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Chapter 5

ELEMENTS OF GROUP 5

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5.1 NITROGEN

5.1.1 Nitrogen and Nitrides

Syntheses with ^{15}N are reviewed in Ott's book.[1] Dehnicke and Strähle[2] have reported on transition metal-nitrogen multiple bonding systems. A detailed account has appeared[3] of the "diimido" type complex, containing the Ta=N-N=Ta grouping, mentioned in last year's Report. Martinengo and coworkers[4] have recently reported the first examples of low-valent metal nitrido (trigonal prismatic) clusters, $M_6N(CO)_{15}^-$, M = Co,Rh; a butterfly configuration has now been reported[5] for the $Fe_4N(CO)_{12}^-$ anion with the nitrogen bonded to all four iron atoms, Figure 1. This ion undergoes protonation to the new imido cluster compound $Fe_3(NH)(CO)_{10}$. The reaction of $TiNMg_2Cl_2$.THF (prepared from $TiCl_3$,Mg and N_2 in THF) with carbon monoxide has been investigated:[6] an intermediate is formed which shows no i.r. absorption characteristic of CO or NCO groups, however Me_2NCOMe is formed from it in 73% yield on treatment with MeI. Partial oxidation of the intermediate with $\frac{1}{2}I_2$ generated TiNMgCl.THF, which is capable of reacting with CO to form the isocyanate complex Ti(NCO)MgCl.THF (50% yield). The crystal structures of bridged imido (t-BuN) complexes of W(VI) and Ti(IV) have been reported:[7] the preference for unsymmetrical bridges in

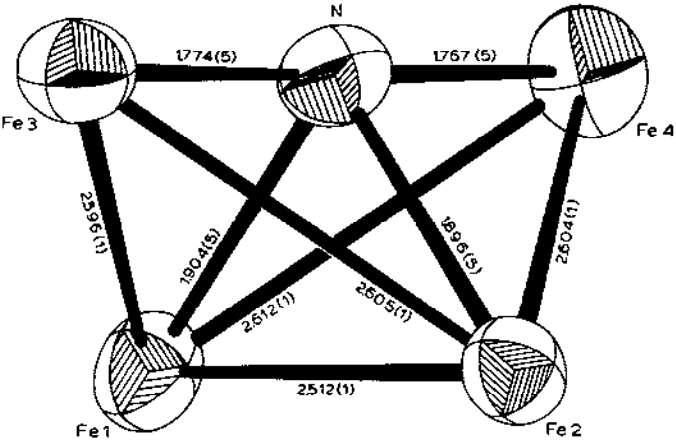


Figure 1. View of the Fe_4N framework; bond distances in Å (reproduced by permission from J. Am. Chem. Soc., 103(1981)1572).

the former and symmetrical ones for the second metal has been related to "anti-aromatic" and aromatic electronic structures of the Hückel models for the two types of compounds.

5.1.2 Bonds to Hydrogen

Shevlin et al.[8] have reported a reaction with possible implication in the extra-terrestrial synthesis of amino acids. They investigated the products of the co-condensation of carbon vapour (arc generated) and ammonia and found glycine, alanine, β-alanine, N-methylglycine and aspartic acid in the hydrolysis products; serine was produced when water was present in the original reaction mixture.

The thermodynamics of reaction (1) in liquid ammonia have been determined electrochemically.[9] The data were then combined with

$$H_2O + e^- \rightleftharpoons \tfrac{1}{2}H_2 + OH^- \qquad ...(1)$$

those for reaction (2) to yield information on the acid/base

$$NH_4^+ + e^- \rightleftharpoons \tfrac{1}{2}H_2 + NH_3 \qquad ...(2)$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-;\ K_3 = 6 \times 10^{-23} \text{ at } -40^\circ C \qquad ...(3)$$

dissociation of H_2O in liquid ammonia. The dissociation constant is much smaller than that in water ($K_3 = 3 \times 10^{-7}$ at 25°C) and this can be attributed mainly to entropy differences. A preliminary study of electrochemical processes in supercritical ammonia has been carried out by Silvestri et al.:[10] compared with subcritical conditions the electrical conductivity of an electrolyte (e.g. NaCl) is lower by one or two orders of magnitude. It was also observed that the conductivity is approximately proportional to the specific weight of the supercritical phase.

The quantitative oxidation of ammonia coordinated to Ru has been described by Thompson and Meyer.[11] Their starting material was $[(NH_3)(trpy)(bpy)Ru]^{2+}$, trpy = 2,2',2"-terpyridine, bpy = 2,2'-bipyridine; fixed potential electrolysis at 0.8v (vs. SSCE) and pH6.8 yielded the nitro compound $[(trpy)(bpy)Ru(NO_2)]^+$ in a six electron change.

5.1.3 Bonds to Carbon or Tin

The controversy continues over the behaviour of quaternary ammonium salts in a mass spectrometer. Cotter and Yergey[12] and Ohashi et al.[13] have confirmed that gaseous quaternary ammonium cations may be generated by heat inside the ion source of a mass spectrometer. Lee et al.[14] however proposed that electron impact is necessary to cause dissociation of the gaseous salts. The latest report[13] confirms that electron impact induced fragmentation of quaternary ammonium salts is also significant.

The basicity of nitrogen in primary and secondary alkyl- and silylalkylamines has been investigated[15] by means of the $\nu(C-D)$ band shift of $CDCl_3$, by mass spectrometrically measured ionisation potentials and from pK data for the conjugate acid. The results show a dependence on electronic and steric effects and throw new light on the α-effect of NCH_2Si. An electron diffraction study of gaseous $N(SnMe_3)_3$ has been carried out;[16] the data are said to be consistent with a planar NSn_3 skeleton with N-Sn bond length of 2.038(3)Å.

Rate constants for the quenching of the cadmium resonance line at 326.1nm by three tertiary amines (Et_3N, N-ethylpiperidine and 1-azabicyclo[2.2.2]octane) have been obtained.[17] Relative rate constants for the formation of an exciplex between an excited Cd atom and these amines as well as quantum yields for the emission from the exciplex were also derived. The heats of formation of gaseous $CH_2NH_2^+$, $MeCHNH_2^+$, $MeNHCH_2^+$, $Me_2CNH_2^+$, $Me_2NCH_2^+$, $MeCHNHMe^+$, $EtNHCH_2^+$ and $EtCHNH_2^+$ have been measured from their appearance energies in ionic dissociations.[18] All these ions can have a quaternary ammonium structure as one of the canonical forms and are consequently more stable than other isomers. Introduction of the $-NH_2$ group into a CH_3^+ ion brings about a decrease of more than 4eV in the heterolytic bond dissociation energy, $D(\overset{+}{R}-\overset{-}{H})$.

The recent report of the production of the phenyl nitrene anion, $PhN^{\overline{\cdot}}$, has prompted the study of a series of ion-molecule reactions, principally with simple carbonyls (aldehydes, ketones and esters), in order to establish the nucleophilic addition mechanism for adduct formation.[19] The nature of N-centred radicals is of considerable interest since the nitrogen must accommodate both an unpaired electron and a lone pair, with the result that the ground electronic state is either a π or a σ state. It has been shown by e.p.r. spectroscopy that N-alkylcarboxamidyl, $R\dot{N}COR'$, radicals have a π ground state with the unpaired electron in a 2p orbital perpendicular to the CNC plane, and yet the acyl group, R'CO, can be twisted out of this plane depending on the extent of steric repulsion between R and the oxygen.[20]

Cyanogen fluoride, FCN, reacts with COF_2, SF_4 and SOF_4 in the presence of nucleophilic catalysts (CsF or dimethylaminopyridine) to form CF_3NCO (8.8%), $CF_3N{=}SF_2$ (54%) and $CF_3N{=}SOF_2$ respectively.[21] Two previously unreported compounds $CF_3N(CN)_2$ (13.8%) and $CF_2{=}NCF_2N{=}SOF_2$ were obtained from the COF_2/FCN and SOF_4/FCN reactions. Cyanogen fluoride reacts with liquid HF at -78°C to produce some CF_3NH_2, whereas, at room temperature, reaction is explosive and mainly polymers are formed. An attractive, alternative route for the conversion of C_3F_6 into perfluoroacetone oxime has been discovered (Scheme 1).[22] The method also works for the conversion of perfluorocyclobutene to the cyclobutanone oxime.

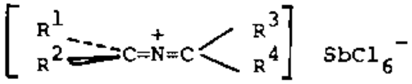
$$CF_3CF{=}CF_2 \xrightarrow{(i)} \underset{85\%}{(CF_3)_2CFNO} \xrightarrow{(ii)} \underset{62\%}{(CF_3)_2C{=}NOH}$$

(i) $KF/CF_3CO_2Ag/MeCN/NOCl$; (ii) $KHSO_3$ aq. 20°C.

Scheme 1

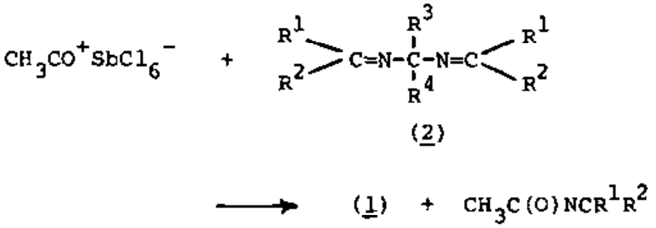
The addition of fluorine to a number of perhalogenated compounds containing the C=N grouping has been investigated by Sekiya and DesMarteau.[23] A high yield of the fluoroamine containing the CF-NF unit was formed in most instances. Two imines, $CF_3CF{=}NF$ and $(CF{=}NF)_2$, were unreactive and two others, $CF_3CF_2CF{=}NF$ and $(CF_3)_2C{=}NF$, reacted explosively. Four novel oxime ethers $RON{=}CF_2$ have been prepared in excellent yield by the dehydrofluorination with KF of $RON(H)CF_3$, R = CF_3, $(CF_3)_2CF$, CH_3, $(CH_3)_3C$.[24] The two new perfluoro compounds dimerise at room temperature in the presence of CsF to give $CF_3N(OR)CF{=}NOR$.

Phenyl substituted dimethyleneammonium(2-azaallenium) salts (1) have the topology and electronic structure of cumulenes.[25] A

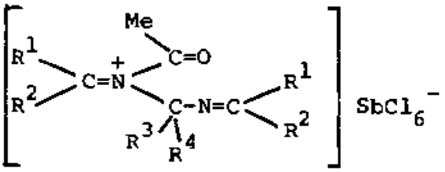


(1)

simple method of synthesis has been reported which starts with the easily accessible N,N'-bisalkylidene diaminomethanes (2). The latter are attacked by acylium salts according to reaction (4), presumably via the non-isolable N-acyliminium salt (3).



$$CH_3CO^+SbCl_6^- + R^1R^2C{=}N{-}CR^3R^4{-}N{=}CR^1R^2 \;(2) \longrightarrow (1) + CH_3C(O)NCR^1R^2 \quad ...(4)$$

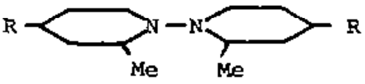


(3)

The ^{14}N n.q.r. spectra of some thiocyanate complexes show a well-defined trend in the coupling constant which is of value in ascertaining the mode of coordination:[26] the field gradients at nitrogen are largest in the S-bound, smallest in N-bound ligands, while ionic groups have intermediate values. The asymmetry parameter was not found to be diagnostic in this context.

5.1.4 Bonds to Nitrogen

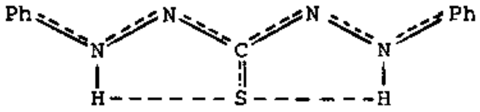
A ^{13}C d.n.m.r. study of meso-1,1'-bi(cis-4-t-butyl-2-methylpiperidine), (4), has revealed that the barrier to the single



(4) R = t-Bu; 79 kJ/mol

(5) R = Me; 74 kJ/mol

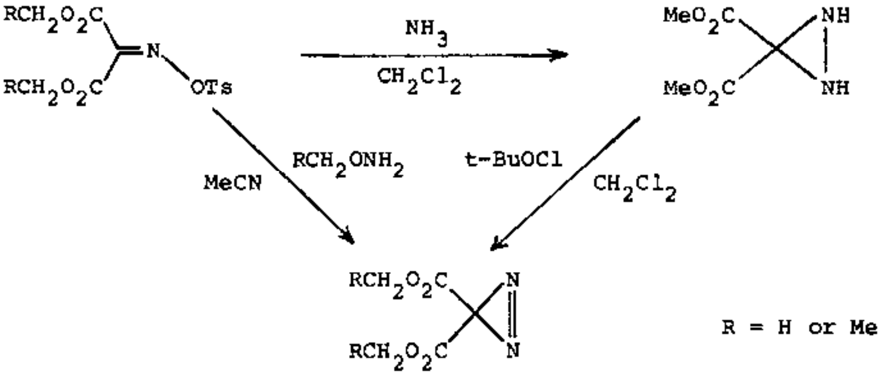
passing rotation about the N-N bond is 79 kJ mol^{-1}.[27] Proton magnetic resonance spectra of dithizone, its ^{15}N-labelled analogue and its alkyl-substituted homologues, as well as the ^{13}C n.m.r. spectrum, suggest that the structure in solution (6) is the same as that in the solid state:[28] there was no evidence for



(6)

the PhN=N·C(SH)=N·NHPh (thiol) $\rightleftharpoons$ PhN=N·C(S)·NH·NHPh (thione) tautomerism.

It has been shown that the 3,3-diazirine dicarboxylates (7) are readily accessible by either of the routes shown in Scheme 2.[29]



Scheme 2 (7)

The esters (7) are colourless materials stable at 0°C. The availability of persistent 1,1-diazenes has prompted Roberts et al.[30] to synthesise N-(2,2,6,6-tetramethylpiperidyl)nitrene labelled with ^{15}N: the ^{15}N chemical shifts were recorded, and that for the nitrene nitrogen is remarkable for a large downfield shift, reflecting the large paramagnetic term. Schultz and Dervan[31] have investigated the photochemistry of N-(2,2,5,5-tetramethylpyrrolidinyl)nitrene.

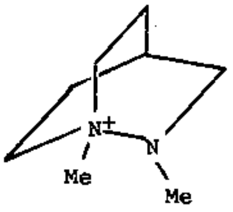
Vanadium(II) reduces nitroamine, NH_2NO_2, to dinitrogen according to reaction (5).[32] On the other hand Cr(II) reduction produces

$$NH_2{}^{15}NO_2 + 2H^+ + 2e^- \longrightarrow {}^{15}NN + 2H_2O \qquad ...(5)$$

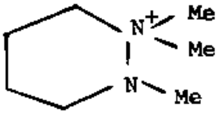
dinitrogen (25%) and NH_3 (ca. 75%).

The ionic species present in aqueous solutions of N_2H_5F and $N_2H_6F_2$, as calculated from data available in the literature, were compared with new information from conductometric measurements.[33] It was shown that a simultaneous determination of both salts is possible by conductometric titration with NaOH. The equilibria and kinetics of proton- and electron-transfer processes on 17 tetraalkylhydrazines have been compared.[34] The most basic hydrazines were found to be the most easily oxidised and the fastest to be protonated and to lose an electron. Under the conditions used (DMSO solvent) the rate of protonation of R_4N_2 was found to be about twice as sensitive to change in the R groups as was the equilibrium constant. It was suggested that a gauche to anti conformational change precedes proton-transfer and thus is a major factor contributing to the anomalous proton-transfer effects. The oxidation of 1,1-dimethylhydrazine by molecular oxygen, in solution in Et_2O or c-C_6H_{12}, has been carried out between 20° and 30°C.[35] The principal product was shown to be formaldehyde dimethylhydrazone. Among the other products identified were 1,1,4,4-tetramethyl-2-tetrazene and N-nitrosodimethylamine. The substitution of chlorine into the phenyl ring of phenylhydrazine lowers the tendency of the molecule to function as a reducing agent and allows the preparation of complexes with metals in higher oxidation states.[36]

Conformational interconversions in pentaalkyl hydrazine cations have been investigated by ^{13}C d.n.m.r.[37] Thus the $\Delta G^{\ddagger}$ for carbon equilibration in (8), (9) and (10) are 9.0(at -70°C), 11.1(at



(8)



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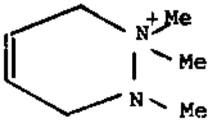


(10)

-20°C) and 10.4 kcal/mol (at -40°C). The kinetics of formation of unsymmetrical dimethylhydrazine from NH_2Cl and Me_2NH has been investigated over the temperature range 25 to 60°C.[38] The reaction is first order in both reagents but shows a dependence on $[OH^-]$ at pH > 12.5, above which pH there is also less competition from side reactions.

