.773 and 1.681Å. The first thiohydroxyphosphorane (212, X = SH) with an almost undistorted trigonal bipyramidal structure has been obtained from (212, X = H) by successive treatment with sulphur in the presence of Et_3N and anhydrous hydrogen chloride.[386] Rather surprisingly in view of its five and six membered rings, the newly prepared (213) also has trigonal bipyramidal geometry.[387]

The novel five coordinate cobalt-complex (214), synthesised from $(C_6H_4O_2)PCl$ and $Na[Co(CO)_3PPh_3]$ in THF at -78°C, decomposes slowly in solution and has a structure with basically trigonal bipyramidal geometry about both cobalt and phosphorus.[388] The phosphorus atom is in an axial position at cobalt while the phosphorus atom has oxygen atoms in axial positions. As in many compounds of this type, the phosphorus geometry is distorted by some 28% along the Berry coordinate toward the square pyramidal alternative.

Hydrolysis of the spirophosphoranes (215, R = H or Me) proceeds



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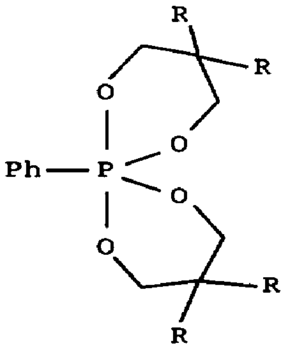

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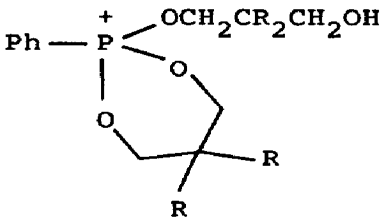
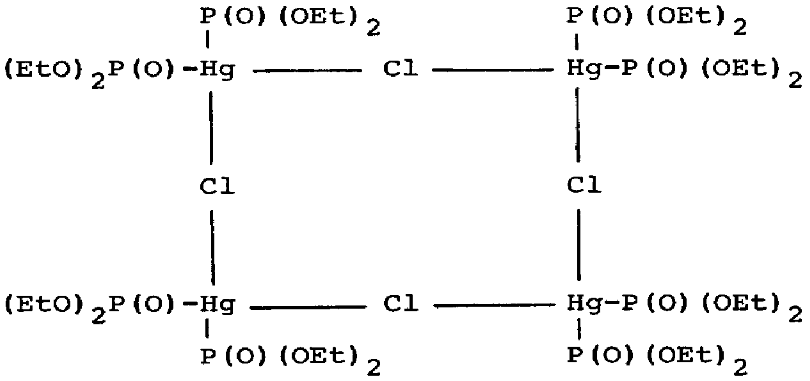


(216)

via a ring opened phosphonium salt (<u>216</u>) which can, in fact, be synthesised.[389]

Both BF_3 and H_3PO_4 form 1:1 addition compounds with the phosphatrane, $O{=}P(OCH_2CH_2)_3N$, where in contrast to the related borine adduct, there is still substantial $N{\rightarrow}P$ interaction.[390] Evidence is presented to suggest that phosphorus is in trigonal bipyramidal coordination and that the compounds are stabilised by the increased electronegativity at the apical atoms as a result of the electron withdrawing properties of the attacking Lewis acids.

Aqueous sodium chloride solution converts $Hg[P(O)(OEt)_2]_2$ into a tetrameric compound (<u>217</u>) containing an almost square, eight membered Hg_4Cl_4 heterocycle.[391] The mercury-phosphorus bonds are almost perpendicular to the ring giving very distorted tetrahedral coordination around mercury and all eight phosphoryl groups are orientated toward the centre of the ring.



(<u>217</u>)

The copper atom in the diphenylphosphato complex, $\{Cu(imidazole)_4[O_2P(OPh)_2]_2\}$, is in square planar coordination with nitrogens from the four imidazole ligands and tetragonally distorted octahedral coordination is completed by oxygens from two unidentate phosphate groups in axial positions.[392] Metal phosphate complexes with the general formula $[(MeO)RPO_2]_nM$, where M = Na, Ca, Ba, Zn, etc; n = 1 or 2; and R = OMe, $OCH{=}CH_2$, $OCMe{=}CHCO_2Me$, etc, can be synthesised by dealkylation of an organo-phosphate or -phosphonate on refluxing with a metal halide in acetone.[393] Coordination of cis- and trans-diphenylphosphoryl ethylene, $Ph_2P(O){\cdot}CH{=}CH{\cdot}P(O)Ph_2$, to $Ph_2Sn(NO_3)_2$ gives, respectively, 1:1 and 1:2 complexes in which the cis isomer is chelating but the trans form behaves as a bridging group.[394] X-ray data point to pentagonal bipyramidal geometry about tin in both compounds with five oxygens occupying the equatorial plane. In the cis compound, there are two oxygens from the ligand and three oxygens from one unidentate and one bidentate nitrate group; in the corresponding trans compound, the two nitrate groups are bidentate and the ligand produces the fifth oxygen atom.

New methods for synthesising the mixed anhydrides, $RR^1P(O)OSO_2R^2$ for R = Bu^t or OEt, R^1 = Ph or OMe and R^2 = Me or CF_3, have been described.[395] In connexion with metal extraction processes, neodymium, $Nd(NO_3)_3.L_2$ and $Nd(NO_3)_3.L_2.2MeCN$,[396] where L = $Ph_2P(O)CH_2C(O)NEt_2$,[396] and erbium complexes $Er(NO_3)_3.L_2.H_2O$, where L = $(Pr^iO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]$, have been synthesised. All the compounds contain three bidentate nitrate groups and the neodymium coordination number is raised to 10 by four further oxygen atoms from the bidentate ligands. The acetonitrile molecules are not coordinated to the metal in the second compound. The erbium atom in the last compound has coordination number nine from oxygens of the nitrate groups, the water molecule and the two P=O groups; the C=O groups on the other hand are either non-coordinated or hydrogen bonded to water and it appears that the phosphonate arms are incorrectly constructed for tripod coordination. The methylenephosphonate ligand $(Pr^iO)_2P(O)CH_2C(O)NEt_2$ chelates via the P=O and C=O groups in its 1:1 complex with MoO_2Cl_2 giving approximately octahedral geometry about the central atom.[398]

Substantial research is again reported on aluminium phosphate cage compounds and related derivatives. For example, compounds designated as $AlPO_4$-12 and $GaPO_4$-12 are isostructural with the formula $M_3(PO_4)_3.H_2O.en$ and result, for the former, from hydrothermal treatment of the gel obtained from a 1:1:1:40 combination of Al_2O_3, P_2O_5, 1,2-diaminoethane(en) and H_2O.[399] The gallium compound is similarly prepared from $Ga_2O_3.\frac{1}{2}H_2O$ and H_3PO_4. The structures are based on sheets of alternate $AlO_4(GaO_4)$ and PO_4 tetrahedra corner linked by slabs of tetramers of Al(Ga) centred trigonal bipyramids cross linked by PO_4 tetrahedra. The details are shown in Figure 8. Sandwiched between these units are diprotonated en molecules giving $[(CH_2NH_3)_2]^{2+}[(MPO_4)(M_2P_2O_9)]^{2-}$ as a more accurate representation of the molecular formula. $AlPO_4$-21 type compounds result using

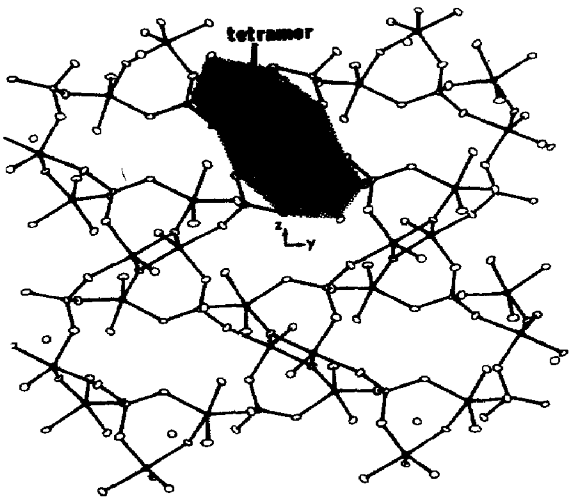


Figure 8. The gallium centred trigonal bipyramidal tetramers, crosslinked by PO_4 tetrahedra, in $GaPO_4$-12 (reproduced by permission from Inorg. Chem., 24(1985)4312).

tetramethyl-1,3-diaminopropane,[400] pyrrolidine[401] and 1,2-diaminoethane as templates. In the first case,[400] X-ray diffraction points to break-up of the template into, most probably, $Me_2NH_2^+$ and propyl units and a novel, complex, anionic framework containing rings based on Al_2P, Al_2P_2 (four types), Al_3P_2 (two types) units. The molecular formula is $4(Al_3P_3O_{10}OH)$.-$1.33(C_7H_{21}N_2)$. The latter compounds have structures described in terms of ribbons of five coordinate aluminium and four coordinate phosphorus atoms forming three and five-membered rings interlinked initially into corrugated sheets and finally into an open network. These compounds can be converted on heating to the sieve $AlPO_4$-25.

Increased catalytic activity of $AlPO_4$ phases can be achieved by adding either ZnO[402] or a cobalt salt[403] to the gel prior to hydrothermal treatment. In the first case, the product which is similar to $AlPO_4$-5 is formulated as $Zn_{0.06}Al_{0.96}PO_4$ together with residual triethylamine used as the template. The cobalt products are blue showing incorporation of the metal into tetrahedral sites.

A further range of gallium analogues of $AlPO_4$-12, -21 and -25 has been synthesised with crystallography showing that the product is strongly dependent on the template (1,2-diaminoethane, pyrrolidine, i-propylamine, Et_4NOH).[404] The powder pattern of a phase formulated as $Pr^iNH_3[Ga_4(PO_4)_4OH]$ is close to that of $AlPO_4$-14 but a full structure shows a new structure type based on a repeating unit of edge and corner sharing GaO_5 and GaO_6 units and PO_4 tetrahedra.

A silico-alumino-phosphate molecular sieve (ZYT-7), prepared from a 1:1:2:1 mixture of P_2O_5,Al_2O_3, morpholine and SiO_2, is $[H_3O]^+[Al_4SiP_3O_{16}]^-.nH_2O$ with a chabazite type structure containing large cavities.[405] The structural units present include 4, 6 and 8-membered rings of AlO_4 and $(Si,P)O_4$ tetrahedra. Multinuclear MAS n.m.r. data of a related silico-alumino-phosphate, SAPO-5, with an $AlPO_4$-5 type structure are now available.[406]

Framework zirconium phosphates, $(NH_4)_xH_{1-x}Zr_2(PO_4)_3.yH_2O$ where $0.6 \leq x \leq 1$, $y \leq 0.3$, have been isolated from hydrothermal reactions between phosphoric acid and $ZrOCl_2$ in the presence of Me_4NBr;[407] heating to between 400 and 640°C converts the products to the acid form $HZr_2(PO_4)_3$ in which the proton can be exchanged by Li^+ or Na^+ but, because of a bottleneck in the $[Zr_2P_3O_{12}]^-$ framework, exchange with K^+ or Cs^+ is not possible. Mixtures of $NH_4Zr_2P_3O_{12}$ and $NH_4Ti_2P_3O_{12}$ heated under reducing conditions in a high pressure vessel give langbeinite-type crystalline phases formulated as $(NH_4)_{1+x}Ti(III)_x[Ti(IV),Zr]_{2-x}P_3O_{12}$ with $x \leq 1$.[408] Langbeinite structures are also proposed for the newly synthesised compounds, $A_2ZrMP_3O_{12}$ for A = K, Rb or Cs and M = Y or In.[409]

$Cd_5(PO_4)_2SiO_4$ and the germanium analogue have the silicocarnotite structure[410] and a three dimensional framework containing tunnels has been observed for the molybosilicophosphate, $CsMoP_{5.8}Si_2O_{25}$, obtained by adding metallic molybdenum to a mixture of $(NH_4)_2HPO_4$, Cs_2CO_3, MoO_3 and SiO_2 previously heated to 873K.[411]

Intercalation of alkylamines[412] into $Sn(HPO_4)_2.H_2O$ as alkylammonium ions between the layers is suggested by i.r. and thermal analysis, but monolayers are formed with pyridine, 4,4'-bipyridine or dimethylsulphoxide.[413] Piperidene, aniline and m-toluidine, on the other hand, give bilayers but other potential guest molecules such as urea, thiourea and formamide do not intercalate.

H^+-K^+ exchange on $Ti(HPO_4)_2.H_2O$ between 25 and 55°C shows no partially substituted phases, the final product is $Ti(KPO_4)_2.3H_2O$.[414] The acid properties of α-$Ti(HPO_4)_2.2H_2O$ affect catalytic activity and they have been followed as a function of different degrees of heat treatment.[415]

Structures for both $ZrNaH(PO_4)_2$[416] and $ZrKH(PO_4)_2$[417] have been reported, the latter by time of flight neutron powder diffraction which allows location of the hydrogen atoms inferred from previous X-ray studies.

α-Zirconium phosphate, $Zr(HPO_4)_2.2H_2O$, like the γ-form, reacts with ethylene oxide, but the extent depends on the degree of crystallinity.[418] With highly crystalline samples reaction occurs only at the surface hydroxyl groups but rapid incorporation between the layers gives products of the type $Zr[O_3PO(CH_2CH_2O)H]_2.xH_2O$ with poorly crystalline materials.

Treating $ZrOCl_2.8H_2O$ with a mixture of H_3PO_4 and $3As_2O_5.5H_2O$ gives a white gel, which on long reflux in nitric acid solution can be converted to crystalline $Zr(HAsO_4)(HPO_4).H_2O$.[419] Heating to 150°C causes loss of one molecule of water and a second is lost at 700°C. The hydrated material is hydrolytically stable and has high ion exchange capacity, its powder pattern is similar to those of $Zr(HPO_4)_2.H_2O$ and $Zr(HAsO_4)_2.H_2O$. A new high pressure phase, β-$Zr(OH)PO_4$, has been synthesised from ZrP_2O_7 and water at 1.5GPa.[420]

Monophosphate structures reported during 1985 include: $Rb_5H_7(PO_4)_4$;[421] a monoclinic form of RbH_2PO_4, prepared in low yield by hydrolysing the tetrametaphosphate, $Rb_4P_4O_{12}$;[422] $Mn(H_2PO_4)_2.2H_2O$;[423] $Ba_3Bi_2(PO_4)_4$, obtained from a melt of $Ba(PO_3)_2.2Bi_2O_3$ at 1373K, showing bismuth in seven fold coordination to oxygen at distances between 2.274 and 2.847Å;[424] and $Na_5Cu_3(PO_4)_2(PO_4HPO_4)$, where two of the four phosphate groups are joined by a very strong O-H...O hydrogen bond (2.388Å).[425]

Dehydration of the following monophosphates, $NaH_2PO_4.2H_2O$,[426,427] $CaHPO_4.2H_2O$,[428] and $Cd(H_2PO_4)_2.2H_2O$,[429] have been investigated in detail.

Tl_2O_3 in phosphoric acid deposits crystals of the mixed valence compound, $Tl(III)_3[Tl(I)_{0.5}(H_2O)_{0.5}]H_{14}(PO_4)_8.4H_2O$ (from an X-ray study), on long standing at room temperature.[430] A series of $M(I)Ta(PO_4)_2$ double salts, where M = Li-Cs, has been isolated by double decomposition from $TaH(PO_4)_2$ and either MCl or MOH.[431] Results consistent with the formation of $[Fe(H_2PO_4)]^{2+}$ and

$[Fe(H_2PO_4)_2]^+$ have been obtained from a study of equilibria and complexation kinetics in the Fe^{3+}-H_3PO_4 system at pH <2.[432]

The monophosphate complex, $[Rh(NH_3)_5PO_4].3H_2O$, can be prepared from $[Rh(NH_3)_5CO_3]ClO_4$ and aqueous phosphoric acid and formation of the diprotonated form $[Rh(NH_3)_5(H_2PO_4)]^{2+}$ from the aquo complex and $H_2PO_4^-/H_3PO_4$ has also been studied.[433] Continuing work on ruthenium ammine complexes as models for biologically important complexes, $[Ru(NH_3)_5(H_2PO_4)][PF_6]_2.2H_2O$ has been synthesised and cyclic voltammetry, pK_a, etc. data reported.[434]

Cation occupancy in $Zn_{3-x}Mg_x(PO_4)_2$ where x = 0-3 has been investigated by ^{31}P MAS n.m.r. spectroscopy showing sensitivity of the ^{31}P isotropic shift to changes in the local environment, particularly at the nearest neighbour cation site.[435] The cation distribution results are comparable to those from diffraction methods and can be obtained in far less time.

A range of amidophosphates, including $Cr(PO_3NH_3)_2NO_3$,[436] $Co(HPO_3NH_2)_2.3H_2O$[437] and $Ni(HPO_3NH_2)_2.5H_2O$, and $Cd(HPO_3NH_2)Cl.\frac{1}{2}H_2O$,[438] $Cd(HPO_3NH_2)_2.1\frac{1}{2}H_2O$, $Hg_2(PO_3N).3H_2O$ and $Hg_3(PO_3NH)_2.5H_2O$ has been synthesised from potassium amidophosphate and an appropriate metal salt in aqueous solution. Formulation as containing the $[PO_3NH_3]^-$ ion follows from i.r. spectroscopy.

Difluorophosphoric acid can be prepared via PO_3F^{2-} by direct fluorination of PO_4^{3-} with HSO_3F.[439] Monosolvated difluorophosphates $M(O_2PF_2)_2.HPO_2F_2$ can be isolated from reactions of metals such as Mn, Co, Ni and Fe with the free acid and a related Cr(III) compound $Cr(O_2PF_2)_3.HPO_2F_2$ has been obtained from a reaction with $CrBr_3$.[440] $FeCl_3$ in ether solution gives an ansolvous product, $Fe(O_2PF_2)_3$ which i.r. spectroscopy indicates is polymeric with bridging difluorophosphate groups. The presence of such bridging groups has been confirmed by X-ray crystal structures for $Co(O_2PF_2)_2.2MeCN$, obtained by recrystallising $Co(O_2PF_2)_2.HPO_2F_2$ from acetonitrile, and $Cu(O_2PF_2)_2$.[441] The cobalt compound is a linear polymer with the metal in octahedral coordination to four oxygen and two nitrogen atoms, while the copper compound forms a three dimensional polymeric structure with four short (1.899-1.984Å) square planar Cu-O bonds and two longer bonds (2.479-2.622Å) completing distorted octahedral coordination about copper. This leads to effective tridentate coordination for the $O_2PF_2^-$ group.

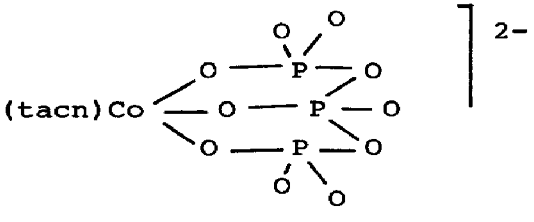
A uranium difluorophosphate, $UO_2(O_2PF_2)_2$, results when $P_2O_3F_4$ reacts with either UO_3 or uranyl nitrate; the compound decomposes on heating eliminating POF_3 to give the monofluorophosphate $UO_2(PO_3F)$.[442] Thermal decomposition of $CaPO_3F.2H_2O$ initially leads to loss of water but in subsequent processes HF and POF_3 loss are important giving α-$Ca_2P_2O_7$ as the final product.[443] The related $Mg(NH_4)_2[PO_3F]_2.2H_2O$ loses NH_3, HF and H_2O on heating but the final product is $Mg_2P_4O_{12}$.[444]

Compounds with the composition $M_xVOPO_4.nH_2O$ where $x \leq 1$ have been isolated following the intercalation of alkali, alkaline earth and transition metal cations into $VOPO_4.2H_2O$ in the presence of reducing agents.[445] Dehydration of $VOHPO_4.\frac{1}{2}H_2O$ leads to two new $VOPO_4$ polymorphs (δ and γ) and a layered (γ) form of $(VO)_2P_2O_7$.[446] The diphosphate which has high selectivity in the catalysis of methacrolein oxidation to methacrylic acid,[447] shows a correlation between degree of crystallinity and magnetic defect density over the temperature range 4-350K.[448]

Association between Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+} or Zn^{2+} with nucleoside di- and triphosphates has been studied by ^{31}P n.m.r. spectroscopy.[449]

$Zn_3Rb_2(P_2O_7)_2$ and the Co(II) analogue are isotypic from recent preparative and structural studies[450] and a neutron diffraction study has been carried out on $2Na_3P_3O_9.Te(OH)_6.6H_2O$ to supplement the previous X-ray study.[451]

It is a curious fact that although triphosphate hydrolysis is slow in aqueous solution, in biological systems it is very fast. Some insight into this has been gained in a study of triphosphate hydrolysis in the complex (218) (tacn is 1,4,7-triazacyclononane) in the presence of $[Co(propanediamine)(OH)(OH_2)]^{2+}$ which is ca. 10^6 times faster than hydrolysis of the uncombined species.[452] A mechanism has been suggested which provides an indication of the roles that metal ions may adopt in enzymatic systems. The structure (218) has been determined.



(218)

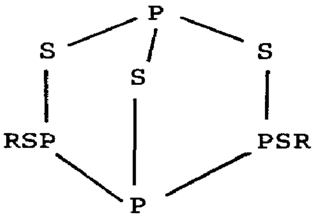
The structure has been determined of $Na(NH_4)_4P_3O_{10}.4H_2O$,[453] and both $KMg_2P_3O_{10}.6H_2O$[454] and $NH_4Mg_2P_3P_{10}.6H_2O$[455] isolated. Steps in the thermal decomposition of $FeH_2P_3O_{10}.2H_2O$ have been followed by X-ray diffraction.[456]

Tetragonal $K_4P_4O_{12}.4H_2O$[457] and $Cs_4Sr_3H_2[P_4O_{12}]_3$[458] have been subjected to single crystal X-ray diffraction; the anion in the former lies in a $\bar{4}$ axis while the latter is structurally similar to $Al_4[P_4O_{12}]_3$ and $Zn_4Na_4[P_4O_{12}]_3$. $Mg_2(NH_4)_2P_4O_{13}.12H_2O$ has been identified in the $(NH_4)_6P_4O_{13}$-$Mg(NO_3)_2$-H_2O system[459] and i.r. and Raman data are now listed for the decametaphosphate, $Ba_2Zn_3P_{10}O_{30}$.[460]

The high temperature form of $LiK(PO_3)_2$ contains infinite PO_3 chains with a period of eight PO_4 tetrahedra[461] while in $Ca(PO_3)_2$ the period in the chain anion is four tetrahedra.[462] A triclinic polyphosphate, $Yb(PO_3)_3$, has been obtained from $YbCl_3$ and $(NH_4)_2HPO_4$, heated initially to 330°C.[463]

5.2.6 Bonds to Sulphur, Selenium or Tellurium

A reinvestigation of the P_4S_3-RSSR (R = Me, Et or Ph) reactions (U.V. irradiation) under less forcing conditions than previously shows successive formation of (219) and (220), designated respectively as the β and α forms by analogy with isomerisation of the related iodide.[464] Mass spectra have been reported for P_4S_3, P_4Se_3 and the arsenic analogues.[465] The exact mode of coordination between P_4S_3 and a transition metal depends on the metal and its oxidation state, with coordination via the apical phosphorus in a number of four coordinate, d^{10} complexes. In the trinuclear compound, $[Pt(\mu\text{-}P_4S_3)(PPh_3)]_3.PhH$, obtained from phosphorus trisulphide and $[Pt(C_2H_4)(PPh_3)_2]$ in acetone, on the other hand, one of the P-P bond is cleaved and the platinum atom inserted.[466] Coordination number four is then achieved by



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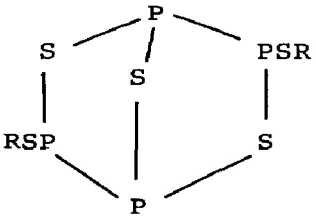
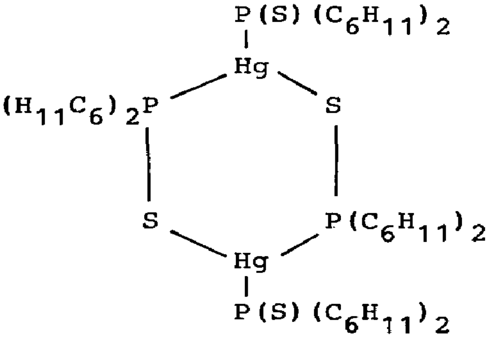


(220)

reaction with phosphorus atoms of Ph_3P and a neighbouring P_4S_3 residue. In two cases the PtP_4 units are almost planar, but in the third there are substantial deviations.