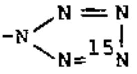
Tetrakis(trifluoromethylthio)hydrazine, $(CF_3S)_4N_2$, prepared by the irradiation of $(CF_3S)_3N$, dissociates homolytically in solution even at 273K into $(CF_3S)_2N\cdot$ radicals.[39] In the course of tracer experiments on the reaction of ^{15}N-enriched hydrazine with excess nitrous acid Phelan and Stedman[40] have obtained evidence for the complete scrambling of ^{15}N between the nitrogen environments in the products, N_2 and N_2O. They propose that a cyclic azide species is formed as a reaction intermediate during the course of the reactions (6) and (7).

$$HNO_2 + N_2H_5^+ \longrightarrow H_3O^+ + HN_3 + H_2O \qquad \ldots(6)$$

$$H^+ + HNO_2 + HN_3 \longrightarrow H_3O^+ + N_2 + N_2O \qquad \ldots(7)$$

Ion cyclotron resonance spectrometry has been used to measure the gas phase proton affinity of the azide ion.[41] The result, 344±2 kcal/mol, is in significant disagreement with the value calculated from the literature and based on indirect methods. The present study also provides the following thermochemical data: $\Delta H_f^\circ(N_3^-(g)) = 48\pm2$, $\Delta H_f^\circ(N_3(g)) = 112\pm5$, $D^\circ(H{-}N_3) = 92\pm5$ kcal/mol. A photodetachment threshold for N_3^- has been obtained which can be equated with the adiabetic electron affinity (62.1±2.8 kcal/mol) of the azide radical.[42] In DMSO solution p-toluenesulphonylazide (TsN_3) reacts[43] with N_3^- to form p-toluenesulphinate and N_2, equation (8). However in CH_2Cl_2 this reaction does not occur;[44]

$$TsN_3 + N_3^- \longrightarrow Ts^- + 3N_2 \qquad \ldots(8)$$

the sole reaction of KN_3 (solubilised with 18-crown-6) with N_3^- is azide ion exchange as has been established using 1,3-^{15}N-labelled azide ion. Surprisingly there is also a slow production of $Ts{-}N{=}^{15}N{=}N$ as well as a consumption of free azide ion by reaction with CH_2Cl_2. Roberts et al. have rationalised the ^{15}N scrambling in N_3 in terms of a hexazene $Ts{-}N^{-}{-}N{=}N{-}^{15}N{=}\overset{+}{N}{=}\bar{N}$ involved in a reversible formation of the N-pentazole $Ts{-}N^{-}{-}$. The i.r. spectrum of gaseous CF_3N_3 and the Raman spectrum of the liquid have been recorded and assigned to a molecule of C_s symmetry with hindered rotation.[45]

The synthesis of additional trialkyltriazenes has been described and the kinetics of their acid-catalysed decomposition investigated.[46] The distribution of products in the decomposition reactions provides evidence that they proceed via either an alkyldiazonium ion or directly to produce a carbonium ion, in situations where the alkyl group is capable of stabilising a positive charge. Trogler et al.[47] have drawn attention to the nature of the bonding in tetraazadiene metallocycles: the molecular structure of $(\eta^5\text{-}C_5H_5)Co(C_6F_5N_4C_6F_5)$, Figure 2, and the results of structural studies on related complexes indicate

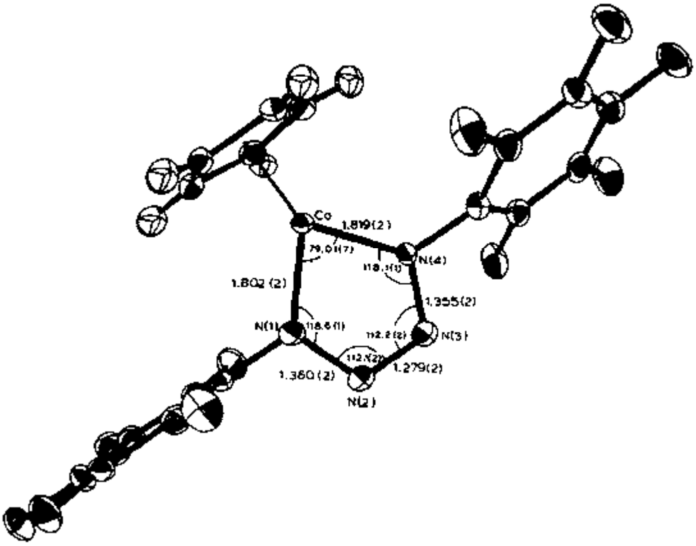
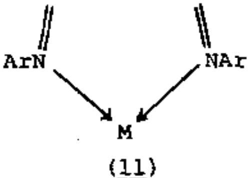


Figure 2. Molecular structure of $(\eta^5\text{-}C_5H_5)Co(C_6F_5N_4C_6F_5)$. Selected distances (Å) and angles (°) are shown: thermal ellipsoids are drawn at the 50% probability level (reproduced by permission from J. Am. Chem. Soc., 103(1981)192).

the diene resonance form (11) to be inappropriate on account of

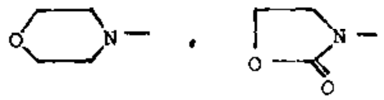


(11)

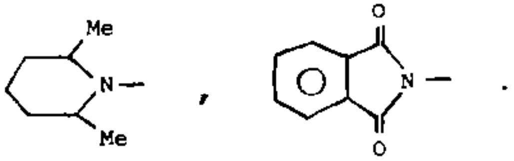
the short N(2)-N(3) bond and, in the cobalt complex, the short

Co-N bonds. The oxidation of 1,1-disubstituted hydrazines, (<u>12</u>), with benzeneseleninic acid, PhSe(O)OH, in methanol affords the corresponding tetrazene, $R_2N\text{-}N\text{=}N\text{-}NR_2$, in high yield.[48]

$R_2N\cdot NH_2$ (<u>12</u>) R_2N =



, $(PhCH_2)_2N$- ,



5.1.5 <u>Bonds to Oxygen</u>

The kinetics of reactions (9) and (10) at room temperature as

$$Cl + ClNO \longrightarrow Cl_2 + NO \qquad ...(9)$$

$$Cl + ClNO_2 \longrightarrow Cl_2 + NO_2 \qquad ...(10)$$

well as the photochemistry of $ClNO_2$ have been studied by Nelson and Johnston.[49] The dominant photodissociation process for $ClNO_2$ at 350nm was shown to be cleavage of the N-Cl bond. The cryogenic reaction between NO and O_3 has been re-examined at 6-20K.[50] Excitation with a CO laser enhances the rate linearly with increasing laser power; this behaviour was attributed to NO vibrational excitation in a one-photon process with low quantum yield. Ray and Watson[51] have studied the same reaction mixture over the temperature range 212-422K using a discharge flow/mass spectrometric technique and have compared their results with those from other studies.

The photolysis of $Re_2(CO)_{10}$ in THF saturated with NO, either in presence or absence of cyclooctatriene, yields ca. 11% of diamagnetic $Re_3(CO)_{14}NO_2$ the trinuclear structure of which, Figure 3, is remarkable for the absence of metal-metal bonding.[52] Significant is the role of the bridging NO_2 group which can be described as a 5 electron donor, if the Re atoms are to have 18 electron environments. The conformer equilibrium of methyl nitrite, MeONO, trapped in an inert matrix has been investigated by i.r. spectroscopy.[53] The enthalpy of conformer interconversion was calculated to be 623 cal/mol.

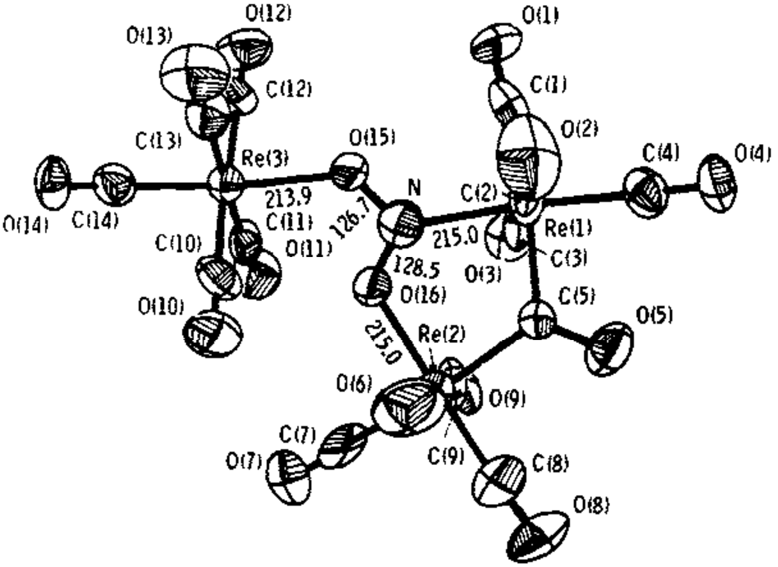


Figure 3. The molecular structure of $Re_3(CO)_{14}NO_2$ projected on to the $NO_2Re(1)$ plane. Bond lengths in pm. (Reproduced by permission from Angew. Chem. Int. Ed. Engl., 20(1981)470).

Bis(triphenylphosphine)iminium nitrite, $(Ph_3P)_2N^+NO_2^-$, has been shown to behave as a mild and versatile nitrosylating agent which finds use in the synthesis of novel transition metal nitrosyl carbonyls.[54] The oxygen exchange between NO_2^- and water has been re-investigated by means of n.m.r. spectroscopy:[55] this approach depends on the large (0.138ppm/^{18}O) isotope effect on the ^{15}N resonance.

Sodium nitrite and thiosulphate interact in aqueous acid to form a yellow species which has been identified as $(O_3SSNO)^-$.[56] Garley and Stedman have studied the reaction and have shown the equilibrium constant $[O_3SSNO^-]/[H^+][HNO_2][O_3SS^{2-}]$ to be 1.66 x 10^7 M^{-2} at 25°C. On the basis of stopped-flow measurements of the kinetics they proposed the existence of parallel reaction pathways involving NO^+ and N_2O_3 as electrophiles. The reaction between nitrite and bisulphite to form hydroxylamine disulphonate, equation (11), has been re-investigated over the pH range 4.5 to

$$NO_2^- + 2HSO_3^- \longrightarrow HON(SO_3)_2^{2-} + OH^- \quad \ldots(11)$$

7.[57] The rate law proposed has three terms and the authors offer a derivation of the rate expression in terms of competing parallel pathways.

The kinetics of reaction (12) have been studied at low partial

$$2NO_2(g) + H_2O(\ell) \longrightarrow 2H^+ + NO_3^- + NO_2^- \quad ...(12)$$

pressures of NO_2 at 22°C.[58] Under these conditions they are consistent with a second order aqueous phase reaction coupled to a mass transport process. Matrix reactions of Mg, Zn or Cd atoms with NO_2 have been examined by McDonald and Andrews.[59] Infrared absorptions in the 1220 cm^{-1} range show isotopic shifts appropriate for $M^+NO_2^-$. Bands near 950cm^{-1} for reactions of Zn were attributed to a different ion pair structural isomer.

From a study of the U.V. absorbances of solutions of nitrous acid in acidified water Schwartz et al.[60] have estimated the equilibrium constant for (13) to be $(3.03\pm0.23) \times 10^{-3}M^{-1}$. The

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \quad ...(13)$$

coefficient of physical solubility of N_2O_3 was calculated to be 0.70±0.05 M atm^{-1} at 22±2°C. Jain et al.[61] have reported that N_2O_3 reacts with $M(PPh_3)_4$, M = Pd or Pt, in the absence of O_2 to form $M(NO_2)_2(PPh_3)_2$; in the presence of O_2 the product is $M(NO_2)(NO_3)(PPh_3)_2$. However no reaction stoichiometries were reported.

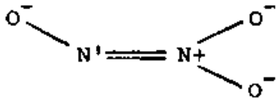
The molecular structures of O-methyl, N-methyl, N,O-dimethyl and N,N,O-trimethyl-hydroxylamines in the gas phase have been determined by electron diffraction.[62] In each instance the anti conformer (about the N-O bond) is dominant. The NO bond length increases with stepwise methyl substitution, from 1.463(3) in NH_2OMe to 1.513(9)Å in Me_2NOMe. Hydroxylamine and SO_2 react in aqueous solution to form sulphamic acid and traces of ammonium bisulphate. The kinetics of these processes have been re-investigated[63] and the enthalpy and entropy of activation evaluated for the two processes. The results are of interest to flue gas desulphurisation or denitrification processes. The kinetics and stoichiometry of the decomposition of NH_2OH in nitric acid have been investigated under conditions where hydroxylamine is functioning as a nitrite scavenger, reaction (14), or as a nitrous acid source, reaction (15).[64] The latter process is

$$NH_3OH^+ + HNO_2 \longrightarrow N_2O + H_3O^+ + H_2O \qquad ...(14)$$

$$NH_3OH^+ + 2HNO_3 \longrightarrow 3HNO_2 + H_3O^+ \qquad ...(15)$$

favoured by an increase in $[HNO_3]$ and in temperature, or a decrease in $[NH_3OH^+]$.

The vibrational spectrum of $Na_2N_2O_3$, (13), trioxodinitrate, has been fully assigned by Bonner et al.[65] Their study also included



(13)

a Raman study of the effect of monoprotonation of the anion. They also reported on the ^{15}N n.m.r. spectrum of the dianion at pH 13 and of the monoprotonated species:[66] this showed that only the N' environment undergoes a shift (24 ppm) on protonation (at pH 8). Furthermore the nuclear Overhauser effect for N' at pH 8 is -2.1. The authors pointed out that the literature chemical shift assignments must be in error and also that the monoprotonated anion, which eventually decomposes to HNO and NO_2^-, is probably protonated on the 2-coordinate N' atom.

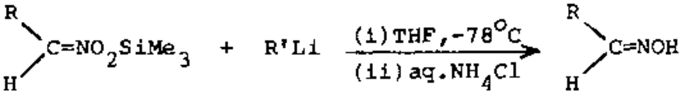
R.T.Barber[67] has reviewed "Nitrates: an environmental assessment", a comprehensive report by the panel on nitrates of the N.R.C. (1978). He remarks that the treatment is not only thorough but also multidisciplinary in its approach: thus it has a section dealing with nitrites, nitrates, and nitrosamines in meat preparations. The reaction of HNO_3 with OH has been studied using the discharge flow-e.p.r. technique.[68] By carrying out a titration of NO_3 radicals with NO it was possible to show that the reaction proceeds according to equation (16).

$$OH + HNO_3 \longrightarrow H_2O + NO_3 \qquad ...(16)$$

Bidentate nitrate and μ-bromato ligands are found in the 8-coordinate Hg(II) compound $K_2Hg(BrO_3)_2(NO_3)_2$.[69] Pernitric acid, $HOONO_2$, has been prepared in solution by the reaction of HNO_3 or

NO_2BF_4 with 90% H_2O_2 at 273K.[70] Gaseous HO_2NO_2 could be carried out of these reaction mixtures in a stream of argon and was identified by its infrared spectrum. Its decomposition in buffered aqueous solution generates O_2 and NO_2^-.

Unlike the corresponding reactions with Grignard reagents silyl nitronates react with organolithium reagents in dilute THF solutions to form oximes, equation (17).[71] In more concentrated solutions the major product is the silyl ester of a hydroxamic acid, equation (18).



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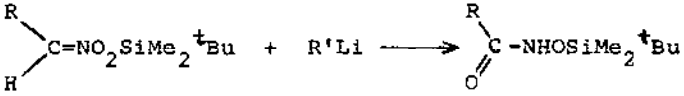


...(18)

5.1.6 Bonds to Sulphur

Gleiter has shown how the classification of SN ring systems is possible within the framework of a MO model:[72] the simple Hückel rule is still applicable. Chivers et al.[73] have developed simple syntheses of ^{15}N-enriched S_4N_4 and other sulphur-nitrogen compounds. These samples were then investigated by ^{15}N n.m.r. spectroscopy to provide information concerning the structure of and electron distribution in S-N rings and cages in solution. A low temperature (-100°C) X-ray crystallographic analysis of S_4N_2 shows that it consists of a six-membered ring in a half-chair conformation with the N atom in the 1,3-positions.[74] A previously unreported substitution product of S_4N_4 has been prepared by the reaction of $S_4N_4Cl_2$ with two moles of Me_3SiNMe_2.[75] The new compound, $S_4N_4(NMe_2)_2$, is stable for months at 0°C; it contains two stereochemically non-equivalent NMe_2 groups as shown in Figure 4.

The unstable dimethyl(thionitroso)amine Me_2N-N=S, displaces THF from $Cr(CO)_5$.THF to form a crystalline product stable at room temperature in which, surprisingly, the novel ligand is bound to Cr via the S atom:[76] the N-N and N-S bond lengths in the complex are 1.279(2) and 1.635(2)Å, respectively, and the NNS angle is

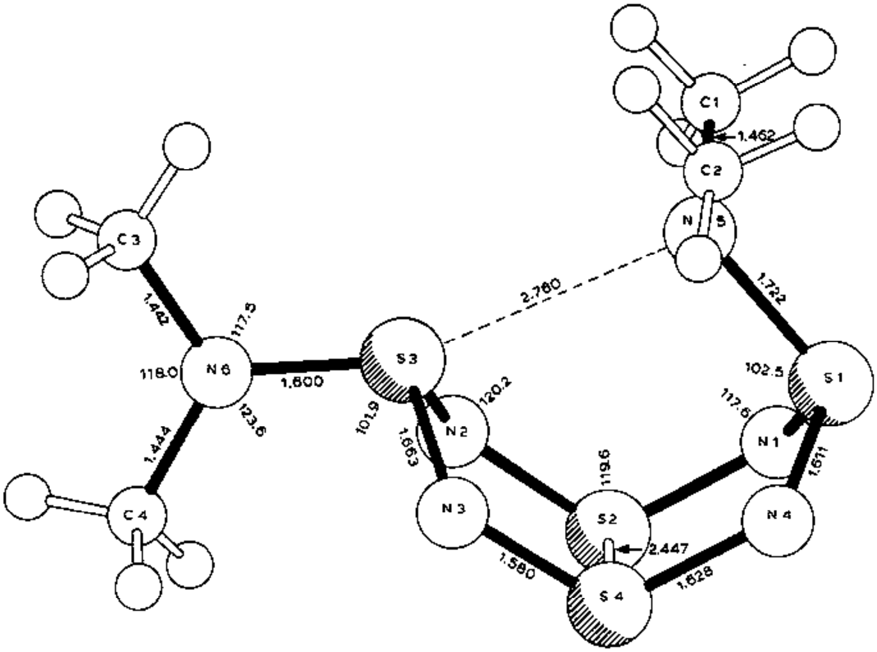


Figure 4. Molecular structure of 1,5-bis(dimethylamino)tetrasulphur tetranitride, with bond lengths (Å) and angles (°); the molecule has C_s symmetry (reproduced by permission from Angew. Chem. Int. Ed. Engl., 20(1981) 592).