Coordination between mercury(II) and the phosphinothioite ligand $[(C_6H_{11})_2PS]^-$ gives the cyclic dimer (221)[467] while mercury halides and the tri-phosphorus ligands $[Ph_2P(S)]_3CH$ and $[Ph_2P(S)][Me_2P(S)]_2CH$ give complexes with the cage structure (222).[468] At ca. 160°C P_4S_{10} reacts with tertiary alkylamines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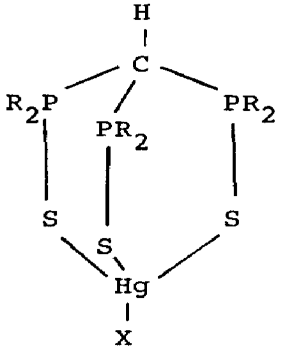
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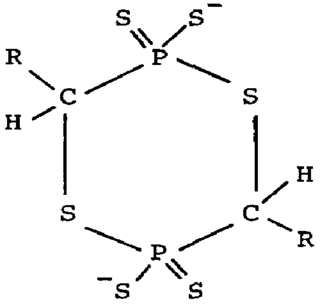
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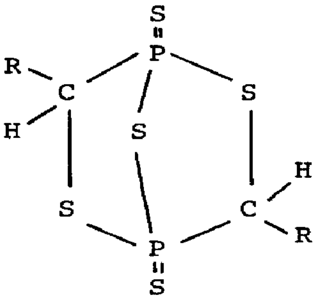

(224)

$(RCH_2)_3N$ to give dialkylammonium salts of the cyclic anion (223);[469] on hydrolysis in vacuum at ca. 190°C the compound with R = Pr^i loses di-i-butylamine and H_2S to give the novel bicycle (224). An X-ray structure shows terminal and bridging P-S distances of 1.92 and 2.11Å respectively with a P-S-P angle of 86.5°.

Electron diffraction, microwave and liquid crystal n.m.r. data have been analysed simultaneously to give the best refinement of the $PF_2H(S)$ parameters:[470]

r(P-F)	1.546(2)Å	F-P-F	99.1(1)°
r(P=S)	1.875(3)	F-P-S	117.2(2)
r(P-H)	1.419	H-P-S	116.4(6)

A crystal structure determination of $Ph_2P(S){\cdot}NH{\cdot}P(S)Ph_2$ with short P-S (1.915, 1.917Å) and long P-N bonds (1.652, 1.700Å) suggests that this formula represents the correct tautomer but the hydrogen atom could not be located.[471] The P-N-P angle is 131.7° and the P=S groups are trans relative to the P-N-P skeleton.

A number of gallium complexes, e.g. $Ga[S_2P(OR)_2]_3$ for R = Et, Pr, Pr^i, Bu and Bu^i, and $Ga[S_2P\overset{O}{\underset{O}{<}}{>}R]_3$ for R = $CH_2{\cdot}CEt_2{\cdot}CH_2$, $CMe_2{\cdot}CMe_2$ and $CMe_2{\cdot}CH_2{\cdot}CHMe$, have been prepared from $GaCl_3$ and an alkali metal salt of the ligand in benzene[472] and in two germanium compounds, $Ph_3GeS_2P(OMe)_2$ and $Ph_2Ge[S_2P(OMe)_2]_2$, the ligands are monodentate with the non-bonded sulphur atom twisted away from possible germanium interaction.[473] A multinuclear n.m.r. study of a series of organotin(IV) dialkyldithiophosphates in $CDCl_3$ solution points to tetrahedral coordination about tin in contrast to the five fold coordination suggested for the solid state by Mössbauer spectroscopy.[474]

The chelates in $Ni[S_2P(OPr^i)_2]_2$ are symmetrical with planar geometry about nickel,[475] while the neodymium complex $[Nd\{S_2P(OPr^i)_2\}_2(Bu_2SO)_3][Nd\{S_2P(OPr^i)_2\}_4]$ chelating ligands raise the coordination numbers of the metal in the cation and anion to seven and eight respectively.[476] Unidentate dithiophosphate, on the other hand, is present in $CpFe(CO)_2[SP(S)(OR)_2]$, obtained when $[CpFe(CO)_2]_2$ is treated with the disulphides, $[SP(S)(OR)_2]_2$ where R = Et or Pr^i.[477] The preparation and e.s.r. spectra are reported for a number of Fe(III), Ru(III) and Os(III) dithiophosphinates.[478]

Recent calculations point to the importance of low lying partially filled metal 3d orbitals in alkali metal intercalation into $FePS_3$ and other MPX_3 species.[479]

$ZnAgPS_4$ prepared from the elements at 700K has a structure based on close packed sulphur atoms with other atoms occupying tetrahedral sites,[480] but in $Cs_2P_2S_6$ and $K_2P_2S_6$ there are discrete $P_2S_6^{2-}$ anions, formed by edge sharing between two PS_4 tetrahedra.[481] The terminal and bridging distances are ca. 1.98

and 2.15Å with an angle of 87.1° at the bridging sulphur atoms for caesium and 85.9° for the potassium salt. A new hexathiohypophosphite, HfP_2S_6 obtained from the elements at 500-900°C is an isotype of TiP_2S_6 with a P-P distance of 2.253Å and P-S distances ranging between 1.965 and 2.067Å.[482]

Mass spectrometry and ^{31}P n.m.r. spectroscopy point to the formation of all members of the $P_{4-n}As_nSe_3$ series in the melt and vapour phase in mixtures of P_4Se_3 and As_4Se_3.[483] The ^{31}P n.m.r. shift of the apical atom, which occurs at 35.1 ppm in P_4Se_3, moves to 86.6 ppm in PAs_3Se_3 while the basal phosphorus atom shift varies between -107.5 ppm in P_4Se_3 and -60.1 ppm in the PAs_3Se_3 isomer with phosphorus atom in the basal triangle. Neutron diffraction has increased the precision of the Tl_3PSe_4 and Tl_3AsS_4 structures;[484] the compounds are potentially useful in acousto-optic devices.

Phosphorus in tris(2-furyl)phosphine selenide is in distorted tetrahedral coordination but the P-C and P-Se distances (1.778 and 2.094Å respectively) are shorter than normal and the C-P-C angles (103.4°) are small.[485] Tri(t-butyl)phosphine can be oxidised quantitatively by elemental selenium or tellurium to give $Bu^t_3PSe(Te)$, but while the corresponding arsine will give Bu^t_3AsSe there is no reaction with tellurium.[486] Complexes containing Bu^t_3PTe can be obtained as fairly air stable, dark red solids by photolysing mixtures of $M(CO)_6$ for M = Cr, Mo or W, and the tellurophosphorane;[487] the presence of a W-Te bond (2.875Å) was confirmed for $W(CO)_5[TePBu^t_3]$ by an X-ray structure.

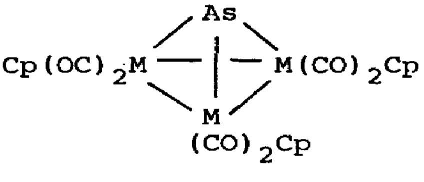
A novel ditellutophosphine, $(Me_3Si)_3CTeTePBu^t_2$, can be prepared when Bu^t_2PCl reacts with the substituted methylditelluride anion, $(Me_3Si)_3CTe_2^-$.[488]

5.3 ARSENIC

5.3.1 Arsenic, Polyarsines and Arsenides

X-ray quality crystals of the readily decomposable diarsene $(Me_3Si)_3CAs{=}AsC(SiMe_3)_3$ can be obtained by repeated chromoatographic separations on silica gel; the trans planar structure is the same as that in the phosphorus analogue and As-As distances in the two independent molecules are 2.245 and 2.243Å.[489]

The isolation of the M_3As cluster (225) from a reaction in which $[CpM(CO)_3]$, for M = Mo or W, was refluxed in xylene with elemental arsenic completes the M_nAs_{4-n} series of tetrahedral clusters,[490] and the versatility of As_2 as a ligand is shown in compounds (226)-(228) for M = Mo or W where it behaves as respectively a four π-electron donor, a six electron donor and an eight electron donor.[491] Compound (229), which can also be considered as containing As_2 as an eight electron donor, arises from reductive coupling of two $[Cp(CO)_2Mn]_2AsCl$ arsinidine units.



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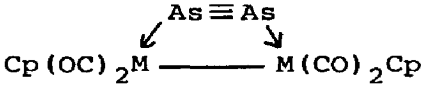

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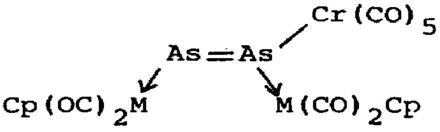

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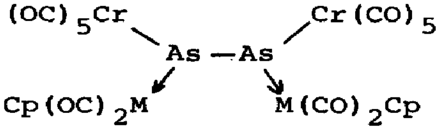

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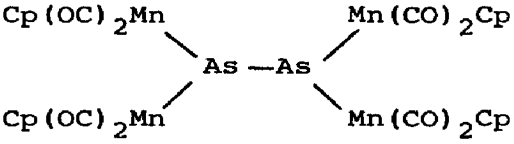
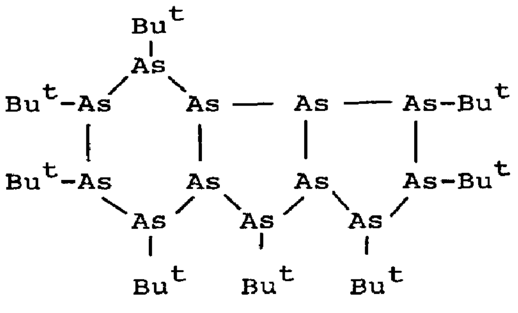


(229)

The As_6^{4-} and As_4^{2-} anions present in solutions of potassium-arsenic alloys in ethylenediamine solution have been characterised by EXAFS which indicates an equilibrium between hexagonal and square planar species.[492]

A new polyarsine, $As_{12}Bu^t_8$, obtained by the magnesium dehalogenation of a Bu^tAsCl_2-$AsCl_3$ mixture in THF has formula (230) on the basis of n.m.r. and mass spectrometric data.[493]

Five distinct solid phases have been identified in a study by X-ray diffraction, DSC and magnetic susceptibility of the MnAs-CrAs phase system.[494]



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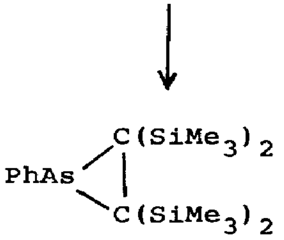
5.3.2 Bonds to Carbon