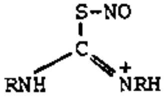
118.5°. The crystal structure study of $NS^+Sb_2F_{11}^-$ at 293K and 121.5K has enabled Sheldrick et al.[77] to analyse the effect of thermal motion on the apparent N-S bond length. The corrected bond length, 1.404(6)Å is shorter than the value, 1.44(1)Å, derived from the vibrational fine structure of the photoelectron spectra of NS in the gas phase. This difference is attributed partly to the discrepancy (0.007(3)Å) between internuclear separation and the distance between the centres of electron density, and partly to stabilisation of form (14a) in preference to (14b) by cation-fluorine (on antimony) interactions in the crystalline state.

$N{\equiv}S^+$

(14a)

$^+N{=}S$

(14b)



(15)

^{15}N n.m.r. studies at -10°C have provided evidence for the formation of thionitrosyl intermediates (<u>15</u>) in the reaction of NO_2^- with thioureas in 1M HCl or HCO_2H.[78] Hydrolysis of (<u>15</u>) leads to the formation of urea derivatives which may then undergo N-nitrosylation. The gas-phase i.r. spectra of methylthionitrite, MeSNO, and of some isotopically substituted analogues have been observed and assigned.[79] The $\nu(SN)$ absorption occurs strongly at 646 cm^{-1} whereas the weaker $\nu(CS)$ band is at higher energy.

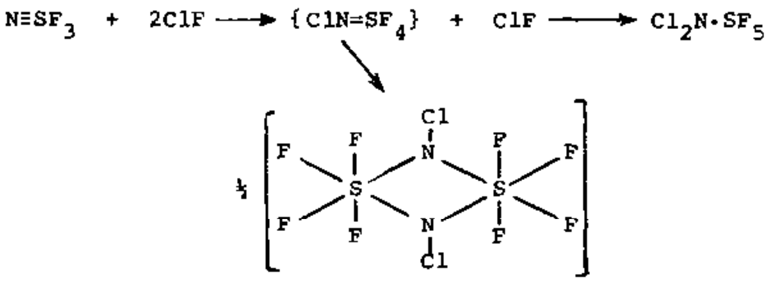
The N-S bond stretching force constant in $MeNSF_3^+$ has been calculated to be 40% higher than in NSF_3 itself.[80] The meaning of this and of the formal bond order value (3.6) were discussed critically. Trifluoromethyl sulphinyl azide, $CF_3S(O)N_3$, synthesised from the acid chloride and NaN_3, starts to decompose at about -10°C, presumably via $CF_3S(O)N$:[81] the reactivity of the latter was such that it could not be isolated. Oligomerisation and other reactions were studied.

The first member of a new class of stable sulphimides, bis[bis(trifluoromethyl)sulphimide], $(CF_3)_2S{=}N{\cdot}N{=}S(CF_3)_2$, has been prepared as a product of the photolysis of $(CF_3)_2S{=}NCl$.[82] The latter compound was formed from $(CF_3)_2S{=}NH$ and ClF in the presence of CsF. The sulphimide, $\overline{CF_2CF_2CF_2CF_2S}{=}NH$, has been prepared by the reaction of $LiNH_2$ with octafluorotetramethylene sulphur(IV) fluoride in the presence of liquid ammonia:[83] the N-halo derivatives were also synthesised by the reaction of the imide with Cl_2 or Br_2 in the presence of KF or CsF. N-alkyl sulphimides were obtained by using primary amines or by reactions of the type shown in equation (19). Abe and Shreeve have also been able to

$$(CF_3)_2SF_2 \; + \; LiN{=}C(CF_3)_2 \longrightarrow \underset{(71\%)}{(CF_3)_2S{=}NCF(CF_3)_2} \; + \; \underset{(trace)}{(CF_3)_2S{=}NC(CF_3)_2{-}N{=}C(CF_3)_2} \quad ...(19)$$

convert the perfluorotetramethylene sulphimide to the analogous sulphoximine $\overline{CF_2CF_2CF_2CF_2S}(O){=}NH$.

Dimeric N-chloroiminosulphur tetrafluoride has been isolated in 3.6% yield in the course of the preparation of SF_5NCl_2 from NSF_3 and 2ClF (Scheme 3):[84] the geometry of the novel cyclodiaza-



Scheme 3

$-\lambda^6$-thiane is probably centrosymmetric. The new xenon(II) compound $Xe[N(SO_2F)_2]_2$ has been reported as one of the products of reaction of XeF_2 with $HN(SO_2F)_2$ at low temperatures.[85] The proportion of the new compound to $FXe[N(SO_2F)_2]$ in the product mixture was controlled by the proportion of the reagents; thus a 1:2 molar ratio yielded 20% of the bis compound (based on XeF_2). The free radical $\cdot N(SO_2F)_2$ is formed (non-photolytically) from the bis compound in $CFCl_3$ near 0°C. DesMarteau et al.[85] have described the e.s.r. spectrum of this radical and have concluded that the unpaired electron is strongly delocalised.

5.1.7 Bonds to Halogens

The e.s.r. spectrum of the 33 electron radical anion F_3NO^- has been reinvestigated.[86] It was concluded that this species is probably of C_{3v} symmetry on the basis of the equivalence of the three fluorines over the temperature range 10 to 110K. Calculations place the bulk of the electron density from the odd electron on the fluorines: moreover, it was observed that the dissociation process forms F_2NO and F^-.

A new route to NF_4^+ salts has been used to prepare $NF_4^+UOF_5^-$;[87] it depends on reaction (20) in which a solution of $NF_4^+HF_2^-$ in HF is used in excess and surplus reagent is subsequently decomposed to NF_3 and F_2 at 40°C. The same technique was applied to the

$$NF_4NF_2 \; + \; UOF_4 \xrightarrow{HF} NF_4UOF_5 \; + \; HF \qquad \ldots(20)$$

preparation of the analogous W(VI) compound.[88] This new compound is a white solid, stable up to 60°C but decomposing at higher temperatures to NF_3, OF_2, WF_6 and $NF_4W_2O_2F_9$. The scope of the metathetical process in liquid HF for the preparation of NF_4^+ salts, as described in earlier reviews in this series, has been successfully applied to the synthesis of salts (e.g. $(NF_4)_2SiF_6$) of F^- ion acceptors (e.g. SiF_4) weaker than the solvent itself.[89] X-ray studies of $(NF_4)_2NiF_6$ have shown that the compound crystallises in a tetragonal form, derived from the K_2PtCl_6-structure.[90] A differential calorimetric study of the decomposition of $(NF_4)_2NiF_6$, equation (21), and NF_4SbF_6 has

$$(NF_4)_2NiF_6 \longrightarrow 2NF_3 + 3F_2 + NiF_2 \qquad \ldots(21)$$

yielded enthalpies of decomposition, 134.7±13.0 and 245.6±28.9 kJ mol^{-1} respectively.[91] The corresponding enthalpies of formation of these compounds were estimated from these data.

Benzene, toluene and nitrobenzene react rapidly with NF_4BF_4 in anhydrous HF to give, almost exclusively, fluorine substituted aromatic compounds.[92] In the first place 4 protons in the nucleus are substituted rapidly at -78^oC; this is followed by much slower addition reactions to form cyclohexadienes and cyclohexenes. The NF_4^+ ion is reduced to NF_3.

The He(I) photoelectron spectra of $(F_3C)_nNF_{3-n}$ and $(F_3C)_{3-n}N(CF_2H)_n$ with n = 1, 2 or 3, and F_2HCNF_2 have been recorded.[93] The assignments are based on comparison of equivalent radical cation states in the individual series assisted by MNDO calculations. The first band results from the N lone pair ionisation and substituent effects can be parametrised successfully. The fluorination of azidotrifluoromethane furnishes CF_3NF_2 in an efficient process which, according to Schack,[94] has clear advantages over previously reported routes. The optimum rate of conversion by F_2 was found to occur at 70^oC.

N,N-Dihaloalkylamines are useful synthetic reagents but only a few are known: Sekiya and DesMarteau[95] have described a high yield synthesis based on reaction (22). On the 3 millimolar scale the

$$RCN + ClF + F_2 \longrightarrow RCF_2NClF \qquad \ldots(22)$$

reactions are slow requiring one or more days for optimum conversion, except for R = Me where the reaction is explosive. A series of N-chloroalkylammonium salts have been prepared by reaction (23).[96] The products (R = Me, Et, n-Pr, i-Pr, i-Bu)

$$R_2NCl \quad + \quad HCl \quad + \quad SbCl_5 \quad \xrightarrow[CH_2Cl_2]{-78^{\circ}C} R_2NH\overset{+}{Cl}\ SbCl_6^- \qquad \ldots(23)$$

may be kept undecomposed at 0°C for weeks but decompose in CH_2Cl_2 especially in the presence of HCl, reaction (24). The analogous

$$R_2NHCl^+ \quad + \quad HCl \longrightarrow R_2NH_2^+ \quad + \quad Cl_2 \qquad \ldots(24)$$

N,N-dichloro ammonium salts could not be prepared from $RNCl_2$, the monochloro ammonium salt being formed instead, reaction (25).

$$RNCl_2 \quad + \quad 2HCl \quad + \quad SbCl_5 \quad \xrightarrow[CH_2Cl_2]{-78^{\circ}C} RNH_2Cl^+SbCl_6^- \quad + \quad Cl_2 \qquad \ldots(25)$$

Equilibria (26), (27) and (28) have been measured by U.V.

$$NH_2X \quad + \quad H_2O \rightleftharpoons NH_4^+ \quad + \quad OX^- \qquad \ldots(26)$$

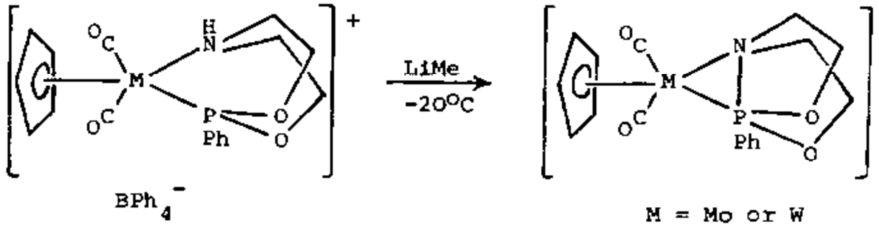
$$2NH_2X \quad + \quad H^+ \rightleftharpoons NHX_2 \quad + \quad NH_4^+ \qquad \ldots(27)$$

$$3NHX_2 \quad + \quad H^+ \rightleftharpoons 2NX_3 \quad + \quad NH_4^+ \qquad \ldots(28)$$

spectrophotometric analysis for X = Cl or Br in aqueous ammonia solution at 25°C.[97] The previously unknown compound $I(NI_4)NH_3$ has been prepared from $NI_3.NH_3$ in the presence of a trace of water. The structure is based on nearly tetrahedral NI_4 units (N-I distances 2.19 and 2.236Å) three corners of which are linked to the additional iodines (I...I, 3.088Å) to form a puckered layer structure.[98] The ammonia molecules are coordinated to the fourth iodines (of the NI_4 units) and also serve to fill the interlayer spaces. The complex formed between Et_3N and I_2 in chloroform has been studied by a number of sporting techniques:[99] the results are consistent with the formulation $(Et_3N\text{--}I^+\text{--}NEt_3)I_3^-$.

5.1.8 Bonds to Phosphorus or Arsenic

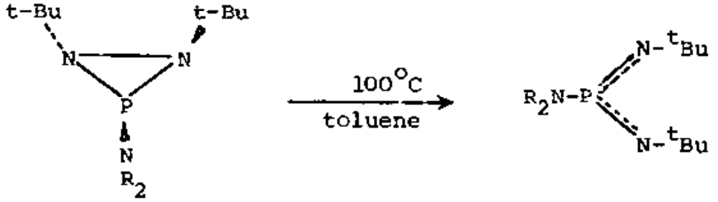
An interesting ring closure process, reaction (29) generates an aminophosphoranide transition metal adduct having the novel $\overline{N\text{-}P\text{-}M}$ ring.[100] 1,2,3λ^3-Diazaphosphiridines, R = $CHMe_2$ or $SiMe_3$, have now been synthesised. At -100°C they isomerise rapidly in toluene, reaction (30), from the trans ground state (16) to give



M = Mo or W

...(29)

the ylidic diiminophosphorane (17).[101] Reaction scheme 4, R = t-Bu, has been used to synthesise the first alkylated iminophosphorane (18).[102] The product, probably the trans isomer, is an intense yellow liquid which is stable for a few days at -40°C. At 0°C rapid dimerisation, a [2+1]-cycloaddition, occurs to form an azadiphosphiridine (19).



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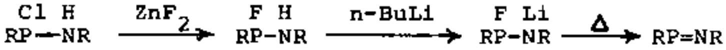
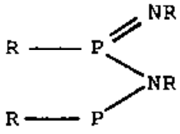
(16) (17)



$$\overset{\text{Cl}\ \ \text{H}}{\text{RP—NR}} \xrightarrow{\text{ZnF}_2} \overset{\text{F}\ \ \text{H}}{\text{RP-NR}} \xrightarrow{n\text{-BuLi}} \overset{\text{F}\ \ \text{Li}}{\text{RP-NR}} \xrightarrow{\Delta} \text{RP=NR}$$

(18)

Scheme 4



(19)

The hitherto unknown and unstable ligands $P(NH-NH_2)_3$ and $P(NH-NMe_2)_3$ have been stabilised as their Cr(0) complexes by the solvolysis of $(OC)_5CrPCl_3$ with N_2H_4 or H_2NNMe_2.[103] The trichloro phosphazo compounds $R_fN{=}PCl_3$, $R_f = CF_3$ or C_2F_5, have been obtained by reaction (31).[104] The azido complex ions $MBr_5N_3^-$,

$$R_fNCl_2 \ + \ 2PCl_3 \longrightarrow R_fN{=}PCl_3 \ + \ PCl_5 \qquad ...(31)$$

M = Nb or Ta, react with PPh_3 in CH_2Br_2:[105] reaction (32) occurs spontaneously for the niobium complex whereas the tantalum complex requires photochemical activation. The analogous reaction of

$$Br_5MN_3^- \ + \ PPh_3 \longrightarrow (Br_5M{=}N{=}PPh_3)^- \ + \ N_2 \qquad ...(32)$$

$AsPh_3$ took place only for the chloroniobium anion $NbCl_5N_3^-$ with photochemical and thermal activation: the product contained the expected $(Cl_5Nb{=}N{=}AsPh_3)^-$ ion.

5.2 PHOSPHORUS

5.2.1 Phosphorus, Polyphosphines and Phosphides

New complexes containing the P_3 unit as an η^3 ligand that have been synthesised during the last year include:
$[(triphos)M^1{-}\mu(\eta^3{-}P_3)M^2(triphos)]Y_n$,[106] where triphos is 1,1,1-tris(diphenylphosphino)methylethane, M^1 = Co,Ni or Rh, M^2 = Rh or Ir, Y = BF_4 or BPh_4 and n = 1 or 2,
$[(triphos)M{-}(\eta^3{-}P_3)]BF_4$,[107] where M = Pd or Pt,
$[(triphos)Pd{-}\mu(\eta^3{-}P_3)Pd(triphos)]BPh_4$,[107] and
$[(triphos)Co{-}\mu(\eta^3{-}P_3)M(etriphos)]Y_2$,[108] where etriphos is 1,1,1-tris(diethylphosphino)methylethane, M = Fe,Co or Ni and Y = PF_6 or BPh_4. Full X-ray structures have been determined for a number of these species.

White phosphorus and tetramethyldistannane react in the dark to produce the novel cage compound $(Me_2Sn)_6P_2$ with the structure shown in Figure 5.[109] The compound, which has D_3 symmetry and consists of three Sn_4P_2 rings sharing three bonds with each other, is unstable in the light when it loses dimethylstannanediyl to give the norbornane compound $(Me_2Sn)_5P_2$.

Compounds containing P=P double bonds have been claimed in the past but until now such products always proved to be oligomers. An authentic P=P species has now been prepared in which steric hindrance plays an important role in promoting stability. The preparation involves treatment of (2,4,6-tri-t-butyl-phenyl)-phosphonous dichloride with magnesium in THF solution from which

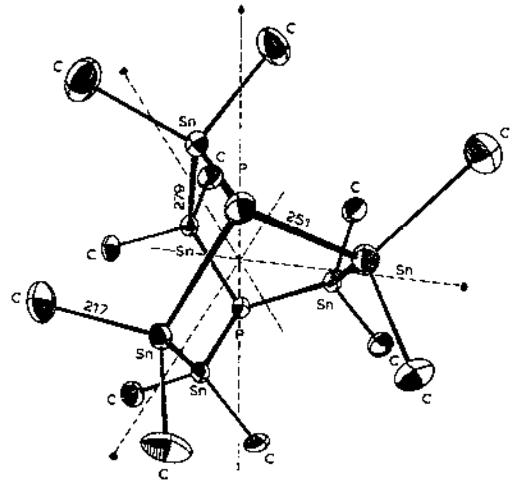
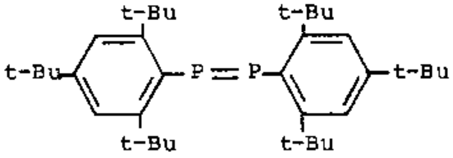


Figure 5. Molecular structure of $(Me_2Sn)_6P_2$ (reproduced by permission from Angew. Chem. Int. Ed. Engl., 20(1981)1029).

can be isolated compound (20) as a thermal and air stable solid.[110] The P-P bond length, 2.034Å, is substantially shorter



(20)

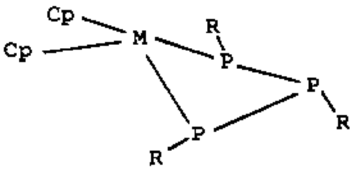
than in other polyphosphines, implying substantial double bond character.