Methyl iodide quaternises only one of the arsenic atoms of $(Ph_2As)_2CH_2$ and the product on treatment with sodium amide in liquid ammonia gives the monoylid $MePh_2As{=}CHAsPh_2$.[495] Quaternisation at both arsenics can be achieved with methylfluorosulphate and the bis(arsonium) salt can be dehydrohalogenated to the carbodiarsorane $MePh_2As{=}C{=}AsPh_2Me$, stable at -40°C. A red, bis(methylene)arsorane (231) has been synthesised at low temperatures as shown in equation 43, but in contrast to the corresponding phosphorus compound it is unstable and rearranges

$$PhAsCl_2 + 3LiC(SiMe_3)_2Cl \rightarrow PhAs[{=}C(SiMe_3)_2]_2$$

(231)



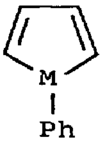
...(43)

(232)

to the isomeric arsirane (232).[496]

1-Phenyl substituted compounds (233), M = As or Sb) can be synthesised from reactions between $PhMCl_2$ and 1,4-dilithium butadiene; the arsenic compound is a light yellow oil, sensitive to oxygen but stable at room temperature under an inert atmosphere, but the antimony analogue is more labile, darkening at room temperature and forming a resin.[497]

Convenient, but low yield, methods have been devised for



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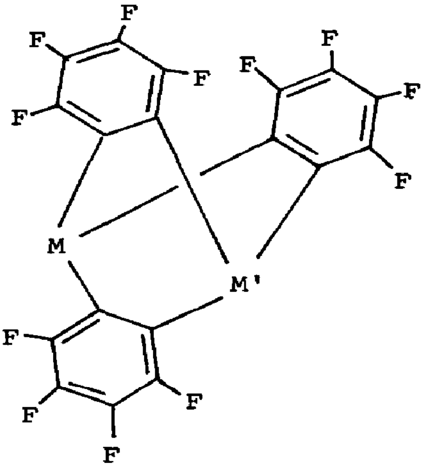

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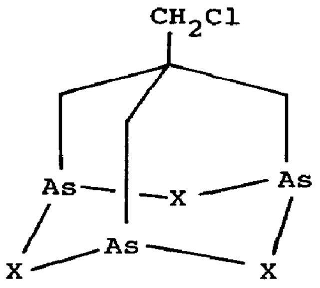
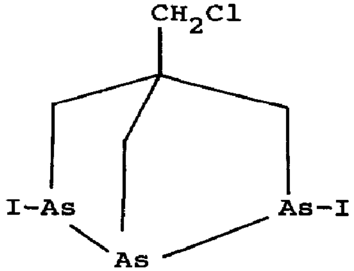


(235)

triptycenes (234) containing two different Group 5 elements.[498] In addition to products in which M = M' = P, As or Sb, compounds with M = P, M' = As or Sb and M = As, M' = Sb have been prepared in a stepwise process between $(C_6F_4Li)_3M$ and $M'Cl_3$.

Only three chlorines in $C(CH_2Cl)_4$ can be substituted by $NaAsPh_2$ groups to give $ClCH_2C(CH_2AsPh_2)_3$ which with anhydrous HI can be converted to $ClCH_2C(CH_2AsI_2)_3$.[499] Further reaction with H_2O or H_2S then leads to (235) with X = O or S respectively, while the iodide on reduction with sodium in THF yields (236) initially but in boiling THF the product is the nortricyclane (237).



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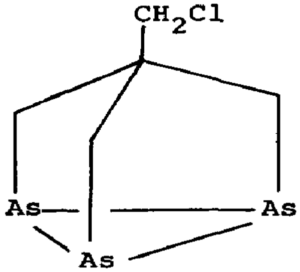
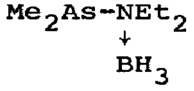


(237)

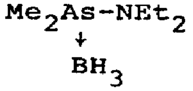
I.r. and Raman spectra of the 1:1 adducts of BX_3 (X = Cl, Br or I) with $MeAsH_2$[500] and Me_2AsH[501] have been analysed on the basis of C_s symmetry. Data are also available for $Me_3As.BX_3$.[502]

Me_2AsNEt_2 on reaction with BH_3.THF at -90°C yields comparable amounts of two new 1:1 addition compounds (238) and (239); on warming, (<u>239</u>) rearranges to (<u>238</u>) which then decomposes to



$\mathrm{Me_2As{-}}\underset{\displaystyle \mathrm{BH_3}}{\underset{\downarrow}{\mathrm{NEt_2}}}$

(<u>238</u>)



$\mathrm{Me_2}\underset{\displaystyle \mathrm{BH_3}}{\underset{\downarrow}{\mathrm{As}}}\mathrm{{-}NEt_2}$

(<u>239</u>)

$Me_2AsH.BH_3$, Et_2NBH_2 and $Et_2NB_2H_5$.[503] At elevated temperatures, bis(trifluoromethyl)nitroxyl, $(CF_3)_2NO$, reacts with $(CF_3)_2AsX$ (X = F or Cl) to give $(CF_3)_2NOAs(CF_3)X$ and $(CF_3)_2NOCF_3$, but with $(CF_3)_2AsBr$ bromine is displaced to give initially $(CF_3)_2NOAs(CF_3)_2$ which adds nitroxyl producing $[(CF_3)_2NO]_3As(CF_3)_2$.[504]

Structures showing coordination of silver by both arsenic and oxygen atoms of a coordinated nitrate group have been determined for the complexes $[Ag(AsPh_3)_nNO_3]$ where n = 1-3, obtained from stoichiometric amounts of $AgNO_3$ and Ph_3As in an acetone-acetonitrile mixture.[505] Two further compounds, $[Ag(AsPh_3)_4][SnPh_2(NO_3)_2X]$ where X = NO_3 or Cl, contain the unusual tetrahedral $[Ag(AsPh_3)_4]^+$ cation (Ag-As 2.643-2.700Å) and can be obtained from AgX in the presence of $Ph_2Sn(NO_3)_2$. Discrete tetrahedral monomers are present in $[Ag(AsPh_3)_3Cl].\frac{1}{2}$(acetone), obtained from Ph_3As and AgCl in an acetone-acetonitrile solvent mixture, while $AgNO_3$ and the diarsine, $Ph_2AsCH_2CH_2AsPh_2$, yield polymeric $(AgNO_3)_2[Ph_2AsCH_2CH_2AsPh_2]$.[506]

A series of platinum complexes PtL_4, where L = $P(OBu)_3$, $AsBu_3$, can be obtained from $Pt(cod)_2$,[507] and $PtMe_2(cod)$ reacts differently with the ligands $Ph_2MCH_2MPh_2$ depending on whether M = P or As.[508] For the former, the product is $PtMe_2(Ph_2PCH_2PPh_2)$ while the arsenic compound gives dinuclear $Me_2Pt[Ph_2AsCH_2AsPh_2]_2PtMe_2$.

A new open trinuclear cluster, capped with a μ_3-$AsBu^t$ group, has been prepared by heating $S(NAsBu^t_2)_2$ with $Os_3(CO)_{12}$.[509]

5.3.3 <u>Bonds to Halogens</u>

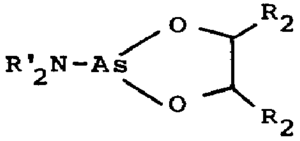
The anion in $[Ph_4P]_2[As_2Cl_8]$, obtained from either an $AsCl_3$-Ph_4PCl reaction or by treating As_2S_5 and Ph_4PCl with hydrogen chloride in dichloromethane, is centrosymmetric with two $AsCl_5$ pyramidal units sharing a common edge.[510] Bridging and terminal As-Cl distances are 2.746, 2.941 and 2.179-2.303Å respectively.

The heavier Group 5 trihalides, $AsCl_3$, $SbCl_3$, and $BiCl_3$ react with toluene-3,4-dithiol ($\equiv LH_2$) to give complexes of the type MClL, [Sb(LH)L], $Et_3NH[BiL_2]$ and $Ph_4P[SbL_3]$.[511] An X-ray structure for AsClL shows pyramidal geometry about arsenic (As-S 2.209, 2.226; As-Cl 2.236Å); the antimony compound is presumed to be similar but the bismuth derivative is probably polymeric. Attempts to remove the final proton in [SbL(LH)] by addition of base gave a purple antimony(V) anion $[SbL_3]^-$.

$As(OTeF_5)_5$ has been reprepared by reacting AsF_5 with $B(OTeF_5)_3$ in SO_2 and the compound shown to give $[As(OTeF_5)_6]^-$ with $CsOTeF_5$.[512]

5.3.4 Bonds to Oxygen

The +3 Oxidation State. Conformational changes in dialkylaminoarsolanes (240, R = H or Me, R' = Me, Et or Pr) as a function of solvent, concentration and temperature have been followed by ^1H



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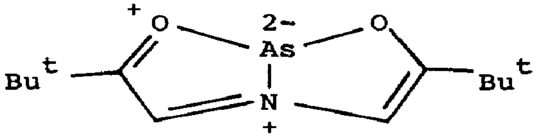
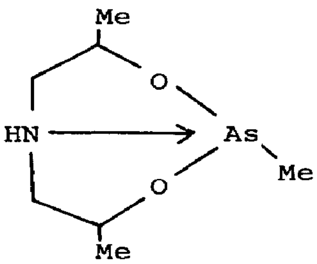


(241)

and ^{13}C n.m.r. spectroscopy.[513]

The bicyclic arsa-octadiene (241), prepared from $AsCl_3$ and the secondary amine $HN[CH_2CBu^t(O)]_2$, is a stable planar compound, similar to the previously prepared phosphorus analogue, representing a system where a 10 electron bonding scheme is preferred.[514] (For related antimony and bismuth compounds, see references 583 and 614.) Staudinger reactions of picryl and tosyl azides with the tetracoordinated arsatrane (242) leads to new arsinimines, still containing the N→As donor bond (243), which can then dimerise to cyclodiarsazanes (244).[515]

A new hydrogen diarsenite, $K_3HAs_2O_5.6H_2O$, has been isolated from a reaction between KOH and As_2O_3 in the presence of a limited amount of water.[516] The structure shows discrete $HAs_2O_5^{3-}$ ions based on corner sharing between two AsO_3 pseudo-tetrahedra in a semieclipsed conformation with one arsenic lone pair sym with respect to an As-O bond at the second arsenic. The mean bridging



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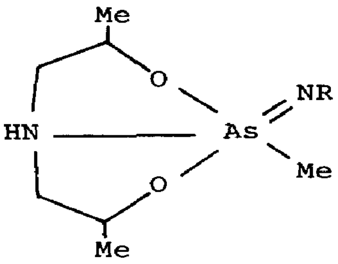

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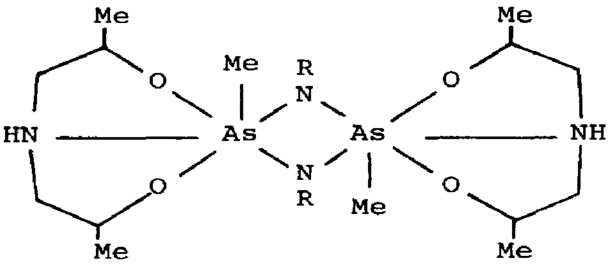
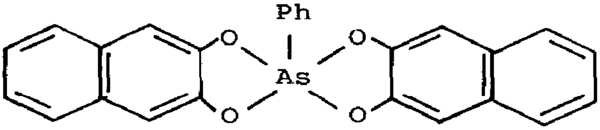


(244)

As-O distance is 1.83Å and terminal distances range between 1.722 and 1.775Å.

The +5 Oxidation State. Structures have been reported for a series (245)-(251) of five coordinate spiroarsoranes containing five membered rings to assess the effect of these groups on the deviation from trigonal bipyramidal geometry.[517,518] Structures



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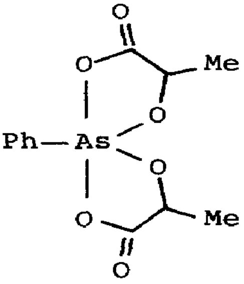

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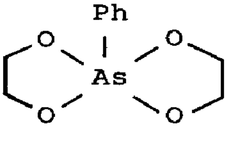

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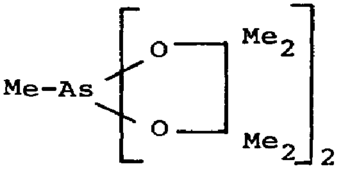

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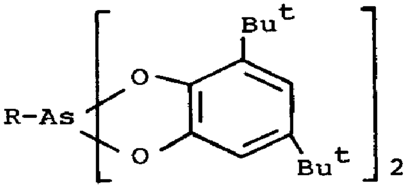
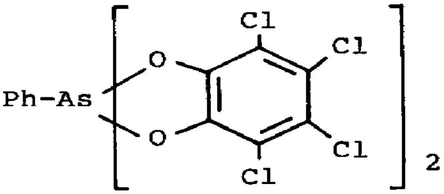


(249, R = Me, OH or Ph)



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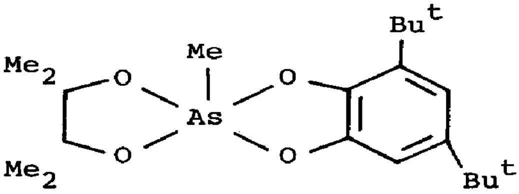
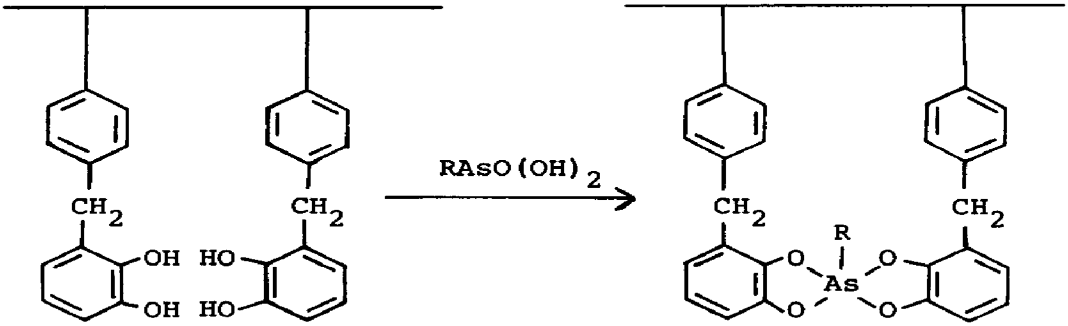


(251)

of (246), (248), and (249, R = Ph) show arsenic geometry close to trigonal bipyramidal while rectangular pyramidal geometry is observed in (245); intermediate character is shown by (247) and (249, R = OH), the latter a hydrogen bonded dimer.

Toxic arsonic and arsinic acids can be readily removed by reaction with pendant catechol groups attached to a polystyrene-divinyl benzene backbone as shown in equation 44.[519] Regeneration of the resin is then by hydrolysis with sodium carbonate solution.

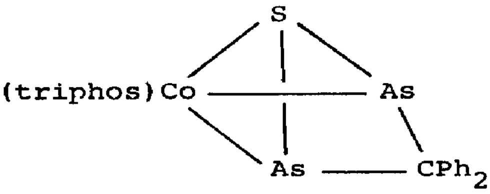


...(44)

$(NH_4)_2H_3(AsO_4)(SO_4)$, obtained from stoichiometric amounts of $(NH_4)_2SO_4$ and arsenic acid, shows ordered AsO_4 and SO_4 tetrahedral positions[520] and a metaarsenate, $Ca(AsO_3)_2$ obtained from mixtures of $CaCO_3$ and arsenic(III) oxide heated eventually to 500°C, is probably isostructural with $PbSb_2O_6$.[521]

5.3.5 Bonds to Sulphur, Selenium or Tellurium

According to X-ray diffraction, the AsS unit in $(Me_5C_5)_2Mo_2(AsS)S_2Co(CO)_2$, obtained from $Co_2(CO)_8$ and $[(Me_5C_5)_2Mo_2S_2As_2S]$ in toluene solution, behaves as a μ_2, η^2 ligand.[522] A series of new-dinuclear metal complexes containing coordinated As_2S and P_2S units have been synthesised by reactions of $[(triphos)Co(E_2S)]BF_4$ with either $[RhCl(cod)_2]$ or $Co(BF_4)_2$.[523] The complexes are formulated as $[(triphos)M(E_2S)M^1(triphos)][BF_4]_2$ and a triple decker sandwich structure has been found for the arsenic derivative with $M = M^1 =$ Rh. The As_2S ring in $[Co(As_2S)(triphos)]BF_4$ has been converted into a four membered thiodiarsete ring in (252) by treatment with a large excess of diphenyldiazomethane.[524]



(252)

Over a 24h period at room temperature, ethylenediamine and As_2S_3 deposit elemental arsenic and give crystals of $[enH_2]_3[As_2S_6]_6.6en$.[525] The anion contains a discrete chair shaped As_3S_3 ring with exocyclic sulphur atoms (As-S 2.15Å) in equatorial positions; the endocyclic As-S distances fall between 2.274 and 2.314Å. A second new anionic arsenic sulphide $As_8S_{13}^{2-}$ has been isolated as the cesium,[526] rubidium[527] and ammonium salts by reactions of As_2S_3 and aqueous alkali carbonate in sealed tubes at ca. 200°C. As shown in Figure 9, the anion in the cesium salt is polymeric, based on eight membered As_4S_4 rings, each connected by As-S-As bridges to three other rings. In the monohydrated Rb^+ and NH_4^+ salts which are isotypes, the anion is again polymeric but based here on As_3S_3 rings interconnected by

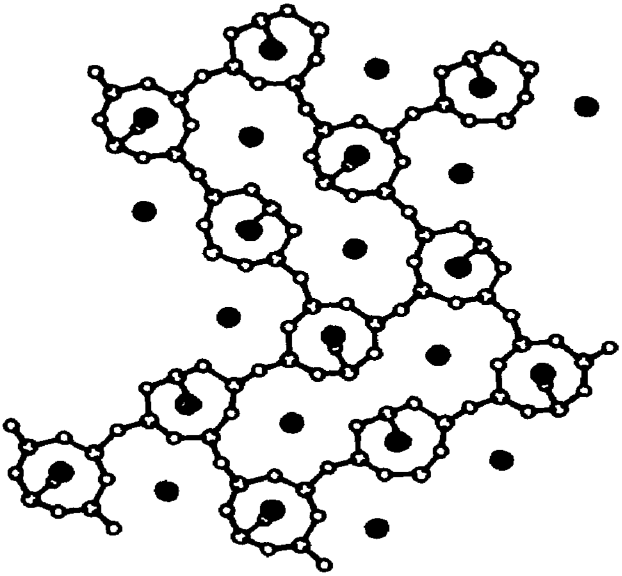
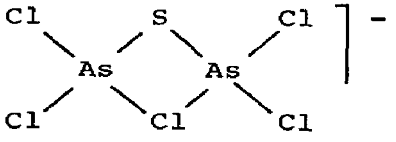


Figure 9. Anion Structure in $Cs_2As_8S_{13}$ (reproduced by permission from Z. Naturforsch., Teil B, 40(1985)571).

AsS_3 pyramids into a complex double chain.

In 1,2-dichloroethane solution, Ph_4PCl reacts with arsenic(III) sulphide and anhydrous hydrogen chloride to give crystals of $Ph_4P[As_2SCl_5]$ (253); addition of a further molecule of Ph_4PCl leads to $[Ph_4P]_2[As_2SCl_6]$ (254).[528] The overall structures can



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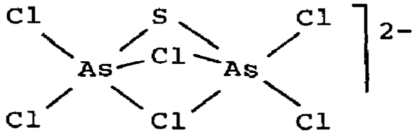


(254)

be described in terms of edge sharing between two distorted pseudo-trigonal bipyramids for (253) and face sharing between two pseudo-octahedral units in (254).

Structures have been determined for the heavier Group 5 tris(i-propylxanthates), $M[S_2COPr^i]_3$ for M = As, Sb or Bi.[529] The arsenic and antimony compounds are isostructural with asymmetrically chelating ligands (As-S 2.305 and 2.978Å, Sb-S 2.508 and 3.006Å) giving distorted octahedral geometry about each central atom. In the bismuth case, strong intermolecular interaction between the $Bi(S_2COPr^i)_3$ units leads to a chain structure in which bismuth is described as showing distorted capped trigonal prismatic geometry. Mixed chloride-xanthates, $PhMCl(S_2COR)$ where M = As or Sb and R = Me, Et, Pr or Pr^i, can be obtained either from reactions of $PhMCl_2$ and KS_2COR in CS_2 solution or by the reorganisation of 1:1 mixtures of $PhMCl_2$ and $PhM(S_2COR)_2$.[530]

$YbAs_4S_7$, $YbAs_2S_4$ and $Yb_3As_4S_9$ have recently been identified in the YbS-As_2S_3 system.[531]

From single crystal X-ray diffraction, $Ba_3(AsS_4)_2.7H_2O$ is obtained when As_2S_5 is treated with aqueous $Ba(SH)_2$; the compound contains isolated $AsS_4{}^{3-}$ ions with a mean As-S distance of 2.17Å and S-As-S angles falling in the range 105.2-112.8°.[532]

Arsenic atoms in As_2Se_3 are in seven-fold coordination to selenium giving a polyhedron described as face sharing between a tetragonal pyramid and a trigonal prism,[533] while As_2Te_3 contains arsenic atoms in both distorted octahedral and seven-fold coordination.[534]

Reaction between As_2Se_3 and strontium chloride in ethylenediamine gives a new orange complex $[Sren_4]_2[As_3Se_6]Cl$, which contains discrete chair shaped anions.[535]

Endocyclic As-Se distances lie between 2.398 and 2.424Å, the corresponding exocyclic distances are ca. 2.29Å.

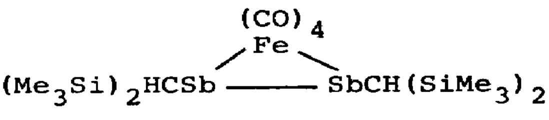
As_5Te_7I, prepared hydrothermally from HI and a stoichiometric mixture of arsenic and tellurium, contains like As_2Te_3, both six and seven coordinate arsenic atoms.[536] Three of the five arsenics are coordinated to six statistically distributed iodine and tellurium atoms.

5.4 ANTIMONY

5.4.1 Polystibines and Antimonides

Although it has not been possible to isolate free distibines, RSb=SbR, they can be stabilised in low oxidation state transition metal complexes such as (255), obtained when $Na_2[Fe(CO)_4]$ reacts with $(Me_3Si)_2CHSbCl_2$.[537] The stibinidine (256) is also produced and together with the cluster compound (257) is a product of the reaction of (255) with $Fe_2(CO)_9$. The Sb-Sb separation in (255) is 2.774Å, substantially shorter than that (2.837Å) in Ph_4Sb_2, supporting the view that a measure of π-bonding remains (see also ref. 548 for a second stabilised distibene).

The first cyclohexastibine, Ph_6Sb_6, isolated as a yellow dioxan



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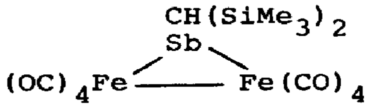

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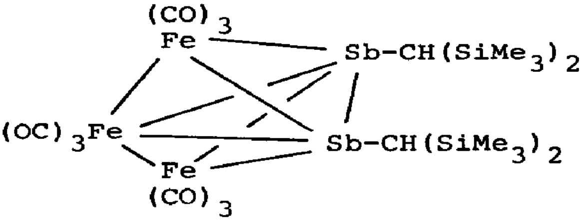


(257)

adduct from a solution of $PhSb(SiMe_3)_2$ in dioxan, is slowly oxidised in air at room temperature.[538] The ring with the chair conformation has equatorial phenyl groups; Sb-Sb distances are 2.84Å and the overall molecular symmetry is close to D_{3d}.