New chiral diphosphines $R(CF_3)P{\cdot}P(CF_3)_2$, where R = Me, CH_2F or CHF_2, have been isolated from reactions between the appropriate phosphines and chlorophosphines in the presence of an HCl acceptor.[111] The ^{19}F n.m.r. spectrum for the particularly stable $Me(CF_3)P{\cdot}P(CF_3)_2$ compound suggests a gauche conformation. The final product of the reaction of $t\text{-}BuP(SiMe_3)_2$ with hexachloroethane is the unsymmetrically substituted diphosphine $t\text{-}Bu(Me_3Si)\text{-}P{\cdot}P(t\text{-}Bu)Cl$, although the previously unknown P-chloro-P-silyl phosphine, $t\text{-}BuP(SiMe_3)Cl$, can be isolated as an unstable intermediate.[112] Instability is associated with loss of Me_3SiCl. Compounds of the type $R_2M^1{\cdot}M^1R_2$, where R = CH_3 or CF_3 and M^1 = P or As, have been treated with Group 4 hydrides Me_3M^2H, where M^2 = Si, Ge or Sn, to study general reactivity and substituted mixed

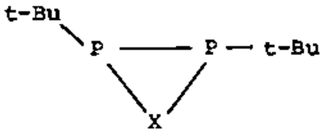
M^1-M^2 species have been isolated.[113]

A cyclo-triphosphine, $(t\text{-BuP})_3$, can be synthesised from 1,3-diiodo-1,2,3-tri(t-butyl)triphosphine by treatment with LiH as in the classic cyclopropane synthesis.[114] Ring cleavage by I_2, Br_2 or PCl_5 leads initially to $X\text{-}(t\text{-BuP})_3\text{-}X$, where X = I,Br or Cl,[115] with the corresponding di- and mono-phosphines, $X\text{-}({}^t\text{BuP})_2\text{-}X$ and $t\text{-BuPX}_2$, as byproducts. The reaction with PBr_5 in toluene at -60°C on the other hand gives the cyclo-tetraphosphine, $(t\text{-BuP})_4$.[115]

Compounds containing a coordinated triphosphanate group (21) can be isolated when a metallocene dichloride is treated with $K_2(PR)_n$



(21)

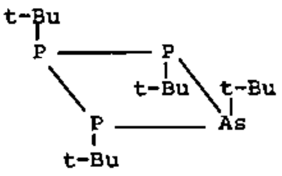


(22)

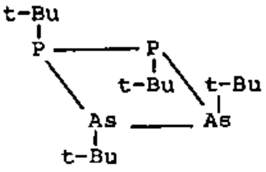
where R = Me, Et, t-Bu or Ph and n = 3-5.[116] Structures with ideal C_s symmetry and a folded chelate ring and equatorial substituents are proposed on the basis of n.m.r. spectroscopy.

A range of substituted cyclo-triphosphines (22) has now been synthesised. These in which $X = BR^1R^2$ result from [2+1] cyclocondensations between $K_2(t\text{-BuP}\cdot\text{Pt-Bu})$ and $R^1R^2NBCl_2$,[117] the structure of one of these, (22, $X = BNEt_2$), showing a trans arrangement of substituents at phosphorus.[118] Dimerisation to tetraphospha-diboracyclohexanes depends on both steric and electronic influences at the ring atoms.[117]

A P_2As heterocycle (22, X = t-BuAs) can be obtained similarly from $t\text{-BuAsCl}_2$ as a mixture of two diastereoisomeric forms;[119] the reaction also yields, the mixed species (23) and (24). Species



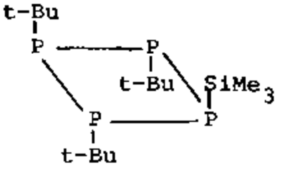
(23)



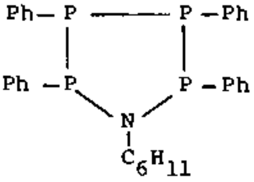
(24)

in which X = S or Se result when the diphosphine dichloride, Cl(t-Bu)P·P(t-Bu)Cl, reacts with either $(Me_3Sn)_2S$ or $(Me_3Sn)_2Se$.[120] HeI p.e.s. have been reported and analysed for a range of P_3 and P_2X species.[121]

The P_4 ring in cyclo-tetra(t-butyl phosphine) is non-planar (torsion angle 24.5°), with mean P-P and P-C bond lengths of 2.212 and 1.884Å;[122] the mean P-P-P angle is 87.3°. P-functional phosphines, e.g. $(Me_3Si)_2P{\cdot}PCl_2$ and $[Me_3Si)_2P]_2PCl$, are obtained when PCl_3 is treated with the lithium compound $(Me_3Si)_2PLi.2THF$ at -78°C, but when the reaction is carried out in the presence of t-BuLi the product is a cyclo-tetraphosphine (25).[123] In an extension of these reactions, PCl_3 was replaced with t-$BuPCl_2$, the initial product being $(Me_3Si)_2P{\cdot}PCl(t\text{-}Bu)$, which on heating to 20°C gave a mixture of the cis and trans cyclo-tetraphosphine $(Me_3Si)_2P_4(t\text{-}Bu)_2$. The related reaction between $(Me_3Si)_3P$ and PCl_3 gives $(Me_3Si)_2P{\cdot}PCl_2$ and, in the presence of t-BuLi at low temperatures, both $[(Me_3Si)_2P]_2PCl$ and $(Me_3Si)_2P.PCl(t\text{-}Bu)$ can be isolated.



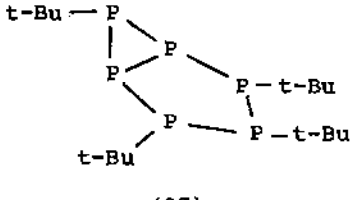
(25)



(26)

A silylated tetraphosphine $Me_3Si(PPh)_4SiMe_3$ can be isolated when $K_2(PPh)_4$ reacts with Me_3SiCl, but the compound is unstable and with time disproportionates to $(PPh)_5$ and the diphosphine, $Me_3Si(PPh)_2SiMe_3$.[124] N.m.r. data point to the presence of four isomeric forms being present in solutions of $Me_3Si(PPh)_4SiMe_3$; on reaction with alcohol, the disilyl-tetraphosphine yields the hydride $H(PPh)_4H$ as the main product. A cyclo-azatetraphosphine (26) has been isolated for the first time as one of the products from a reaction between N,N-dichloro-cyclohexylamine and an excess of $K_2(PPh)_4$.[125]

New hexa-, hepta- and higher phosphines have also been announced during the year. A hexaphosphine $(t\text{-}Bu)_4P_6$ with the structure shown in (27) is one of the range of products obtained by dehalogenation of PCl_3-t-$BuPCl_2$ mixtures with magnesium metal.[126] The bicyclo[3.1.0]hexaphosphine structure was confirmed by a full X-ray determination. A similar preparative method but using PCl_3-$MePCl_2$ or PCl_3-Me_5P_5 mixtures with magnesium has yielded P_7Me_5 and P_9Me_5 and there is evidence for three further compounds, i.e. P_7Me_3, P_8Me_6 and $P_{11}Me_5$, among the complicated mixture of reaction products.[127] The P_7 compound has the norbornane type structure (28) while a noradamantane structure (29) is found for the P_9 species. MINDO/3 calculations on the P_7^{3-} anion point to an activation enthalpy toward rearrangement of 59.13kJ mol^{-1}, in agreement with variable temperature ^{31}P n.m.r. data, and suggest that cleavage of a basal P-P bond is the initial step.[128]



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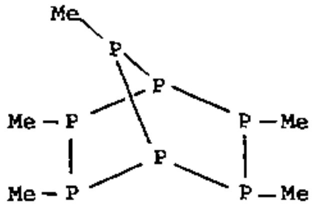

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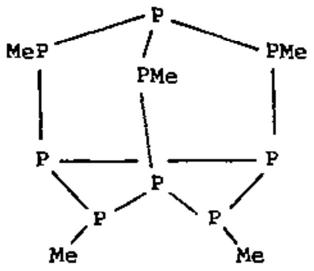


(29)

Cyclo-octa-phosphines and -arsines have been synthesised by the reactions shown in equations (33) and (34);[129] in each case lower cyclic species were also produced as by-products. As shown in

$$2H(t\text{-}Bu)P\cdot P(t\text{-}Bu)H + P_2I_4 \longrightarrow (t\text{-}Bu)_6P_8 + 4HI \qquad \ldots(33)$$

$$6t\text{-}BuAsCl_2 + 2AsCl_3 + 9Mg \longrightarrow (t\text{-}Bu)_6As_8 + 9MgCl_2 \qquad \ldots(34)$$

Figure 6 the octaphosphine consists of two P-P bonded non-planar P_4 rings while the corresponding octa-arsine structure is based

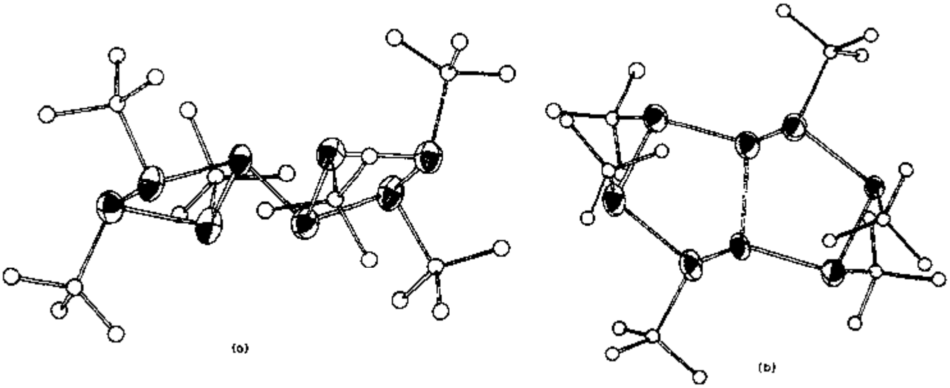


Figure 6. a) Structure of $(t\text{-Bu})_6P_8$, b) Structure of $(t\text{-Bu})_6As_8$ (reproduced by permission from Angew. Chem. Int. Ed. Engl., 20(1981)406).

on two fused As_5 rings in the twist envelope conformation.

Red crystals of Na_3P_7 on treatment with Ph_4PCl in THF solution give the tetraphenylphosphonium salt of the novel anion P_{16}^{2-},[130] with a structure consisting of two P_7 units joined by a common P_2 unit. In Ba_2P_7Cl,[131] the structure is related to that of sodium chloride in which half of the anion positions are occupied by P_7^{3-} units with P-P bonds of 2.264, 2.145 and 2.172Å respectively in the three membered ring, the ring to bridge bonds and the bridge atoms to bridgehead arom. The compound was obtained initially as a by-product from a Ba-red phosphorus-$AlCl_3$ reaction but it can also be obtained directly from barium, phosphorus and barium chloride.

A review on cluster chemistry in the Main Group element area deals with the general problem of homoatomic bonding and the incidence of polycation and polyanion formation;[132] von Schnering's treatment covers, inter alia, the Group 5 elements.

The metal rich part of the scandium-phosphorus system shows the formation of Sc_7P_3 and Sc_3P.[133] A single crystal study for $Zr_{14}P_9$ shows the presence of nine non-equivalent PZr_6 trigonal prisms with 1 to 3 further zirconium atoms above the rectangular faces.[134] Two new polymorphic modifications of MnP_4 have been identified, one of which is a stacking variant of a previously reported modification.[135] AgP_3 previously identified in the Ag-P system has been shown recently to be, in fact, Ag_3P_{11} in which tetrahedral AgP_4 units (Ag-P 2.47 to 2.61Å) are linked by sharing phosphorus atoms into infinite chains along the a axis.[136] Further interactions link the chains into a two dimensional infinite polyanion.

Three dimensional networks are present in the structures of the new ternary compounds $BaGe_2P_2$ and $BaGe_2As_2$ in which the germanium and phosphorus (arsenic) atoms are in four and two fold coordination respectively.[137] The ternary $CeSiP_3$ has been isolated from a reaction between CeP and iodine in a quartz ampoule,[138] and two series of manganese compounds LiMnX and NaMnX, where X = P,As,Sb or Bi, have been obtained from the elements at high temperature.[139] Detailed structures are available for a number of the compounds. A single crystal X-ray study for $Ti_{11+x}Cu_{1-x}P_8$, where x = 0.34, shows the presence of trigonal prismatic PTi_6 and distorted body centred cubic $CuTi_8$ structural units.[140] New κ-phases in the HfMoP, HfMoAs and HfWP ternary systems have been shown to crystallise in the hexagonal space group $P6_3/mmc$.[141]

Compounds with the stoichiometry Cd_3PX_3[142] and Cd_3AsX_3,[142] where X = Cl,Br or I, Cd_4PI_3,[143] Cd_4AsI_3,[143] $Cd_7P_4Cl_6$[144] and $CdAs_2I_3$[k44] have been prepared either by vapour transport of $Cd_3P_2(As_2)$-CdX_2 mixtures or fusion of Cd_3As_2 with the appropriate cadmium halide. A number of structures have been determined showing, for example, that $Cd_7P_4Cl_6$ and $Cd_4As_2I_3$ should be represented respectively as $(Cd^{2+})_7(P^{2-})_4(Cl^{1-})_6$ and $(Cd^{2+})_4(As^{3-})(As_2^{2-})(I^{1-})_3$.[144] A mixed phosphorus-arsenic compound Cd_4PAsBr_3 has been isolated from vapour transport with a stoichiometric mixture of $Cd_4P_2Br_3$ and $Cd_4As_2Br_3$;[145] its structure has been determined.

5.2.2 Bonds to Carbon

The +3 Oxidation State. The number of compounds containing multiple bonds between carbon and phosphorus continues to increase and both this section and the related section dealing with phosphorus in the +5 oxidation state (see page 314) begin with a discussion of these species. Phospha-alkene and -alkyne chemistry has been reviewed,[146] stressing that many of these compounds have stability comparable to that of the olefins.

Microwave spectroscopy for phosphaethene, $CH_2{:}PH$ which has a half-life of ca. 11 minutes and five of its isotopically substituted species gives the following parameters.[147]

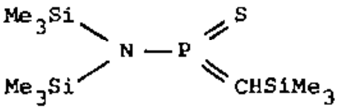
r(C-P)	1.671Å	$H-C-P_Z$	124.5°
r(P-H)	1.425Å	$H-C-P_E$	119.1°
r(C-H)	1.082Å	C-P-H	95.5°

Dehydrofluorination of $(CF_3)_2PH$ with trimethylamine probably proceeds via $CF_3P{:}CF_2$ but subsequent reactions give diphosphines such as $R(CF_3)P{\cdot}P(CF_3)_2$, where R = CHF_2 etc., and a new triphosphine $(CF_3)_2PCH_2P(CF_3)P(CF_3)_2$.[148] New methylenephosphines result from the reactions outlined in equations (35),[149] (36),[150] and (37).[151] The compounds are thermally stable liquids which may be cis-trans isomer mixtures. Spectroscopic investigation of the product from equation (35) points to the presence of one form, probably the trans isomer, and as for similar compounds it reacts either by addition across the P=C double bond or by oxidation of phosphorus to the +5 state. With sulphur in refluxing benzene, for example, the product is the methylenethioxophosphorane (<u>30</u>), with the thiaphosphirane (<u>31</u>) as a by-product.[152]

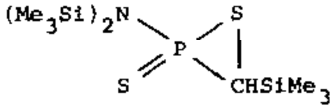
$$(Me_3Si)_2NPCl{\cdot}CH_2SiMe_3 \xrightarrow[-HCl]{LiN(SiMe_3)_2} (Me_3Si)_2N{\cdot}P{:}CHSiMe_3 \quad \ldots(35)$$

$$\begin{tikzcd} RPCl_2 \ + \ LiC(SiMe_3)_3 \arrow[r] & (Me_3Si)_3CPClR \arrow[d, "\Delta"', "-Me_3SiCl"] \\ R = t\text{-}Bu \text{ or } Ph & (Me_3Si)_2C{:}PR \end{tikzcd} \quad \ldots(36)$$

$$(Me_3Si)_3CPCl_2 \xrightarrow[-Me_3SiCl]{\Delta} (Me_3Si)_2C{:}PCl \quad \ldots(37)$$

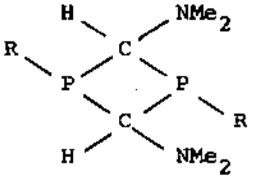


(<u>30</u>)



(<u>31</u>)

Reaction between $RP(SiMe_3)_2$, where R = Me, t-Bu, Ph or mesityl, and dimethylformamide is very slow but, in the presence of sodium hydroxide, elimination of $(Me_3Si)_2O$ to give $RP{:}CHNMe_2$ is complete in a few days.[153] The products with R = Me or Ph are unstable and readily dimerise to the corresponding substituted diphosphetan (32). Similar reactions with benzophenone in place of dimethylformamide are also catalysed by sodium hydroxide giving $RP{:}CPh_2$ compounds; the mesityl compound is stable but again the P-phenyl compound readily dimerises. A P-hydrido substituted methylidene phosphine results from the reaction in equation (38),[154] the intermediate (33) rearranging to the E and Z isomers



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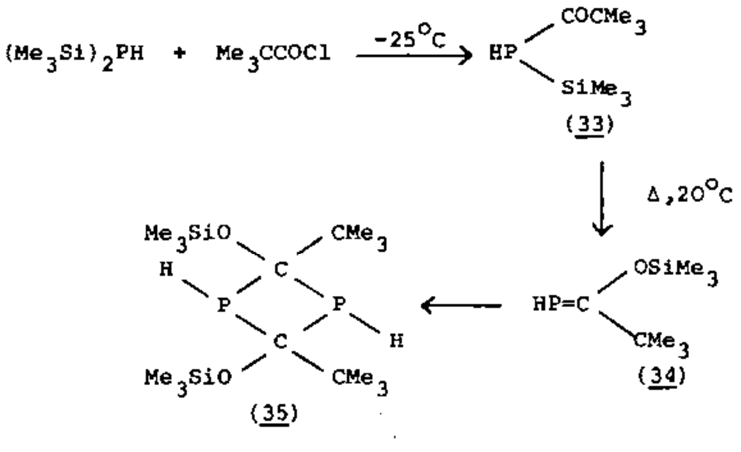


...(38)

of (34) on gentle heating. Compound (34) dimerises on standing in daylight to the diphosphetane (35), which has a centrosymmetric structure with long (1.903Å) P-C bond lengths.[155] This indicates substantial ring strain and in agreement the dimer is reconverted to the isomeric mixture of the monomer (34) in solution. Compound (33) after lithiation at low temperature reacts with Me_3SiCl to give $Me_3Si{\cdot}P{:}C(OSiMe_3)(CMe_3)$.[154]

The first coordination complexes with $(mesityl)P{:}CPh_2$ (≡L) as a ligand have been reported; among these are cis-$M(CO)_4L_2$ where M = Cr,Mo or W, trans-$RhCl(PPh_3)_2L$, cis-PtX_2L_2 where X = Cl,I or Me, and cis- and trans-$PtCl_2(PEt_3)L$.[156] The structure of a further compound $Cr(CO)_5L$ has been determined[157] showing that bonding is via the phosphorus atom.

Further information is also now available for compounds containing a phosphorus to carbon triple bond. One compound which is unusually stable results when the substituted propylidene phosphine, $(Me_3SiO)(Me_3C)C{:}PSiMe_3$ mentioned above,[154] is treated with a small amount of sodium hydroxide.[158] As in similar reactions, hexamethyl disiloxane is eliminated leaving 2,2-dimethylpropylidene phosphine $Me_3C{\cdot}C\vdots P$, a monomer in freezing benzene with a boiling point of 61°C. The phenyl analogue, $Ph{\cdot}C\vdots P$, is much less stable ($t_{\frac{1}{2}}$ ca. 7 mins. at 0°C) and has been obtained by high temperature vacuum pyrolysis of $(Me_3Si)PhC{:}PCl$.[159]

Electron diffraction and microwave spectroscopy give the following parameters for $Me_3C{\cdot}C\vdots P$.[160] This compound also gives

r(P-C)	1.536Å	C-C-C	109.0°
r(C-C)	1.473Å		
$r(C-CH_3)$	1.543Å		

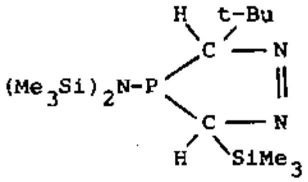
coordination complexes but, in contrast to those from phospha-alkenes, an X-ray structure for $Pt(PPh_3)_2(Me_3C{\cdot}C\vdots P)$ as a benzene solvate shows that the ligand bonded in a side-on fashion (P-C 1.67Å).[161] With $Co_2(CO)_8$, the ligand gives an oil formulated as $Co_2(CO)_6(Me_3C{\cdot}C\vdots P)$.

The synthetic uses of C-lithiated phosphines have been reviewed.[162]

A number of new two coordinate phosphorus cationic compounds have been isolated from chloride ion abstraction reactions by aluminium trichloride. Among these species are the nitrogen substituted cations $(Me_2N)t\text{-}BuP^+$, $Me_2N[(t\text{-}BuMe_2Si)_2N]P^+$, $Me_2N[(Me_3Si)_2N]P^+$, $[(Me_3Si)_2N]_2P^+$ and $ClP(Nt\text{-}Bu)_2P^+$,[163] and one compound containing two P-C bonds derived from diferrocenyl chlorophosphine.[164] After replacement of one chlorine atom in $(C_5Me_5)PCl_2$ using Me_3SiNMe_2, the resulting $(C_5Me_5)PCl(NMe_2)$ can be converted to the $(C_5Me_5)PNMe_2^+$ cation by treatment with $AlCl_3$ in dichloromethane.[165] A similar series of reactions take place with the corresponding arsenic derivative and a further arsenium salt results when $AlCl_3$ reacts with $(C_5Me_5)(C_5H_5)AsCl$.

Microwave data have been interpreted to show that the conformer present in vinyldifluorophosphine is that with a plane of symmetry containing the phosphorus atom and the vinyl group.[166] U.v. p.e.s. have been measured for a series of phenyl substituted phosphines to assess the extent of conjugation between the phosphorus lone pair and the π-system of the phenyl group;[167] similar data are also available for the t-butyl acetylene derivatives t-BuC⋮CPX_2 where X = H,Cl or NEt_2.[168]

Nitrogen elimination from the 1,2,4-diazaphospholine (36) leads to the phosphorinane (37) rather than the ylid isomer $(Me_3Si)_2NP(:CHt\text{-}Bu)(:CHSiMe_3)$.[169]



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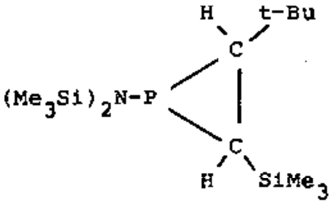


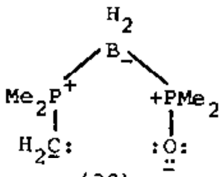
(37)

Preparation of di(o-tolyl)phosphorus chloride and its subsequent conversion to $(o\text{-tolyl})_2P\text{-}(CH_2)_n\text{-}P(o\text{-tolyl})_2$, where n = 1-4, 6 and 8, has been described.[170] At -35°C, tetramesityl diphosphine shows C_2 molecular symmetry with an anti-conformation and there are strong structural similarities with 1,1,2,2-tetramesityl disilane;[171] there is thus little evidence that the ground state structure is influenced by conjugation between the aryl π-system and the phosphorus lone pair.

α-Trimethylsilyl substituted methylphosphines $PhRPCH_2SiMe_3$ and $PhRPCH(SiMe_3)_2$ where R = Me,Et,i-Pr or Ph, have been synthesised[172] and undergo oxidative ylidation with carbon tetrachloride to give $PhRPCl{:}CR'(SiMe_3)$.

Electron diffraction and vibrational spectroscopic data for $Me_3P.BBr_3$ give r_g(P-B) as 1.946Å and assess the rotation barrier about the P-B bond as ca. 10 kcal mol^{-1}.[173] Vibrational data and force constant calculations are available for $Me_2PH.BX_3$, where X = Cl,Br or I, and for the deuterated compound.[174]

The novel B-P ligand (38) has been synthesised from BH_3.THF via $Me_3P.BH_2Cl$ in a multistep process;[175] complex formation with $BeCl_2$ is described. The stability of the $Ph_3P.SO_3$ complex is associated with the fact that, according to a recent structure determination,[176,177] the S-O bonds are shielded by the propeller like arrangement of P-Ph bonds. The molecule has three fold symmetry and contains a long (2.176Å) P-S bond.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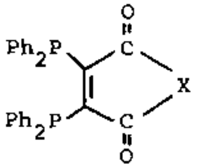
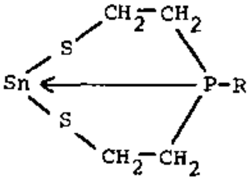
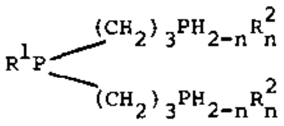
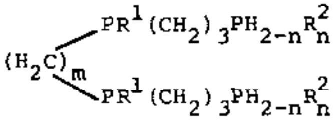

(39, X = O,S,CH_2 or NMe)


(40)

Triphenylphosphine reacts with the niobium azide complex, $Ph_4P(NbBr_5N_3)$, liberating nitrogen to give the phosphiniminato complex $Ph_4P(Br_5Nb:N:PPh_3)$.[178] The analogous tantalum complex reacts similarly and it is possible in these reactions to substitute $AsPh_3$ for PPh_3 when the products are $(Br_5M:N:AsPh_3)^-$ species.

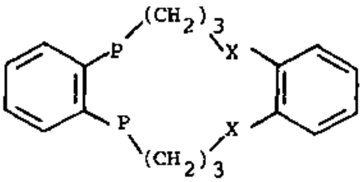
The formation of radical anions from bis(diphenylphosphino)-maleic anhydride (39) and its derivatives has been investigated;[179] the observed low reduction potentials are associated with the presence of π-orbitals which are extended to include the phosphorus atoms.


(41, R^1,R^2=Me or Ph ; n=1 or 2)

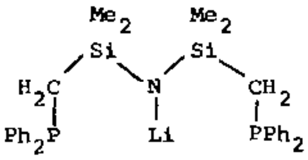

(42, R^1,R^2=Me or t-Bu m = 2 or 3, n = 1 or 2)

Monomeric stannylenes formulated as in (40) are obtained from reactions between tin(II) alkoxides and $RP(CH_2CH_2SH)_2$ according to n.m.r. and mass spectrometric data.[180]

Among the new polydentate P(III) ligands synthesised this year are the triphosphaalkanes (41),[181] the chiral tetraphospha analogues (42)[182] and a series of 14 membered ring compounds (43).[183] In the latter the donor groups are arranged to promote square planar coordination about a central metal atom. Finally a multidentate ligand (44), containing both hard and soft donor centres has been synthesised and used to prepare Ni(II) and Pd(II) complexes.[184]



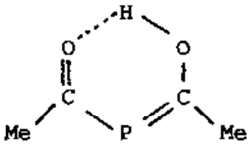
(43, X=PPh,NMe,O or S)



(44)

1:1 Stoichiometry is observed for the complexes formed between $M(SbF_6)_2$, where M = Sn(II) or Pb(II), and phosphines such as $Ph_2P(CH_2)_2PPh_2$, $PhP[(CH_2)_2PPh_2]_2$ and $MeC(CH_2PPh_2)_3$ in nitromethane solution.[185]

Triacetyl phosphine, $P(COMe)_3$, can be isolated when tris(trimethylsilyl)phosphine reacts with acetyl chloride at 0°C,[186] the compound on treatment with alcohols being converted to the di- and mono-acetyl phosphines, $HP(COMe)_2$ and $H_2P(COMe)$.[187] For the former there is an equilibrium with the enol tautomer (45) but the latter appears to solely in the keto form. Diphenylchlorophosphine reacts with sodium acetate,[188] sodium benzoate[189] or silver pentafluorobenzoate[189] to give the appropriately substituted acyloxy-phosphine (46), R = Me, C_6H_5 or C_6F_5). Analogous dimethylphosphorus compounds can be prepared using perfluorocarboxylic anhydrides,[188] but the products are generally thermally unstable and reorganise to the isomeric phosphine oxides (47).



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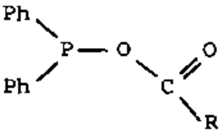

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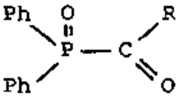


(47)

Phosphine carbonic esters have been prepared, see equations (39) and (40);[190] n.m.r. parameters are discussed and reactions with

$$R^1PH_2 \; + \; ClCOOR^2 \xrightarrow{K_2CO_3} R^1PHCOOR^2 \; + \; HCl \qquad ...(39)$$

$$R^1PH_2 \quad + \quad 2ClCOOR^2 \xrightarrow{K_2CO_3} R^1P(COOR^2)_2 \quad + \quad 2HCl \qquad \ldots(\underline{40})$$

R^1 = Ph or cyclohexyl
R^2 = Me, Et,Bu or Ph

MeI, etc. are described.

Vibrational spectra for the cyanomethylphosphine, $P(CH_2CN)_3$, have been assigned on the basis of C_3 symmetry and compared with data for $PX(CH_2CN)_3$ where X = O, S or Se.[191] The coordination characteristics of the ligands Ph_2PCH_2CN and Ph_2PCH_2COOEt have been investigated.[192]

Details are now available for the preparation of novel organocyanophosphide and mixed phosphorus(III) cyanide bromide anions. The former, given the formula $RP(CN)^-$, where R = Me, Et or Ph, are obtained from $RP(CN)_2$ and Et_4NCN in dichloromethane solution, via an adduct, $RP(CN)_3^-$, which readily loses cyanogen.[193] The bromide-cyanide species again require a large cation, e.g. R_4N^+ or a crown ether-sodium cation, for stabilisation and result from reactions in equations (41) to (44).[194] The missing $P(CN)Br_3^-$ could not be obtained and

$$P(CN)_3 \quad + \quad Br^- \longrightarrow P(CN)_3Br^- \qquad \ldots(41)$$

$$P(CN)_2^- \quad + \quad BrCN \longrightarrow P(CN)_3Br^- \qquad \ldots(42)$$

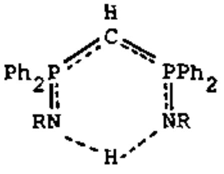
$$P(CN)_2^- \quad + \quad Br_2 \longrightarrow P(CN)_2Br_2^- \qquad \ldots(43)$$

$$PBr_3 \quad + \quad Br^- \longrightarrow PBr_4^- \qquad \ldots(44)$$

although $P(CN)_4^-$ can be observed at low temperatures it decomposes via reductive elimination of cyanogen to give $P(CN)_2^-$. Full X-ray structures are reported for $P(CN)_3Br^-$ and $P(CN)_2Br_2^-$.

<u>The +5 Oxidation State</u>. Species containing phosphorus-carbon multiple bonds are considered first. Methanidobis(phosphonium) salts, $[(R^1R^2N)Ph_2P\overset{\ldots}{=}CH\overset{\ldots}{=}PPh_2(NR^1R^2)]Cl$ where R^1 = Me, Et, n-Pr or Ph and R^2 = H, Me, Et, n-Pr can be readily obtained from reactions between $Ph_2P{\cdot}CH_2{\cdot}PPh_2$ and carbon tetrachloride in the presence of the appropriate amine.[195,196] Dehydrohalogenation with sodium hydride gives diaminocarbodiphosphoranes

$(R_2N)Ph_2P{:}C{:}PPh_2(NR_2)$ with secondary amine derivatives,[196] but imido compounds (48) from precursors with primary amine functions.[195] A cyclic carbodiphosphorane (49) has been prepared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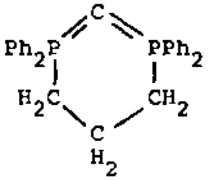
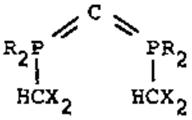

(49)

from bis(diphenylphosphino)methane and 1,3-dibromopropane via a diphosphonium salt and transylidisation with $Me_3P{:}CH_2$.[197] From X-ray diffraction this compound contains the smallest P-C-P angle (116.7°); the P-C distances are 1.645 and 1.653Å.[198] For comparison, the P-C-P angle and the P-C bond length in $MePh_2P{:}C{:}PPh_2Me$ are 121.8° and 1.648Å respectively.[198]

Substituent effects on isomerisation in the carbodiphosphorane (50)-[(phosphoranylidene)methyl]methylene phosphorane (51) system have been investigated both by n.m.r. spectroscopy and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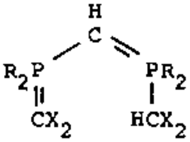
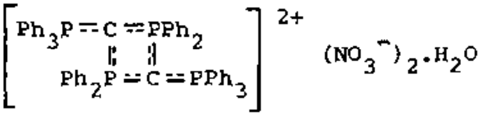
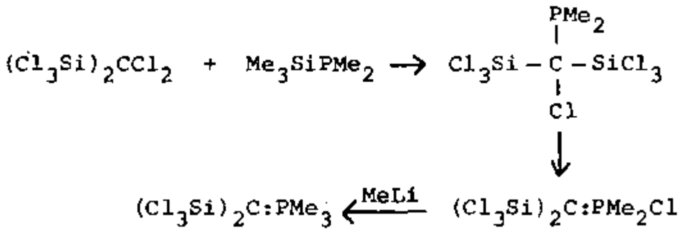

(51)

preparative methods;[199] compounds containing benzyl or fluorenyl substituents, for example, exist in the conjugated ylid form (51) while for those with methyl or phenyl substituents only isomer (50) is observed.

The relationship between triboluminescence and the two phases of hexaphenylcarbodiphosphorane has been investigated, showing that triboluminescence is associated with crystallisation in a polar space group.[200] The structure has been determined for compound (52), which contains a stabilised diphosphacyclobutadiene unit.[201] The cation,which is centrosymmetric, shows complete delocalisation of both the charge and double bond character.


(52)

Compounds which rearrange to ylids are the products when perchlorinated carbosilanes react with either Me_3SiPMe_2 or $LiPMe_2$.[202] Some of the reactions investigated are summarised in equations (45) and (46); full X-ray structures for compounds (53),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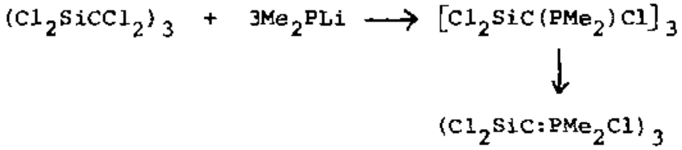
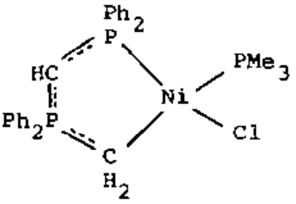

(55) ...(46)

(54) and (55) show short P-C and Si-C bonds equivalent to bond orders of ca. 1.33.