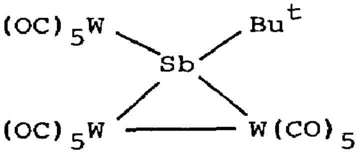
The technique of stabilising Zintl anions by using alkali metal cations complexed with cryptands has been applied in the formation of $[2,2,2\text{-crypt-K}]_2[Pb_2Sb_2]$.en, which is isostructural with $[Sn_2Bi_2]^{2-}$.[539] There is a difference, however, as the Pb-Sb anion is only partially disordered, with lead occupancies ranging between 27 and 67%.

A number of new binary and ternary antimonides, usually prepared from the elements at high temperature, have been isolated during 1985. Among these are: Ba_2Sb_3[540] (an isotype of Sr_2Sb_3 and containing discrete Sb_6^{8-} anions); Ba_3GaSb_3,[541] Ca_3GaAs_3 and Ca_3InP_3 (the antimony compound contains isolated Ga_2Sb_6 groups formed by edge sharing between two distorted $GaSb_4$ tetrahedra); $Ca_5Ga_2Sb_6$,[542] $Ca_5In_2Sb_6$ and $Sr_5In_2Sb_6$ (with structures containing strings of fused 10 membered rings); $Ca_{11}InSb_9$[543] (containing Sb^{3-}, Sb_2^{4-} and isolated $InSb_4^{9-}$ anions); $LaZn_{0.52}Sb_2$,[544] $LaCo_{0.68}Sb_2$, $LaMn_xSb_2$ ($0.65 \le x \le 0.76$) and $LaCu_xSb_2$ ($0.82 \le x \le 0.87$), (compounds show the tetragonal $CaMnBi_2$ structure).

5.4.2 Bonds to Carbon

Organo-antimony chemistry for 1983 has been reviewed.[545]

Reactions between $(Bu^tSb)_4$ and $Fe(CO)_5$ in a sealed tube at 403K give $[Fe(CO)_4(SbBu^t_3)]$, a trigonal bipyramidal molecule with antimony in an axial position (Sb-Fe 2.547Å, $Sb\text{-}Fe\text{-}C_{axial}$ 175.9°).[546] Reactions of Bu^tSbCl_2 with $Na[M(CO)_3Cp]$ (M = Mo or W)[547] or $Na_2W_2(CO)_{10}$[548] give stibinidene products, in the first case via $Cp(CO)_3MSbBu^tCl$ which disproportionates in solution to give the antimony bridged species $[Cp(CO)_3M]_2SbBu^t$. A similar product is obtained with $Na_2W_2(CO)_{10}$, i.e. $[(OC)_5W]_2SbBu^t$ which has Lewis acid character and can be converted into $[W(CO)_5]_3SbBu^t$ (258).[548] A stabilised distibene complex (259) has been isolated from a related reaction between Bu^tSbCl_2 and $Na_2Cr_2(CO)_{10}$.



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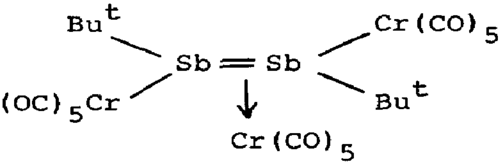
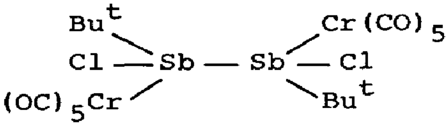


(259)

By contrast, in the presence of zinc metal, this reaction leads via reductive coupling to the distibine complex (260).[549] Similar compounds (261) and (262) are found in reactions of $RSbCl_2$ (R = Me, Bu^t or Ph) with $Cp(CO)_2Mn$ and $Cp(CO)_2FeSbBr_2$ with $Na_2Cr_2(CO)_{10}$ respectively.



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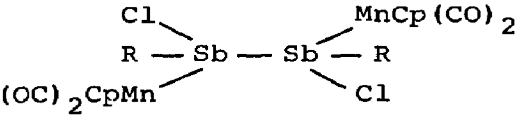

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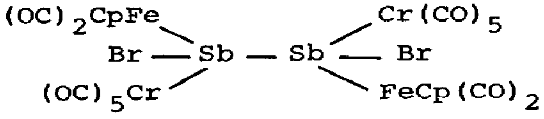
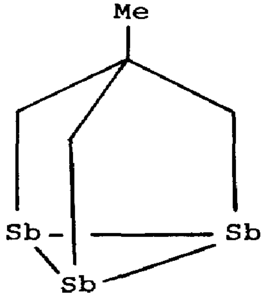


(262)

An unusual dimeric antimony(V) oxide, $(Ph_2SbBrO)_2$, soluble in a range of organic solvents can be isolated by oxidation of

Ph_2SbBr in dichloromethane solution with atmospheric oxygen or, better, with t-butylhydroperoxide.[550] The structure is based on two trigonal bipyramidally coordinated antimony atoms sharing axial and equatorial positions.

In liquid ammonia solution, Ph_2SbNa reacts with $MeC(CH_2Cl)_3$ to give Ph_4Sb_2, but with the bromide, $MeC(CH_2Br)_3$ the product is a mixture of the distibine and $MeC(CH_2SbPh_2)_3$.[551] As with the phosphorus and arsenic analogues, the latter reacts with gaseous hydrogen chloride giving $MeC(CH_2SbCl_2)_3$ and the cyclotristibine (263) can be obtained on reduction with sodium in THF. The tristibine which has C_s symmetry forms complexes with $M(CO)_5.THF$ (M = Cr, Mo or W).[552] The chelate (264) is formed when



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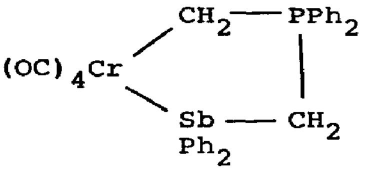


(264)

$Ph_2PCH_2SbPh_2$ reacts with the sulphur ylid complex $(OC)_5Cr[CH_2S(O)Me_2]$ but reaction with $Ph_2SbCH_2SbPh_2$ gives $(OC)_4Cr[Ph_2SbCH_2SbPh_2]$.[553]

Difficulties have been experienced in preparing 1,6-distibatriptycene, although compounds containing halogen substituents on the rings [see (234)] are well known. The compound has now been isolated albeit in low yield by pyrolysis of an antimony-o-phenylene-mercury trimer mixture at 260°C.[554] Oxidation of $(C_6F_5)_3Sb$ with ICl, IBr, thiocyanogen and sulphur gives the expected products, and $(C_6F_5)_3SbX_2$, where X = NCS or NCO, can be prepared by metathesis reactions between $(C_6F_5)_3SbCl_2$ and either AgSCN or KNCO.[555] An oxygen bridged compound $[(C_6F_5)_3SbN_3]_2O$ is the product from $(C_6F_5)_3SbCl_2$ and sodium azide in water.

Reactions of Ph_3SbBr_2 with a range of potentially bidentate ligands, including the acetylacetone, 8-hydroxyquinoline, salicylaldehyde, o-hydroxyacetophenone and 2-hydroxy-1-naphthaldehyde anions, give products of the type $Ph_3Sb(OMe)L$ when the solvent is a benzene-methanol mixture.[556] The compounds are monomers suggesting that the anions are bidentate giving octahedral coordination about the central antimony.

Treatment of Ph_4SbOH with the appropriate sulphonic acid in methanol gives sulphonates Ph_4SbO_3SR, where R = Ph, Me, CF_3, CH_2CH_2OH, 4-MeC_6H_4 and 2,4-$(NO_2)_2C_6H_3$.[557] An X-ray structure for $Ph_4SbO_3SPh.H_2O$ shows that the sulphonate is unidentate giving distorted trigonal bipyramidal coordination about antimony. The "long" Sb-O bond (2.506Å) suggests substantial ionic character. The structure of $[Ph_3SbOSO_2(CH_2)_2OH]_2O$, recently obtained from a sulphonic acid reaction with Ph_3SbO, contains a linear Sb-O-Sb system and antimony again in trigonal bipyramidal coordination with a unidentate sulphonate group and the bridging oxygen in axial positions.[558]

By analogy with the ethanol reaction, Ph_3SbO with 2-methylaminoethanol would be expected to yield $Ph_3Sb(OCH_2CH_2NHMe)_2$ but the product is the bridged species $MeHNCH_2CH_2OSbPh_2(OH)$-$OSbPh_2(OH)OCH_2CH_2NHMe$[559] arising from loss of one phenyl per antimony.

5.4.3 Bonds to Halogens

The hydrated fluoride, $MnF_2.2SbF_3.6H_2O$, which readily loses water to a dihydrate, can be obtained from mixtures of the components in aqueous HF.[560] A second (β) form of the complex $6SbF_3.5SbF_5$ results when $SbF_3.SbF_5$ is reduced by PF_3 in AsF_3.[561] The compound is one of a series based on a complex antimony(III) cation and the SbF_6^- anion. The cation here is $Sb_6F_{15}^{5+}$, composed of strongly interacting $Sb_2F_5^+$ and SbF_2^+ units.

The SbF_6^-, previously known to coordinate only to SbF_5 and Me^+ has been shown to be weakly coordinated to the metal in both $W(CO)_3(NO)(Me_3P)SbF_6$[562] and a (meso-tetraporphinato)iron(III) complex,[563] recently examined by X-ray diffraction. In the latter the Fe-F distance is 2.105Å and the Fe-F-Sb angle 150.4°.

Two series of compounds $BiF_5(SbF_5)_n$, where n = 1.5, 2 or 3, and $(BiF_5)_nSbF_5$, where n = 1, 1.5, 2, 3 or 20.6, have been identified in a reinvestigation of the SbF_5-BiF_5 system in liquid tungsten hexafluoride as solvent.[564] The $BiF_5.(SbF_5)_n$ compounds are isomorphous with $(NbF_5)_4$ and probably consist of disordered tetramers while disordered trans bridged polymeric structures equivalent to that of BiF_5 itself are suggested for the

$(BiF_5)_nSbF_5$ products.

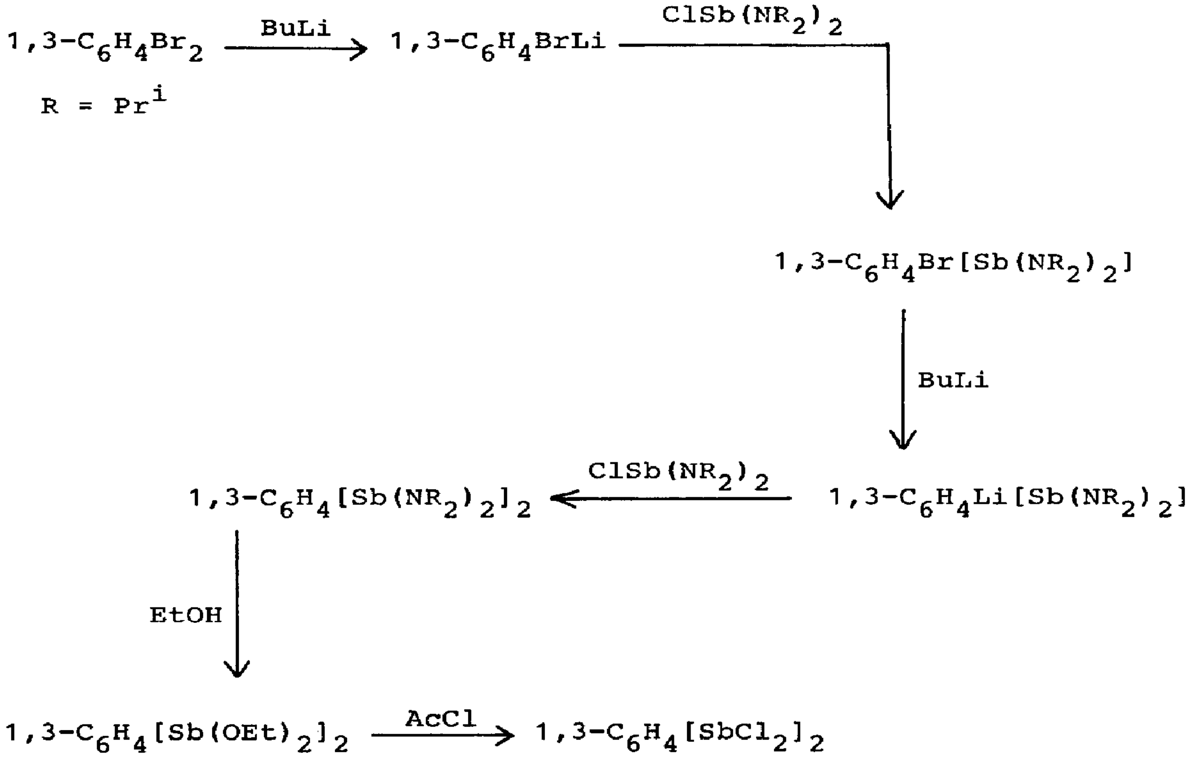
1:2 adducts are formed in the pyrene-$SbCl_3$ and phenanthrene-$SbBr_3$ systems.[565] In the former, antimony atoms lie on different sides of the hydrocarbon with 3.284Å being the closest Sb...C contact. Both antimonys lie on the same side of the phenanthrene molecule in the second product and bonding involves interaction between the aromatic π-system and the antimony atom (3.15-3.23Å). In both structures there are a number of Sb-halogen contacts that are well within the van der Waals radii. Benzo[b]thiophene and 2,2'-dithienyl both also give 1:2 complexes where the antimony atoms are, respectively, 3.25 and 3.16Å from the aromatic rings.[566]