Treatment of the ylid $MePh_2P{:}CH{\cdot}PPh_2$ with $Na(K)NH_2$ generates the new ligand $(H_2CPh_2CHPPh_2)^-$ which on displacement of trimethylphosphine from $(Me_3P)_2NiCl_2$ gives the new complexes (56) and (57).[203] A platinum ylid complex cis-$[Pt(PPh_3)_2(CH_2PPh_3)Cl]Cl$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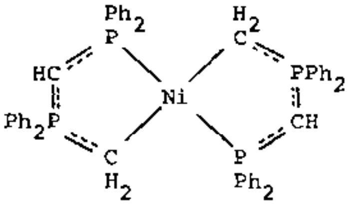
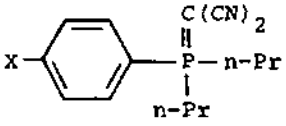

(57)

has also been isolated.[204] Crystal structures are available for two phosphonium dicyanomethylides (58, X = OMe[205] and NMe_2),[206] which show P-C bond lengths of 1.722 and 1.729Å respectively.



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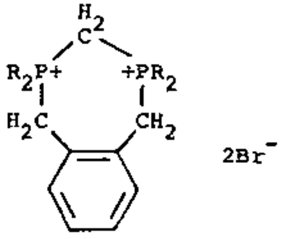
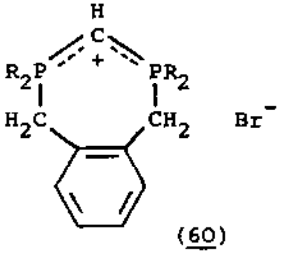


(59)

Three mixed cyclopropylmethyl phosphonium salts, $[Me_n(c\text{-}C_3H_5)_{4-n}P]^+X^-$ where n = 1 to 3, and the corresponding ylids, $Me_n(c\text{-}C_3H_5)_{3-n}P{:}CH_2$ where n = 0 to 2 have been synthesised.[207] The analogous benzyl phosphonium salts, $[R_2P(CH_2Ph)_2]^+Br^-$ where R =Me,Ph or $PhCH_2$, can also be converted to the corresponding ylids.[208] Reactions of the bis(phosphino)methanes, $Me_2P{\cdot}CH_2{\cdot}PMe_2$ and $Ph_2P{\cdot}CH_2{\cdot}PPh_2$, with 1,2-bis(bromomethyl)benzene give the corresponding diquaternary salts (59) which on treatment with a strong base yield mono- (60) and di-ylids (61).[209]



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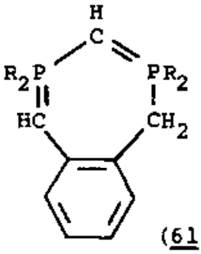


(61)

Finally a series of highly fluorinated phosphonium salts and their ylids, including $(n\text{-}C_6F_{13}PMe_3)I$ and $R_3P{:}CHC_6F_5$, has been prepared.[210]

Oxiranes and thiiranes react with triorganophosphorus dichlorides to yield isolable chloro-(thio)alkoxyphosphonium chlorides $[R^1_3P{\cdot}X{\cdot}CHR^2CH_2Cl]^+Cl^-$ where X = O or S and R^2 = H, Me or CH_2Cl.[211]

X-ray structures for tris(2-cyanoethyl)phosphine oxide,[212] sulphide[213] and selenide[213] show a different packing pattern for the oxide; the sulphide and selenide are isostructural.

5.2.3 Bonds to Halogens

The +3 Oxidation State. Matrix isolation techniques have yielded the first information for the PF_4^- ion, prepared from a gas phase reaction between PF_3 and CsF;[214] i.r. spectroscopy suggests that the symmetry is no higher than C_{2v} and a structure similar to that of SF_4 is thought most probable. Replacement of CsF by CsCl leads to PF_3Cl^- but it was not possible to obtain either PCl_3F^- or PCl_4^-.

Phosphorus trifluoride will react with the normally inert SF_6 at high temperatures and pressures to give PF_5 and SPF_3.[215]

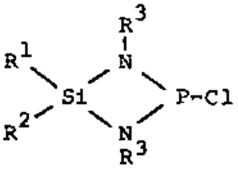
Electron diffraction measurements on a number of substituted phosphorus (III) fluorides including $PF_2(NCSe)$,[216] $PF_2{\cdot}N(SiH_3)_2$,[217] $(PF_2)_2{\cdot}NSiH_3$,[217] and $(PF_2)_2NGeH_3$[218] have been reported. Coordination about nitrogen in the last three compounds is planar with longer Si(Ge)-N bonds than in other silyl or germyl amines. This shows that PF_2 groups have a greater tendency than the $Si(Ge)H_3$ group to accept electron density from the lone pair p-orbital on nitrogen.

Exchange reaction between the mixed fluoride bromide, PF_2Br, and Me_2PSiMe_3 or $P(SnBu_3)_3$ lead to respectively the unstable diphosphine, PF_2PMe_2, and a triphosphine, thought to be $P(PF_2)_2(SnBu_3)$.[219] Platinum complexes, singly bridged by PF_2 groups have been isolated from reactions between PF_2X, where X = Cl, Br or I, and $PtHX(PEt_3)_2$,[220] and complexes containing coordinated difluorothio- and difluoroseleno-phosphonate groups of the type $[Pt(PEt_3)_2(PF_2Y)]$, where Y = S or Se, are the products when $PF_2H(Y)$ reacts with trans-$PtH(PEt_3)_2Cl$.[221]

The first example of a strongly π-accepting, tridentate ligand has been isolated from an unusual reaction between $PhN(PF_2)_2$ and $(MeCN)_3Mo(CO)_3$.[222] The initial product is $(OC)_3Mo(PF_2{\cdot}NPh{\cdot}PF_2)_3$ which loses two mols of PF_3 to give tris[phenyl(difluorophosphino)-amino]phosphine $P(NPh{\cdot}PF_2)_3$.

Recent experiments show that PCl_3 can be completely fluorinated in ca. 80% yield by sodium fluoride in refluxing acetonitrile.[223]

A series of reactions between non-metal halides and lithium aminofluorosilanes, $R^1R^2SiF(NR^3Li)$ where R^1=R^2=Me, t-Bu or Ph and R^3 = t-Bu or mesityl, leads initially to unstable substituted products but halosilanes are subsequently lost with formation of cyclic compounds.[224] For example, with PCl_3 the product is compound (62) while with AsF_3 it is possible to obtain either (63) or (64) depending on the ratio of the reactants. Monomeric



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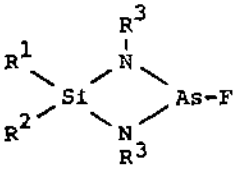

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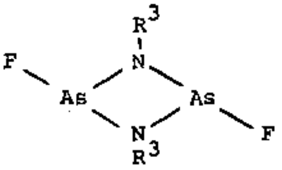


(64)

entities can also be obtained, particularly when bulky groups are attached.

Dichloro(methyl)phosphine is now readily available and a recent review considers its use in preparing a range of phosphonic, phosphinic and phosphonous acid derivatives.[225]

P_2Br_4 is unknown as a free molecule but it has recently been stabilised in the carbonyl complex, $(OC)_5Cr(PBr_2PBr_2)Cr(CO)_5$.[226] The compound results either from photolysis of a $Cr(CO)_6$-PBr_3 mixture in THF solution or by HBr replacement of the amine groups in $(OC)_5Cr[P(NEt_2)_2P(NEt_2)_2]Cr(CO)_5$. An improved synthetic route to a phosphorus-mesoporphyrin uses a PBr_3-pyridine intermediate with the free base mesoporphyrin dimethyl ester;[227] a similar technique can be used to prepare the analogous phosphorus(III) phthalocyanine.

Replacement of the iodine atoms in P_2I_4 by AgCN, PCl_3 and PBr_3 has been followed by ^{31}P n.m.r. spectroscopy;[228] with the first reagent, evidence was obtained for $P_2I_{4-n}(CN)_n$ where n = 1 to 4 and all mixed $P(I/CN)_3$ species. With the trihalides (PX_3), evidence is available for P_2I_3X and $P_2I_2X_2$ but, whereas only the symmetrically substituted isomer is present for $P_2I_2Cl_2$, the corresponding bromide gives both isomeric forms.

The +5 Oxidation State. A salt containing the $PH_2F_2^+$ cation has been isolated from a PH_2F_3-AsF_5 reaction and although the product cannot be stored in glass apparatus there is no noticeable decomposition in polyethylene after several days.[229]

According to powder X-ray data, the "hexahydrates" of HMF_6, where M = P, As or Sb, are probably isostructural and recent ^{19}F n.m.r. spectroscopy points to the presence of one molecule of HF per MF_6^- anion.[230] The formulae should then be $HMF_6 \cdot HF \cdot 5H_2O$, with disordered MF_6^- ions occupying clathrate cages formed by hydrogen bonding between H_2O, H_3O^+ and HF. The dimethylacetamide (L) complexes, $HMF_6.2L$ for M = P, As or Sb, contain the hydrogen-bonded cation $(DMA)_2H^+$ on the basis of X-ray data for the isomorphous phosphorus and antimony compounds.[231] The O...O distances in the cation are 2.419 and 2.443Å respectively while the MF_6^- anions are disordered with high thermal motion.

Substituted fluorophosphonium salts, such as $R_3PF^+Br^-$ for R = Et, i-Pr or n-Bu and $Me_n(R_2N)_{3-n}PF^+Br^-$ for R = Me and n = 0 or 1 or R = Et and n = 0, are products from respectively R_3PBr_2-R_3PF_2 reactions in dichloromethane and fluorination reactions between $Me_n(R_2N)_{3-n}PBr_2$ and sodium fluoride.[232] Compounds of the type $R_3PF^+PhPF_5^-$, where R = i-Pr or n-Bu, can be isolated from fluoride ion transfer reactions in dichloromethane; full n.m.r. data are available for all these compounds.

Direct fluorination to phosphorus(V) species has been observed for the first time with the phenoxy-phosphorus(III) derivatives $(PhO)_2PR$, where R = Me, Ph or F, $(PhO)_3P$ and $PhOPF_2$.[233] Similar results were obtained with a number of alkoxy derivatives.

Bis(phosphonic difluorides), $F_2P(O)$-X-$P(O)F_2$, where X = CH_2, CH_2CH_2, trans-CH:CH, are obtained on reaction of the corresponding chlorides with arsenic trifluoride;[234] conversion to the bis(tetrafluorophosphoranes), F_4P-X-PF_4 can be achieved by treatment with SF_4.

Reactions between $P_2O_3F_4$ and V_2O_5 at the boiling point of the former lead to $VO_2PO_2F_2$.[235]

Although treatment of PCl_5 with either lithium or sodium azide leads to $N_3P_3Cl_6$, the pyridine adduct of PCl_5 gives the series of mixed species $PCl_{5-n}(N_3)_n.py$, where n = 1 to 4, according to a ^{31}P n.m.r. study.[236] Similar reactions with a number of phosphorus-catechol species are also described.

Hydrogen dichloride salts of the phosphorus(V) cations $R^1R^2PCl_2^+$ and $R^1PCl_3^+$, where R^1 = Me or Ph and R^2 = $MeOC_6H_4$, together with the dinuclear species $[(MeOC_6H_4)PCl_2 \cdot X \cdot P(MeOC_6H_4)Cl_2]^{2+}$, where X = $(CH_2)_4$ or 1,4-C_6H_4, have been prepared as moisture sensitive solids.[237] Crystal structures are available for $[(MeOC_6H_4)MePCl_2]HCl_2$ and $[(MeOC_6H_4)PCl_3]HCl_2$ showing the presence of symmetrical HCl_2^- anions.[238] Although the monophosphorus species on treatment with hydrogen bromide give $R^1R^2PBr_3$ and R^1PBr_4, the diphosphonium compound yields $[RPBr_2 \cdot X \cdot PRBr_2][HBr_2]_2$.[237]

^{31}P n.m.r. shifts for $OPCl_3$ and a range of organophosphorus(V) compounds in liquid hydrogen chloride solution are, in general, downfield in comparison with those in non-acidic media, in agreement with (partial) protonation of the phosphoryl oxygen atom.[239]

Phosphoryl chloride when treated with alkylaluminium dichlorides can be converted directly to alkyl phosphonic acid derivatives.[240]

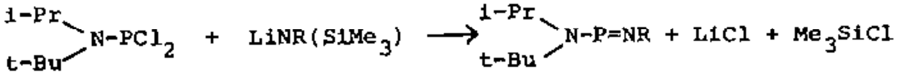
$Cl_3NO_2P_2$, previously obtained from the $POCl_3$-NH_4Cl reaction, on refluxing with PCl_5 in phosphoryl chloride gives the cyclochlorophosphazenes, $(NPCl_2)_n$, where n = 3 to 7, and the monomeric $Cl_2P(O)(NPCl_2)Cl$ as products soluble in n-heptane.[241] The insoluble residue consists of $Cl_2P(O)(NPCl_2)_nCl$ where n = ca. 5.

The molybdenum atom in $POCl_3.MoO_2Cl_2$, which has a polymeric chain structure, is in distorted octahedral coordination to one oxygen and two chlorine atoms as terminal ligands, the $OPCl_3$ molecule which is trans to the terminal oxygen, and two bridging oxygen atoms.[242] A Raman investigation of the laser solution $POCl_3$-$SnCl_4$-$Nd(H_2O)_n^{3+}$ shows a complicated mixture with lines that can be associated with coordinated $POCl_3$, $P_2O_3Cl_4$ molecules and $PO_2Cl_2^-$ ions.[243] E.p.r. data have been obtained for the polymeric $[Cu(O_2PCl_2)_2]_n$.[244]

Phosphorus pentabromide, sublimed from 273K to 15K, gives a Raman spectrum interpreted as showing the PBr_4^+ and Br_3^- ions together with PBr_3.[245] On warming, the Br_3^- and PBr_3 bands disappear suggesting a solid phase reaction leading to $PBr_4^+\ Br^-$. There is no evidence for covalent PBr_5 with a trigonal bipyramidal structure. The thermal decomposition of PBr_5 has been investigated by noting the temperature dependence of the pressure of decomposition products.[246]

5.2.4 Bonds to Nitrogen

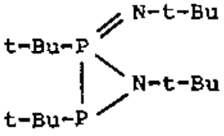
The +3 Oxidation State. Compounds containing P-N double bonds are considered first. New monomeric phosphazenes with coordination number two for phosphorus have been isolated following the reaction in equation (47).[247] The intermediate, (i-Pr)(t-Bu)N·PCl·NRSiMe$_3$,



$$(i\text{-}Pr)(t\text{-}Bu)N\text{-}PCl_2 + LiNR(SiMe_3) \longrightarrow (i\text{-}Pr)(t\text{-}Bu)N\text{-}P{=}NR + LiCl + Me_3SiCl$$

R = i-Pr, t-Bu or SiMe$_3$ ...(47)

can be isolated only when R = i-Pr. The P-t-butyliminophosphine, t-BuP:Nt-Bu, isolated by pyrolysis of t-BuPF·NLit-Bu as a yellow liquid, susceptible to both oxidation and hydrolysis, is stable for some days at -40°C but at 0°C it dimerises to the azadiphosphiridine (65).[248] Loss of trimethylchlorosilane from t-BuPCl.N($SiMe_3$)t-Bu is also a route to -P:N- compounds. Tri-



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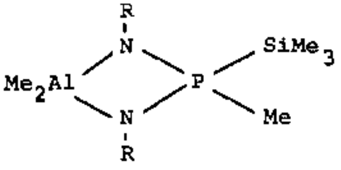

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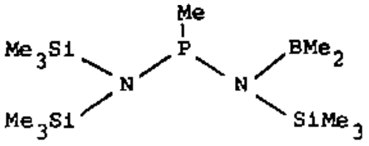
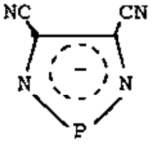


(67)

methyl-boron and -aluminium react with such iminophosphines by different routes.[249] The latter with (Me_3Si)RN·P:NR, where R = t-Bu or Me_3Si, gives the heterocycle (66) but, while the analogous boron compound is produced with BMe_3 and the t-Bu substituted starting material, an acyclic derivative (67) results with the Me_3Si substituted reactant.