I.r. and n.m.r. spectroscopic data suggest similar structures for the 1:1 addition compounds of $SbCl_3$ with a series of N,N'-disubstituted dithiomalonamides $RHNC(S)CH_2C(S)NHR$, for R = Me, Et, Pr^i, Bu or cyclohexyl.[567] In the ethyl compound, the antimony is attached to both sulphur atoms of the ligand (2.66 and 2.74Å) in addition to the three chlorines (at 2.344, 2.580 and 2.576Å). Preparation and structure determinations for the toluene-3,4-dithiol complexes SbClL and $Ph_4P[SbL_3]$ have already been mentioned.[511] In the $SbCl_3.2L$ adducts with two azolethiones, primary coordination gives a tetragonal pyramidal arrangement about antimony but with 3-methylbenzthiazole-2-thione the chlorines occupy fac positions while they are in a mer arrangement with 3-methylimidazole-2-thione.[568] The compounds are in fact dimeric in the solid state and the structural differences arise as a consequence of the different secondary bonds in the crystals.

Slow evaporation of aqueous solutions of Me_3NHCl and $SbCl_3$ give crystals of $(Me_3NH)_3Sb_2Cl_9$ which contain polymeric anions based on three independent antimony atoms.[569] Each antimony is in distorted octahedral coordination forming three short (2.401-2.473Å) and three long (2.883-3.316Å) antimony-chlorine contacts.

Chlorine and antimony n.q.r. data for $Ph_2NH_2Cl.SbCl_3$ show a phase transition at 108K; the ^{35}Cl lines disappear above ca. 275K although antimony lines can be seen at room temperature suggesting that there is cation motion at room temperature and/or reorientation of the $SbCl_3$ group.[570]

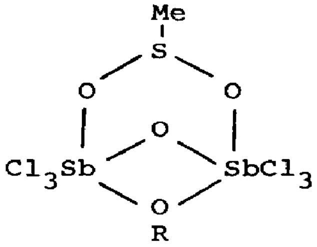
1,3-Phenylene bis(dichlorostibine) has been synthesised as shown in Scheme 8; the related 1,4-analogue can be obtained similarly.[571]



Scheme 8

Powder neutron diffraction[572] and phonon[573] spectroscopy (inelastic neutron scattering) have been used to investigate a series of mixed valence compounds $A_2M(III)_{0.5}Sb(V)_{0.5}X_6$ where A = Rb or Cs, M = Sb, Bi, In, Tl, Fe or Rh and X = Cl or Br. Five of the compounds, A = Cs, M = Sb, Bi or Tl, X = Cl and A = Rb or Cs, M = Sb, X = Br, show a superlattice ordering of the SbX_6^- and MX_6^{3-} units (space group $I4_1/amd$) while the remainder are disordered (space group Fm3m). Order or disorder correlates with the average M(III) M(V)-X bond length with those greater than 2.478Å being ordered and those less than 2.448Å being disordered. As the M(V)-X bond lengths are essentially constant in the current series, the controlling factor appears to be the difference in size between the $M(III)X_6^{3-}$ and SbX_6^- ions.

The structure of $HSbCl_6.4\frac{1}{2}H_2O$, obtained from concentrated solutions of the acid, contains pairs of asymmetrically coordinated, strongly hydrogen bonded, $H_5O_2^+$ ions bridged by water molecules (O-H...O 2.682Å) to give centrosymmetric six membered rings.[574] Two new bridged basic antimony(V) chlorides, (265) and (266) have been isolated from reactions of water-alcohol adducts of $SbCl_5$ and either methane sulphinic acid or methane sulphonic acid.[575] An alternative preparative method is the reaction of $SbCl_5.H_2O.ROH$ with the tetrachloroantimony derivatives $[SbCl_4.O_2SMe]_2$ or $[SbCl_4.O_3SMe]_2$.



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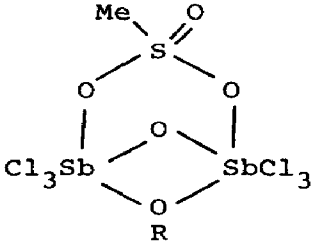


(266)

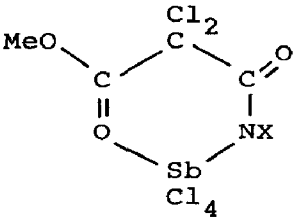
The dimethylsulphoxide adduct with $SbCl_5$ is statistically disordered with two positions for oxygen and sulphur; the Sb-Cl bond trans to coordinated oxygen is shorter (2.29Å) than the remainder (mean 2.36Å).[576] A series of 1:2 adducts, behaving as 1:1 electrolytes in DMF solution, has been obtained from $SbCl_5$ and a number of Schiff bases[577] and the $SbCl_5$ adducts with a number of chloro- and amino-benzonitriles show weak i.r. and Raman bands at ca. 215 cm^{-1} assigned to Sb-N stretching.[578]

5.4.4 Bonds to Nitrogen

The amine substituted antimony(III) compound, $MeSb[N(SiMe_3)_2]_2$, is the surprising product from a reaction between $SbCl_3$ and three mols of $Na[N(SiMe_3)_2]$ in benzene solution; in addition the reaction produces Me_3SiCl and $+SiMe_2-N(SiMe_3)+$oligomers.[579] The monomeric product can be oxidised by sulphuryl chloride to trigonal bipyramidal $MeSbCl_2[N(SiMe_3)_2]_2$. Chlorine atoms occupy axial positions (2.469Å) and Sb-C and Sb-N distances are 2.116 and 1.991Å respectively. Mass spectra have been reported for Cl_2SbNMe_2, $ClSb(NMe_2)_2$, $Sb(NMe_2)_3$, $Sb(NEt_2)_3$ and $ClSb(OMe)NMe_2$.[580]

Me_2SbN_3 and Et_2SbN_3, which are monomeric in benzene, have been prepared from silver azide and the corresponding antimony bromide in ether solution.[581] In the solid state the antimony atoms in the methyl compound are linked into zig-zag chains via the α-nitrogen atoms with Sb-N distances of 2.32 and 2.43Å. In the related bismuth compound, which has the same structure, the metal-nitrogen distances are equal.

New cyclic Sb(V)-N compounds can be obtained by the oxidative addition of N-chloroamides to antimony(III) chloride (267, X = H or Cl) or by thermolysis of mixtures of $SbCl_5$ with N-silylated amides (268).[582]



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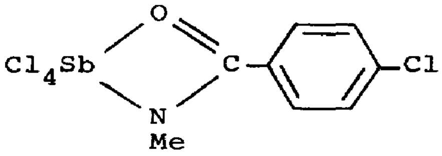

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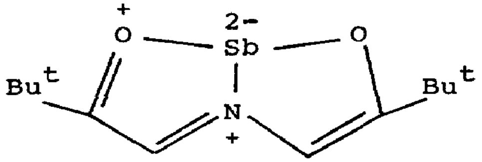

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5.4.5 Bonds to Oxygen

Like the previously reported phosphorus and arsenic[514] analogues, compound (269) is planar, showing thermochromism at the melting point; it is thermally stable but reacts with water and oxygen.[583] The complex cation in $[(\text{catecholato})Sb(1,10\text{-phen})_2]^+[BF_4]^-$, obtained from $[(C_6H_4O_2)SbCl.\text{phen}]$, $NaBH_4$ and 1,10-phen in methanol, contains three chelating ligands with Sb-O distances of 2.023 and 2.020Å and relatively long Sb-N distances (2.426/2.694 and 2.467/2.592Å).[584] The ligands are effectively located in only half of the coordination sphere with obvious space to accommodate the antimony lone pair . Some confirmation of the presence of an active lone pair comes from the relatively large, positive values for eQV_{zz} from the Mössbauer spectrum.

Stoichiometric compounds, $LaSb_3O_6$ and $LaSbO_3$, together with variable composition phases, $2La_2O_3.xSb_2O_3$ where $3 \leq x \leq 4$ have been observed in the sub-solidus region of the La_2O_3-Sb_2O_3 system.[585] The thermal stabilities of $LnSbO_3$ (Ln = La, Pr or Nd)[586] and X-ray powder data for $LnSb_5O_{12}$ (Ln = La - Lu)[587] have been reported.

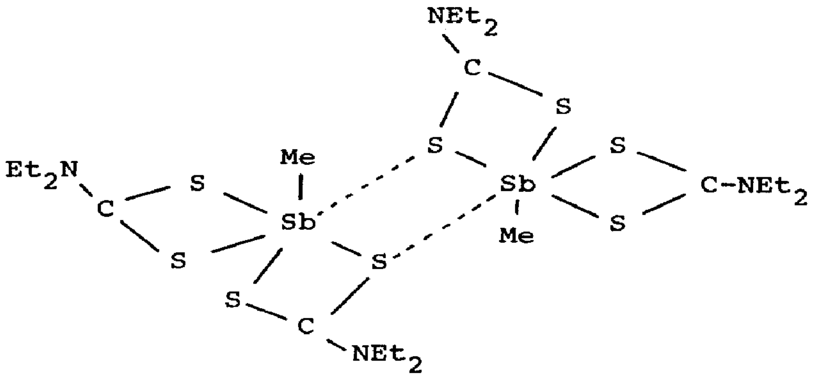
An unusual mixed oxide halide, Sb_3TeO_6Cl, isolated from a mixture of TeO_2 and Sb_2O_3 in concentrated hydrochloric acid, has a layer structure based on infinite two dimensional $(Sb_3TeO_6)_n^+$ units perpendicular to the c axis separated by chloride ions.[588] It was not possible to distinguish between the antimony and tellurium atoms. The α→β phase transition of Sb_2O_4 is lowered from 935 to 850°C in the presence of molybdenum trioxide with molybdenum dissolving into the β-phase.[589] EXAFS and Raman data are interpreted in terms of interstitial molybdenum occupying channels of high electron density from the antimony(III) lone pairs. Reaction of α-Sb_2O_4 with manganese at 950°C gives $MnSb_2O_4$ with the $ZnSb_2O_4$ structure.[590]

Two non-stoichiometric vanadium antimonate samples, obtained by calcining an Sb_2O_3/V_2O_5 mixture in respectively air and oxygen-free nitrogen, have been examined by ^{121}Sb Mössbauer spectroscopy and magnetic susceptibility measurements and can be formulated as respectively $V(IV)_{0.89}Sb(V)_{0.89}O_4$ and oxygen deficient $V(III)_{0.72}V(V)_{0.28}Sb(V)_{0.72}O_{3.58}$.[591] Two new mixed antimony-tellurium oxides, $Sb_2Te_2O_9$ and Sb_2TeO_7, with tellurium in the +4 oxidation state have been obtained by heating mixtures of TeO_3 with either Sb_2O_3 or Sb_2O_5.[592]

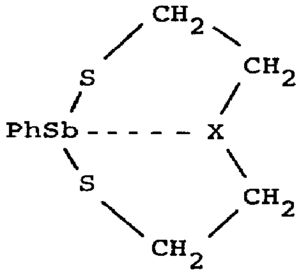
Selectivity sequences have been determined for the alkaline earth metals and transition metals in the +2 oxidation state on tin(IV) antimonate, an inorganic ion exchanger.[593]

5.4.6 Bonds to Sulphur, Selenium or Tellurium

Dithiocarbamates, $MeSb(S_2CNR_2)_2$, R = Me or Et, RR = $(CH_2CH_2)_2O$, can be prepared from $MeSbBr_2$ and NaS_2CNR_2 in methanol at -78°C;[594] in the diethyl derivative the ligands are asymmetrically bonded (Sb-S 2.554/2.960 and 2.538/2.904Å) but there are short intermolecular Sb-S contacts (3.847Å) giving dimers (<u>270</u>) in the solid state. Chelation in the pyrrolidine dithiocarbamate, $ISb[S_2CN\text{-pyrrolidine}]_2$, is less asymmetric (Sb-S 2.521/2.665 and 2.502/2.697Å) but here Sb-I bridges give a chain structure and there is probably no active antimony lone pair.[595] A redetermination of the $Sb(S_2COEt)_3$ structure shows three short (2.511Å) and



(270)



(271)

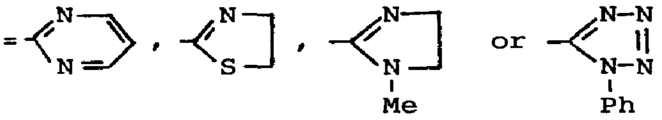
three long (3.002Å) Sb-S distances and a structure isomorphous with the arsenic analogue.[596] In $Sb(S_2COEt)(oxin)_2$ obtained from $Sb(S_2COEt)_2Br$ and potassium oxinate, antimony is in pentagonal pyramidal coordination; two sulphur atoms, an oxygen and nitrogen of one oxine group and a nitrogen of the second oxine form an approximately pentagonal plane with the oxygen of the second oxine occupying the apical position. Asymmetric coordination in $Sb(S_2COPr^i)_3$[529] and the preparation of $PhSb(S_2COR)_2$[530] have been mentioned earlier.

Oxadithia- and trithiastibocanes (271, X = O or S) have been prepared from $PhSbCl_2$ and $X(CH_2CH_2SH)_2$; in the oxygen compound, the Sb...O transannular interaction is 2.94Å with chair-chair conformations but for X = S, interactions in the two independent molecules are 3.31 and 3.36Å with a boat-chair ring conformation.[597] In each case there are Sb...S intermolecular contacts raising the antimony coordination numbers to, respectively, five and six (for the bismuth analogues, see ref. 623).

New antimony and bismuth dithiolates have been synthesised, see equation 45, and examined by ^{1}H n.m.r. spectroscopy.[598]

$$RSb(OEt)_2 + 2R'SH \rightarrow RSb(SR')_2 + 2EtOH \qquad \ldots(45)$$

R = Me or Ph R' =

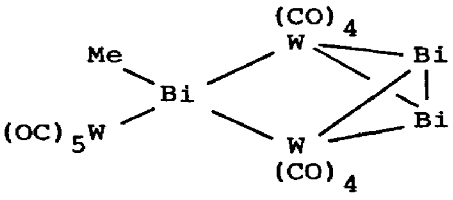


The Sb_2Se_3 structure has been redetermined as being isostructural with Sb_2S_3 and Bi_2Se_3 with antimony atoms in both six and seven fold coordination.[599] $SnSb_2S_4$ and $SnSb_2Se_4$ are isostructural consisting of ribbons of edge sharing $MS(Se)_5$ polyhedra; the tin and antimony atoms are randomly distributed over the available metal sites.[600]

A new antimony selenide complex, $[CpFe(CO)_2(Se{=}SbMe_3)]BF_4$, was isolated by displacing the THF in $[CpFe(CO)_2(THF)]BF_4$ by Me_3SbSe_2.[601] Two ternaries, $TlSbFe_2$ and Tl_9SbTe_6 have been observed but there is no confirmation of $TeSbTe_3$ previously reported as forming in the Tl-Sb-Te system.[602]

5.5 BISMUTH

Bi_2 units behaving as η^2 groups are present in two compounds obtained when $(Me_3Si)_2CHBiCl_2$ is treated with $Na_2[W(CO)_5]$ in THF solution.[603] One compound, the previously known $\{[W(CO)_5]_3(\mu_3\text{-}\eta^2\text{-}Bi_2)\}$, contains Bi_2 behaving as a six electron donor while in the new compound (<u>272</u>), it is a four electron donor. The Bi-Bi distance, 2.795Å, implies a high degree of double bond character.



(<u>272</u>)

Reaction of $Et_4N[BiFe_3(CO)_{10}]$ either under pressure with carbon monoxide or with Ph_3P in dichloromethane solution gives a mixed Zintl-metal carbonyl cluster, $(Et_4N)_2[Bi_4Fe_4(CO)_{13}]$.[604] Central to the structure is a Bi_4 tetrahedron with three faces capped by $Fe(CO)_3$ units; the fourth iron atom is associated with an $Fe(CO)_4$ unit bonded to the apical bismuth atom. X-ray diffraction has identified the product of the complex reaction of $NaBiO_3$ and $Fe(CO)_5$ in methanolic KOH as $Bi_2Fe_3(CO)_9$ and not $Bi_2Fe_5(CO)_{20}$ as previously reported.[605] The structure is disordered but contains a trigonal bipyramidal Bi_2Fe_3 core with bismuth atoms in apical positions; each iron carries three terminal CO groups.

A review of organo-bismuth chemistry for 1983 has been published.[606] Alkyl halides react with Me_2BiNa to give a series of triorganobismuths, Me_2BiR for R = Et, Pr, Bu, Pr^i, and allyl, while with dichloromethane the product is $Me_2BiCH_2BiMe_2$.[607] The corresponding aryl substituted compounds were also prepared and although the latter are more stable, both types of compound reorganise to Me_3Bi-$MeBiR_2$ mixtures.

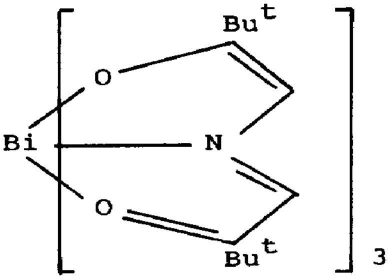
The anion in $[Et_2NH_2][BiCl_4]$ is polymeric with $BiCl_6$ octahedra sharing cis edges; each bismuth forms two short terminal bonds (2.493 and 2.559Å) and four longer Bi-Cl bridging bonds (2.688, 2.747, 2.917 and 3.007Å).[608] Hydrogen bonding to the cation accounts for the longer bonds, which is also a factor in the $[Et_2NH_2]_3[BiBr_6]$ structure. Here bismuth lies on a three fold axis with Bi-Br distances of 2.749 and 3.006Å;[609] the anion bond angles do not support stereochemical activity of the lone pair of electrons.

Among the new bismuth(III) halide complexes with 1,10-phenanthroline (≡L), 2-pyridinecarboxaldehyde-2-pyridyl hydrazone (≡L') and diphenylphosphynoethane (≡L") are $BiCl_3.L_{1.33}$ (possibly formulated as $[BiCl_2L_2]_2[BiCl_5]$) $BiBr_3.L$, $BiI_3.L$, BiX_3L' and $BiX_3.L"$ (X = Cl, Br or I).[610]

Ternary iodides recently isolated include $3RbI.2BiI_3$,[611] $BaBiI_5$,[612] $AgBiI_4$[613] and Ag_3BiI_6.

Hydrazoic acid in ether reacts with $Me_2Bi[N(SiMe_3)_2]$ to give Me_2BiN_3 with a polymeric structure similar to that of the antimony analogue.[581]

Bismuth(III) chloride is reduced to metallic bismuth and the complex (<u>273</u>) on reaction with the secondary amine $HN[CH_2CBu^t(:O)]_2$ in the presence of triethylamine.[614] Coordination about bismuth is tricapped trigonal prismatic with oxygen atoms at the corners (Bi-O 2.51Å) and nitrogens at the capping positions (Bi-N 2.54Å). (For related arsenic and antimony



(273)

compounds, see refs. 514 and 583).

The $Bi(NO_3)_3.5H_2O$ structure, recently redetermined, shows substantial differences from the earlier measurement in that the central atom is in 10-fold coordination to four water molecules, oxygens from two almost symmetrically chelating nitrates and one asymmetrically chelating group.[615] The fifth water molecule is hydrogen bonded to two of the coordinated waters. A proton n.m.r. study of the Bi^{3+}-OH^- system in acetone-water at low temperatures in agreement with X-ray data confirms the stoichiometry of the basic complex as $[Bi_6O_4(OH)_4]^{6+}$ rather than $[Bi_6(OH)_{12}]^{6+}$.[616]

The structure of Bi_3ReO_8 (prepared from Re_2O_7 and Bi_2O_3 at high temperatures) is related to the fluorite structure from a combination of single crystal X-ray and powder neutron diffraction data.[617] The perovskite-related $Ba_2Bi_2O_6$,[618] two new sillenite type phases, $Bi_{11.5}Fe_{14.5}O_{39}$ and $Bi_{9.5}Co_{16.5}O_{38}$[619] and the oxide chlorides[620] $Bi_{24}O_{31}Cl_{10}$, Bi_3O_4Cl and $Bi_{12}O_{17}Cl_2$ have been reported.

$NaBiO_3.2H_2O$ loses water molecules successively at 177 and 267°C while oxygen loss begins at 345°C to give the metastable δ-form of bismuth oxide ($Bi_2O_{3.33}$) and finally α-Bi_2O_3.[621]

Novel iron-bismuth compounds result by treating $[Cp(CO)_2Fe]_2$ with either $RBi[S_2CNEt_2]_2$ or $RBi[S_2COMe]_2$ (R = Me or Ph) in refluxing benzene.[622] Carbon monoxide is not substituted but either ethane or biphenyl is eliminated and the products are $Cp(CO)_2FeBi[S_2CNEt_2]_2$ and $Cp(CO)_2FeBi[S_2COMe]_2$. The former contains a five coordinate bismuth atom with bonds to iron (2.641Å) and sulphur atoms of two chelating ligands (2.713/2.997 and 2.719/3.000Å); in addition there is a Bi...S intermolecular contact at 3.467Å. The structure of $Bi[S_2COPr^i]_3$ has been discussed previously.[529]

Oxadithia- and trithiabismocanes, analogous to the antimony compounds (<u>271</u>),[597] can be obtained from $RBi(OEt)_2$ and the dithiols $X(CH_2CH_2SH)_2$ where X = O or S.[623] The ring in the R = Ph and X = O product has a chair-chair conformation and, in addition to bonds to phenyl, two sulphur atoms (2.560, 2.602Å) and the transannular Bi-O contact (2.97Å), there are intermolecular Bi...S contacts at 3.440 and 3.509Å.

Quantitative yields of the tellurobismuthine, (p-tolyl)TeBiBu$_2$, the first of a new class of compounds, are obtained by redistribution of equimolar quantities of (p-tolyl)$_2$Te$_2$ and Bu_4Bi_2.[624] A new ternary, orthorhombic $Tb_3Bi_4Te_9$, has been identified in the Bi_2Te_3-TbTe system.[625]

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