Condensation at room temperature between $P(NMe_2)_3$ and diamino-maleodinitrile (H_2N)(CN)C:C(CN)(NH_2) gives the anion (68) containing a two-coordinate phosphorus atom, and this yields the neutral N-methyl derivative (69) on reaction with methyl iodide.[250] An X-ray structure of the 1:2 complex from $Cr(CO)_6$



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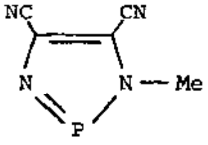
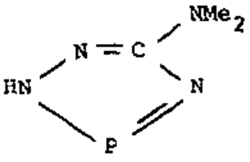


(69)

and the triazaphosphole (70) indicates the formation of a "tetramer" with the structure shown in (71),[251] while a related



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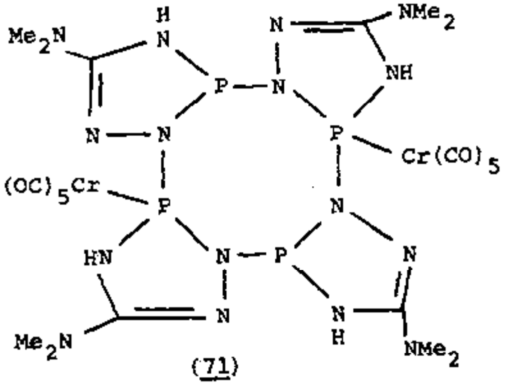
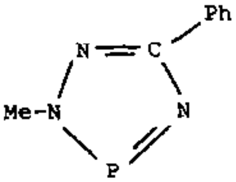


(71)

phosphole (72) on reaction with azodicarboxylic esters probably gives initially the spirophosphazene (73), which dimerises to the pentacyclic product (74) that is actually isolated.[252]



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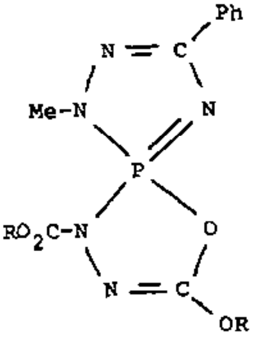

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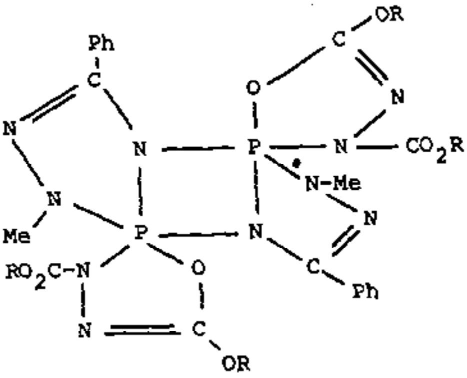
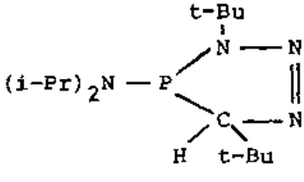


(74)

Cycloaddition between diisopropylamino(t-butylimino)phosphine and 1-diazo-2,2-dimethylpropane gives compound (75), which loses nitrogen at 40°C yielding the iminomethylene phosphorane (76).[253]



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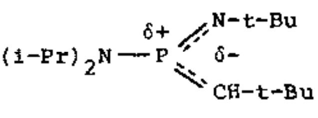

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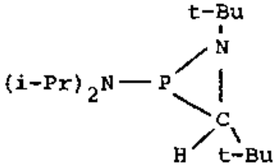


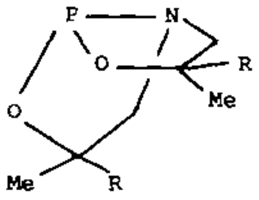
(77)

Isolation by rapid distillation is possible but its isomerisation to (77) can be followed by ^{31}P n.m.r. spectroscopy.

Ammonolysis of $(CF_3)_2PH$ leads to $CH_2F(CF_3)PNH_2$, $CHF_2(CF_3)PNH_2$ and $(CF_3)_2PNH_2$, which can be converted to the corresponding chlorides on treatment with hydrogen chloride.[254]

The coordinating ability of the aminophosphine ligands (78), in which the nitrogen atom is forced to remain pyramidal, has been assessed in the formation of a series of molybdenum and tungsten complexes $M(CO)_{6-n}L_n$ where n = 1 to 3.[255] From n.m.r. data it appears that coordination is via the phosphorus atom only. $Fe(CO)_4$ complexes containing coordinated $(R_2N)_2PCl$ groups (R = Et or i-Pr) have recently been isolated from direct reactions with $Fe_2(CO)_9$ in hexane solution.[256] In addition, the following compounds were also isolated: $Me_2NPCl_2.Fe(CO)_4$, $(Me_3Si)_2NPCl.Fe(CO)_4$ and $t\text{-}Bu(Me_2N)PCl.Fe(CO)_4$; treatment with $AlCl_3$ leads to salts containing the coordinated phosphenium ion and $AlCl_4^-$ (see also references 163-165).

A new four membered P-N-S ring system (79) has been obtained from a reaction between phosphorus trichloride and the sulphamide derivative $(t\text{-}BuNH)_2SO_2$.[257] The chlorine atom can be



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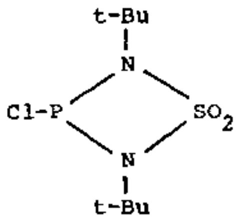


(79)

substituted by fluorine or NMe_2 and with sodium the corresponding diphosphine is produced.

Analysis of the variable temperature n.m.r. spectra for the diphosphinoamines, $(X_2P)_2NR$ where X = Ph and R = H, Me, Et or i-Pr, X = Cl and R = Me, t-Bu or CH_2t-Bu and X = F and R = Me or t-Bu gives values of $^{2}J_{PNP}$ in the range -23.9 to 731.9 Hz, the sign and magnitude being related to the local symmetry of the P-N-P skeleton.[258]

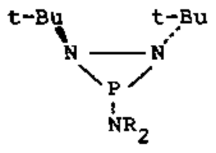
Previously unknown methylamino-fluoroalkylphosphites have been prepared from the reactions in equations (48) and (49).[259]

$$ROPFCl + (Me_3Si)_2NMe \longrightarrow MeN(SiMe_3)PFOR + Me_3SiCl \qquad ...(48)$$

$$2ROPFCl + (Me_3Si)_2NMe \longrightarrow MeN(PFOR)_2 + 2Me_3SiCl \qquad ...(49)$$

R = Me or Et.

The diazaphosphiridine (80) can be obtained from 1,2-bis(t-butyl)hydrazine and R_2NPF_2, where R = i-Pr or $SiMe_3$, as an air stable solid;[260] a crystal structure of the i-propyl compound shows the t-butyl groups in trans-positions with endocyclic P-N lengths of 1.709 and 1.737Å. These species, stabilised kinetically by the exocyclic groups, rearrange slowly in toluene at 50°C to the valence isomers (81). Related azadiphosphiridines (82) where R=$SiMe_3$ or $CHMe_2$, can be prepared



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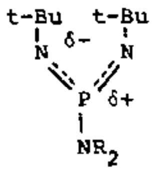

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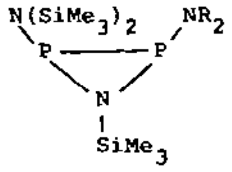
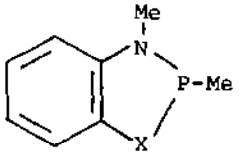


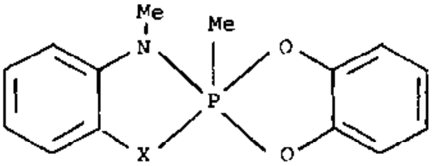
(82)

by either the base induced loss of HX from a phosphanylaminophosphine, $(Me_3Si)_2NPH{\cdot}NSiMe_3{\cdot}PX(NR_2)$ or by treatment of an iminophosphoranylphosphorane, i.e. $(Me_3Si)_2N{\cdot}PH(:NSiMe_3){\cdot}PXNR_2$ with methyl lithium.[261,262]

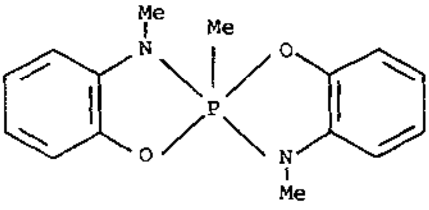
Transamination reactions lead to compounds (83, a X=O and b X=NMe), which on treatment with o-benzoquinone yield the corresponding spirocyclic derivatives (84).[263] If (83a) is treated with aluminium trichloride, it disproportionates to (85) while treatment of (83b) with bromine and N,N'-dimethyl-o-phenylenediamine gives (86), with a trigonal bipyramidal structure.[264]



(83a X=O, b X=NMe)



(84a X=O, b X=NMe)



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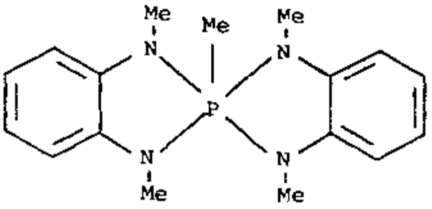


(86)

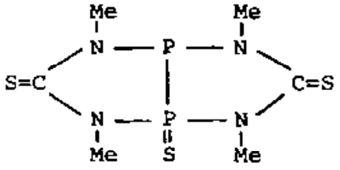
MNDO-SCF calculations for $(Me_2N)_3P$ point to greatest stability for the conformer with C_3 symmetry and dihedral angles of 61° between the phosphorus and nitrogen lone pairs,[265] and in this context the structures of the iron carbonyl complexes $(Me_2N)_3P{\cdot}Fe(CO)_4$ and $[(Me_2N)_3P]_2{\cdot}Fe(CO)_3$ are of interest.[266] Both compounds show trigonal bipyramidal geometry about iron with the phosphine groups in axial positions. In the first compound the donor has close to C_3 symmetry with two NMe_2 groups close to planarity and twisted in the same direction, the third group is more tetrahedral. The ligands in the disubstituted complex are quite different, one being very similar to that above while in the second the ligand conformation approaches that of the C_s form.

^{13}C n.m.r. spectra have been reported for $P(NR_2)_3$ and $PX(NR_2)_3$, where X = O, S or Se and R_2 = Me, Et or morpholine, piperidine or pyrrolidine residues,[267] while photoelectron spectra for related phosphorus(III) species have been interpreted in terms of possible conformations.[268]

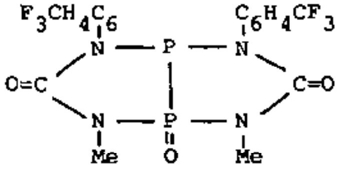
Neutral compounds containing six-coordinate phosphorus atoms chelated by carbamato and thiocarbamato groups can be obtained by insertion of CO_2, COS and CS_2 into the P-N bond in $Me(CF_3)PNMe_2$.[269] Detailed n.m.r. data are given together with an X-ray structure for $Me(CF_3)PO_2CNMe_2$.

On thermal decomposition complexes of the type $(OC)_5MP(NH_2)_3$, where M = Cr or Mo, give derivatives of the unknown $P_4(NH)_6$ with the formula $[(OC)_5MP]_4(NH)_6$.[270] The metal carbonyl groups can be displaced in the molybdenum compound on treatment with sulphur giving the previously unknown species $P_4S_4(NH)_6$ but desulphurisation of the latter was not possible. Hydrazinophosphorus(III) compounds such as $P(NHNH_2)_3$ and $P(NHNMe_2)_3$ are unstable but, following the reactions above, they have been stabilised in the chromium carbonyl derivatives which result when $Cr(CO)_5PCl_3$ is solvolysed with either hydrazine or N,N-dimethylhydrazine.[271]

New compounds containing a P-P bond between phosphorus atoms in the +3 and +5 oxidation states have been reported. One such compound (87) results from the reaction between phosphorus trichloride and N,N'-dimethylthiourea,[272] while compound (88) is obtained on reaction with the silylurea, $3\text{-}CF_3C_6H_4(Me_3Si)N{\cdot}C(O){\cdot}N(SiMe_3)Me$.[273] The P-P bond lengths are

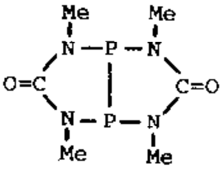


(87)



(88)

2.191 and 2.172Å respectively. In contrast, the PCl_3-$[(Me_3Si)Me]_2CO$ reaction leads to the analogue (89), with two three coordinate phosphorus atoms.[273] This can be oxidised by potassium permanganate or sulphur giving (90) and (91)



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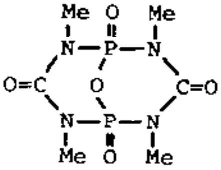
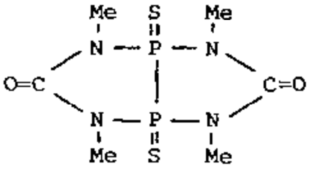


(90)

respectively; an X-ray structure is available for the former.[274] The diazaphospholidinone-oxide (92) has been isolated from pyrolysis of the P(III)-P(V) spiro compound (93).



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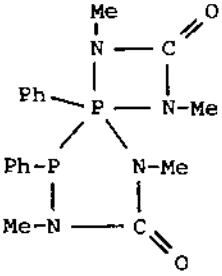

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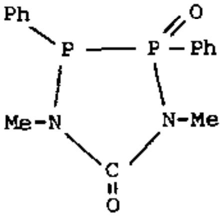
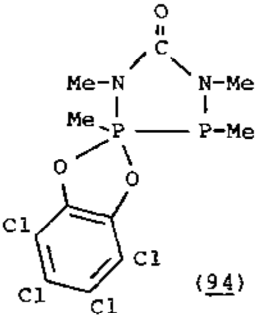


(93)

The first example of a compound containing a bond between phosphorus atoms in four- and five-fold coordination has been isolated from a series of reactions in which the λ^5-λ^3 compound (94) is an intermediate.[275] Addition of sulphur then gives the novel compound (95) and from an X-ray structure the geometry at the five-coordinate centre is midway between the trigonal bipyramidal and square pyramid alternatives.



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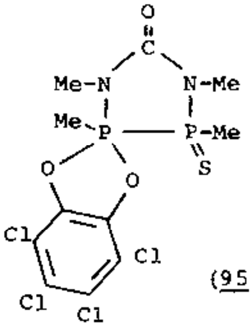
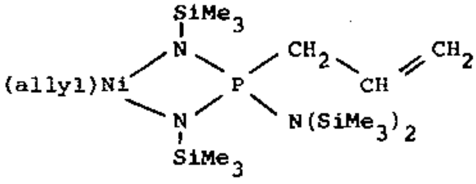


(95)

The +5 Oxidation State. A new ethylene polymerisation catalyst (96) is produced in the reaction between the amino-bis(imino)-phosphorane $(Me_3SiN:)_2PN(SiMe_3)_2$ and bis(allyl)nickel;[276] a similar palladium complex has also been isolated for which an X-ray structure was carried out. The reactivity of



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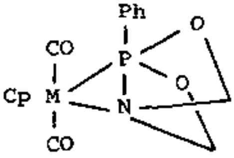


(97, M = Mo or W)

trichlorophosphazophosphorus dichloride, $Cl_3P:NPCl_2$, towards SbF_3, SO_2, S_8, $n\text{-}Bu_3P$, etc has been assessed[277] and a reinvestigation of the ^{31}P n.m.r. spectrum of its phosphoryl derivative, $Cl_3P:NP(O)Cl_2$, shows a single AB type spectrum in contrast to the more complex spectrum reported previously.[278]

The structure of the unusual transition metal-aminophosphoranide complex (97) contains, in addition to a three membered MPN ring, a trigonal bipyramidal phosphorus atom with oxygen atoms in equatorial positions.[279]

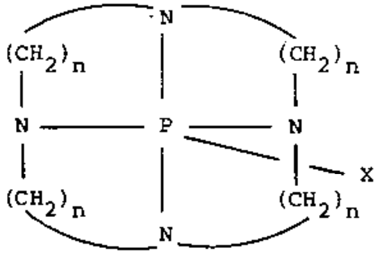
Dimethylformamide catalyses the reaction between thionyl chloride and $(Me_2N)_3PO$ to give the chlorophosphonium chlorosulphite $[(Me_2N)_3PCl]^+SO_2Cl^-$, which is a mild condensation reagent for peptide synthesis.[280]

Structures for two phosphinic amides, $Ph_2P(O)NHCH_2CH_2Ph$ and $Ph_2P(O)NMeCH_2CH_2Ph.H_2O$, show P-N bond lengths of 1.64Å indicating a degree of π-bonding but this is not sufficient to reduce the basicity of the nitrogen atoms which are markedly non-planar.[281] A slightly shorter P-N bond length 1.630Å has been observed in $Ph_2P(O)NH_2$.[282]

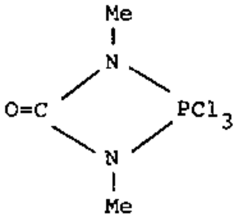
Complex formation with di- and mono-hydrazido-thiophosphoric acid derivatives, $(H_2NNH)_2P(S)OPh$ (L) and $(H_2NNH)P(S)(OPh)_2$ (L'), leads to compounds of the type ML_2Cl_2, NiL'_4Cl_2 and CdL'_2Cl_2 etc.[283]

Full details are now available on the preparation and structure of the P(V)-P(V) compound, bis(cyclenphosphorane) $(C_8H_{16}N_4)_2P_2$,[284] illustrated in last year's report (see p.319).

This type of ring system is also involved in the series of polycyclic tetrakis(substituted amino)phosphonium compounds (98), which can be obtained with peripheral ring sizes varying between



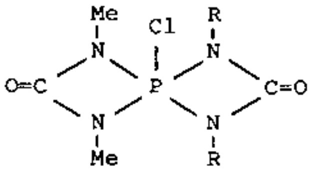
(98, n = 2 or 3; X = H, F, Cl or I).



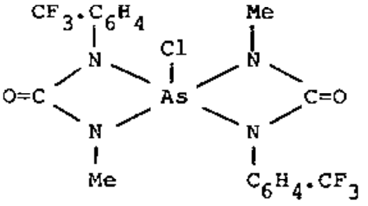
(99)

12 and 16.[285] In the series of fluorides (98, X = F), ^{19}F n.m.r. data show that there is no spin coupling in compounds with peripheral ring sizes of 15 and 16 and, unusually, the fluorine must be considered as ionic.[286]

Reaction of the phosphorus(V) compound (99) with an N,N'-disubstituted urea leads to the spirocyclic derivative (100);[287] the related arsenic(V) compound (101) is the product



(100, R = Me or Ph)

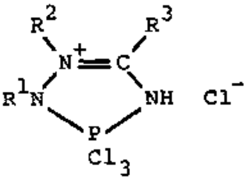


(101)

from $AsCl_3$ and the substituted urea, $OC[N(SiMe_3)(C_6H_4CF_3)]_2$.

Condensation between PCl_5 and amidrazone hydrohalides, $[(R^1NH)R^2N{:}CR^3(NH_2)]X$, leads to 1,2,4,3$\lambda^5$-triazaphospholes such as (102),[288] and with (102, R^1 = H, R^2 = Me) there is further HCl loss followed by dimerisation giving (103). From a full crystal structure for (99, R^3 = Ph) the geometry about phosphorus is half way along the Berry coordinate between the trigonal bipyramidal and square pyramidal extremes.[289] The structure of the corresponding difluoride has also been determined.

P-N Ring Compounds. The PCl_3-aniline reactions gives the substituted diazadiphosphetidine (104), which is also a thermolysis product of $[(PhNH)_2P]_2NPh$.[290] X-ray diffraction of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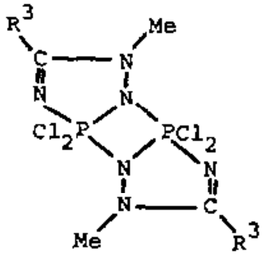
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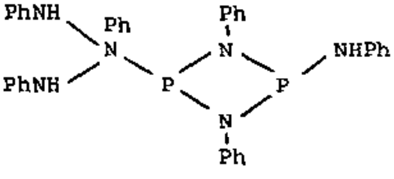
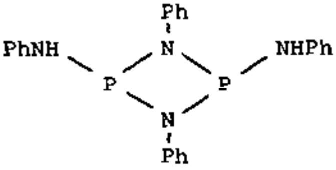

(104)

the ethanol solvate shows an almost planar P_2N_2 ring with the substituents at phosphorus in cis positions. On heating to >80°C, the trimer (104) is slowly converted into the dimer (105). Complete substitution of bromine atoms in the cyclotriphosph(III)-azane (106) occurs on reaction with alcohols, phenols and the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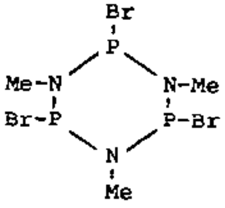
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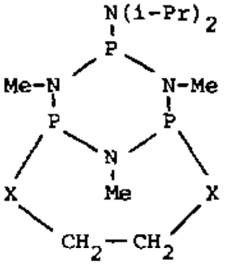
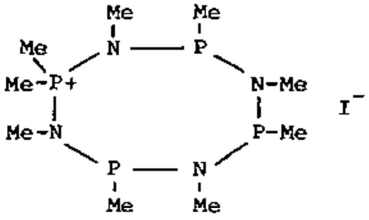

(107, X = NMe or O)

secondary amines, Me_2NH, Et_2NH and PhMeNH;[291] with di-isopropylamine only one halogen is substituted but the remainder can be removed by either N,N'-dimethylethylenediamine or tetramethylethylene glycol to give the bicyclic compounds (107). Reactions of the related tetrameric compound $(MePNMe)_4$ with methyl iodide in a 1:1 ratio at -70°C and with an excess at 20°C lead to products (108) and (109) with respectively one and two phosphorus(V) atoms.[292] From an X-ray structure P(V)-N distances are 1.647 and 1.657Å compared with values of 1.751 and 1.746Å for the P(III)-N bonds in the centrosymmetric cation (109).



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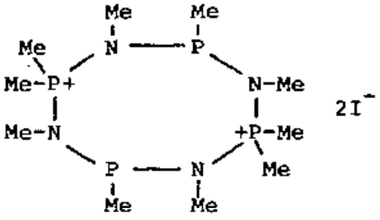

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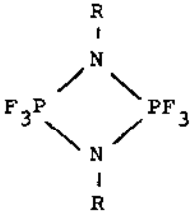
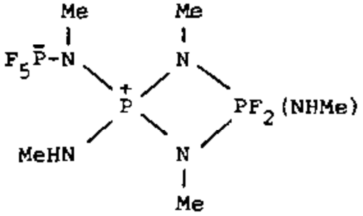


(110, R = Me,Et,n-Pr, n-Bu or i-Pr).



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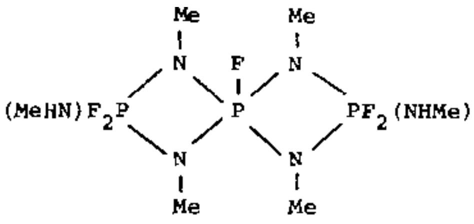

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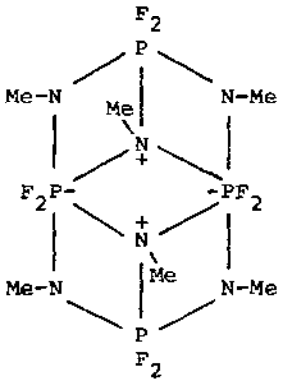


(113)

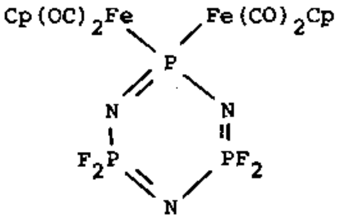
One or two fluorine atoms in (110), the latter giving the non-geminal isomer, can be replaced on treatment with N-trimethylsilylmethylamine; in addition two by-products (111) and (112) have been isolated.[293] A new synthetic route to the zwitterionic compound $(MeN)_6P_4F_8$(113) involves reaction of (110, R = Me) with heptamethyldisilazane and N,N'-dimethylurea.[294]

The methods shown in equations (50) and (51) have been used to synthesise a range of substituted dithiodiphosphazanes.

$$2PhP(S)(NHAr)_2 \xrightarrow{\Delta} [PhP(S)NAr]_2 + 2ArNH_2 \qquad ...(50)$$

$$2PhP(S)Cl_2 + 2ArNH_2 \xrightarrow{py} [PhP(S)NAr]_2 + 4pyHCl \qquad ...(51)$$

Reactions of $N_3P_3F_6$ with p-dimethylamino-phenyl Grignard and lithium reagents proceed in moderate yields only to give the non-geminal substitution compounds $N_3P_3F_{6-n}(C_6H_4NMe_2)_n$ where n = 1 to 3.[296] Although approximately equal amounts of the cis- and trans-disubstituted compounds are formed, only the trans trisubstituted product was isolated. The sodium salt, $Na[Fe(CO)_2Cp]$, can replace two fluorine atoms in $N_3P_3F_6$ to give initially (114), which is photochemically unstable and decomposes with loss of CO giving (115);[297] both compounds have been investigated by X-ray crystallography.



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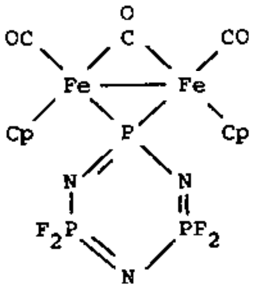


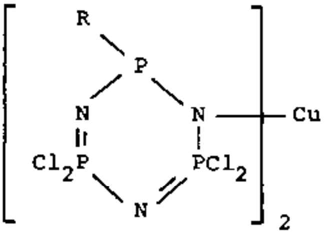
(115)

Mass spectra for the gem-, cis- and trans-isomeric forms of the mixed fluorobromotriphosphazenes, $N_3P_3Br_nF_{6-n}$ where n = 2 to 5, show significant differences for the gem and non-gem series of isomers, but the mass spectra do not provide a basis for distinguishing between the cis- and trans- forms.[298] Substitution of fluorine atoms in $N_3P_3F_6$ by dimethylamino groups leads to a marked decrease in ionisation energy, e.g. from 11.59eV for $N_3P_3F_6$ to 8.17eV for $N_3P_3F_2(NMe_2)_4$.[299] Similar, but less pronounced, changes occur on substitution by either chlorine or bromine.

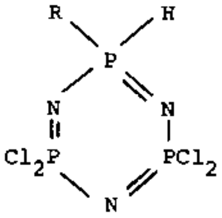
X-ray crystallographic data are available for the geminal isomer

$N_3P_3Me_2F_4$, which has a crystallographic mirror plane perpendicular to the ring,[300] and both ^{31}P and ^{15}N n.m.r. measurements have been carried out for gem-$N_3P_3Cl_4X_2$, where X = F, NH_2 or SEt.[301]

The copper-phosphazene intermediates (116), obtained by treating $N_3P_3Cl_6$ with a Grignard reagent in the presence of $(n\text{-}Bu_3P.CuI)_4$ can be converted into either 1,1-dialkyl derivatives on reaction with an alkyl halide[302] or to compounds with acetylenic side chains on treatment with prop-2-ynyl bromide.[303] The latter reaction gives in addition the isomeric form where the side chain is the $-CH{:}C{:}CH_2$ group. The first phosphazene compound containing a P-I bond has been isolated from a reaction between the hydrido-phosphazene (117) and iodine in carbon tetrachloride solution;[304] similar reactions take place with chlorine and bromine. The products are volatile solids, stable towards moisture, which react with nucleophiles to replace the halogen atom gem to the alkyl group.

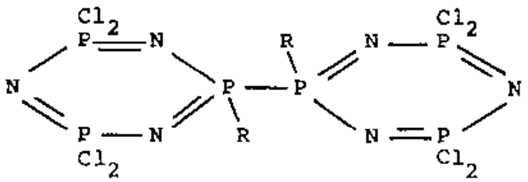


(116, R = Me,Et,n-Pr,n-Bu,
i-Pr,i-Bu,t-Bu, etc)



(117)

Recent experiments point to the ready formation of bicyclic phosphazenes (118) from reactions between $N_3P_3Cl_6$ and organomagnesium chlorides. This is in contrast to the ring cleavage reactions which are usually observed with PhMgBr, Ph_2Mg or PhLi.[305]



(118)

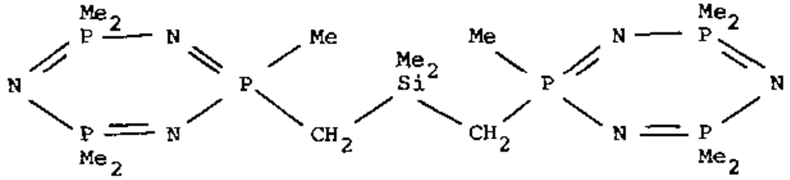
New kinetic measurements have elucidated many of the aspects of the course of amine substitution reactions with $N_3P_3Cl_6$. For example, in THF solution, the reaction between dimethylamine and a range of monosubstituted derivatives $N_3P_3Cl_5(NR^1R^2)$, where R^1 = n-Bu, R^2 = H; $R^1 = R^2$ = n-Bu; R^1 = i-Pr, R^2 = H; and $R^1R^2 = C_5H_{10}$, shows small steric effects as both the second order rate constants and activation parameters vary little.[306] With $R^1 = R^2$ = Me, the product is a mixture of cis- and trans- $N_3P_3Cl_4(NMe_2)_2$ with the latter predominating. The rate data show that $\Delta S^{\ddagger}(trans) > \Delta S^{\ddagger}(cis)$ and this is explained in terms of a substituent solvating effect.[307] The formation of geminal di-substitutttion products in $N_3P_3Cl_5NHMe$ - R^1R^2NH systems can be enhanced if the reactions are carried out with an increased base concentration in agreement with a proton abstraction mechanism.[308] Equilibration between the three pairs of cis-trans isomers, $N_3P_3Cl_{6-n}(NMe_2)_n$ where n = 2 to 4, has been investigated in acetonitrile and chloroform solutions over a range of temperatures.[309]

Selective fluorination is known to occur when SbF_3 or KSO_2F react with the non-geminal isomer $N_3P_3Cl_4(NMe_2)_2$, and this work has been extended to other substrates in which the amine residues are NEt_2, piperidine, NHMe, NHEt and NHi-Pr.[310] With SbF_3, substitution occurs only at the PCl(amine) groups while KSO_2F, if the substituent is a secondary amine, reacts only at only at the PCl_2 centre. Primary amine derivatives on the other hand are completely fluorinated by KSO_2F, and with the geminal compound $N_3P_3Cl_4(NHt\text{-}Bu)_2$ both SbF_3 and KSO_2F lead to the corresponding tetrafluoride. Spiro compounds are the products when 1,3- and 1,4-diaminopropane and N-methylethanolamine react with $N_3P_3Cl_6$.[311] The bis- and tris- derivatives of the latter were both found in two isomeric forms. Similar reactions were carried out with $N_3P_3Cl_4Ph_2$ and $N_4P_4Cl_8$. A tris spiro compound, isolated as an adduct with HCl and water, has been obtained from the reaction of N,N'-dimethylurea with $N_3P_3Cl_6$.[312]

Imidazole reactions with $N_3P_3Cl_6$ follow both geminal and non-geminal paths with the latter predominating, and the hydrolytic stability of the hexa-substituted compound is of interest as a model for the linear polymeric phosphazene, which has potential as a biodegradable carrier macromolecule.[313] Interaction between the anticancer drug $N_3P_3(aziridinyl)_6$ and DNA has been followed by Raman spectroscopy.[314] Reactions of aziridine with $N_3P_3Cl_5R$, where R = pyrrolidino, piperidino or morpholino, show that the phosphorus centre is deactivated as a result of electron release from the nitrogen atom.[315]

Full crystal structures have been determined for two triphenylphosphazo derivatives, i.e. gem-$N_3P_3Cl_4(NPPh_3)_2$[316] and gem-$N_3P_3Cl_4(NEt_2)(NPPh_3)$;[317] the conformations of the exocyclic groups are of particular interest.

Methyl phosphazenes, such as $N_3P_3Me_6$, $N_3P_3Ph_2Me_4$ and $N_4P_4Me_8$, are deprotonated to carbanions on treatment with alkyl lithium derivatives.[318] They can then react with monofunctional electrophiles giving phosphazenes with side chains such as CH_2Me, CH_2Br, CH_2I, CH_2COPh, CH_2COOH, $AsMe_2$ or $SiMe_3$. With difunctional electrophiles, e.g. Me_2SiCl_2, two phosphazenyl groups can be linked giving compounds of the type (119).

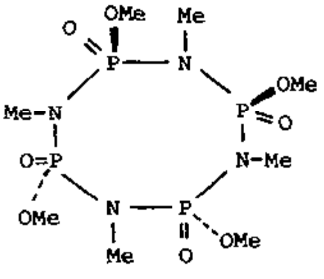


(119)

A new tetrameric diamido derivative, $N_4P_4Cl_6(NH_2)_2$ with a geminal arrangement of substituents, has been isolated from the reaction of $N_4P_4Cl_8$ with aqueous ammonia in ether;[319] further reaction gives a trisubstitution product with a 2,2,6-arrangement of NH_2 groups. The chlorine atoms in the geminal isomer, $N_4P_4Cl_4(SEt)_4$, have been substituted by NH_2, OMe and OEt groups and the isomeric composition of the products determined.[320]

The methoxy derivatives, $[NP(OMe)_2]_n$ where n = 3 to 6, rearrange to N-methyl-cyclophosphazanes on heating to 150-160° at 1-2mm Hg pressure.[321] Two isomeric forms can be isolated for n = 4 and a full structure for the less abundant isomer shows a cis-cis-trans-trans arrangement of substituents (120).[322] The pentameric compound gives three isomers and there is a complex mixture for n = 6. Both partially (121) and fully (122) rearranged products are observed with the trimeric compound, $N_3P_3Ph_2(OMe)_4$.[321]

Methylated higher phosphazenes, e.g. $N_6P_6Me_{12}$[323] and $N_8P_8Me_{16}$[324] serve as ligands, the former yielding the palladium complex shown



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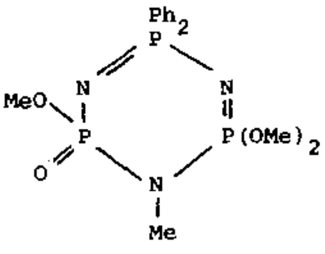

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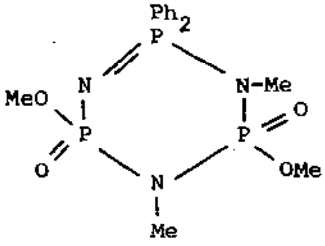


(122)

in Figure 7. With the latter, cobalt nitrate gives the complex $[N_8P_8Me_{16}.Co(NO_3)]^+ NO_3^-$, where the coordination sphere of the metal atom contains four nitrogen atoms from the phosphazene and two oxygen atoms from an unsymmetrically bidentate nitrate group.

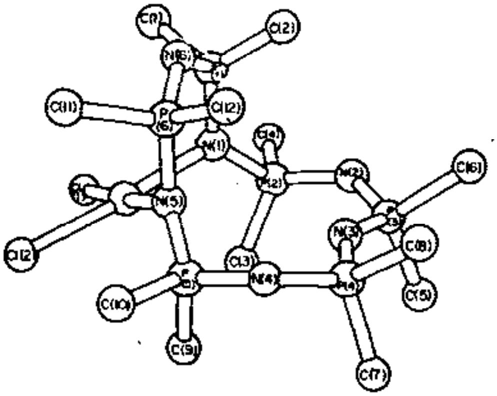
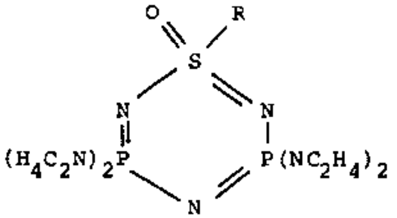


Figure 7. Molecular structure of $PdCl_2.N_6P_6Me_{12}$ (reproduced by permission from Can. J. Chem., 59(1981)2429).

Aziridine derivatives of the mixed P-N-S ring system (123) have been prepared for R = F or Ph by reactions which follow basically a geminal substitution path;[325] the compounds show pronounced activity against animal tumours. The compound (123, R = NC_2H_4) can be isolated in two forms which melt at 357 and 376K and crystallise in the space groups $P2_12_12_1$ and $P2_1/c$ respectively.[326] Detailed crystallographic investigation shows that in each form the ring is nearly planar and differences arise from different conformations of the aziridine residues.



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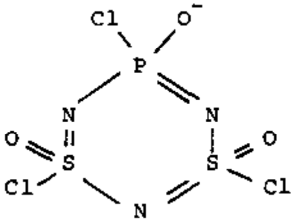
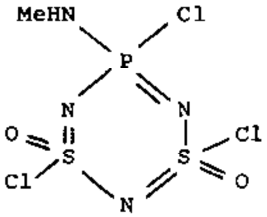


(124)

Salts of the new anion (124) result when cis-$(NSOCl)_2NPCl_2$ is hydrolysed with either hydrated Ph_4AsCl or Me_4NCl-H_2O;[327] a structure determination shows a slight chair conformation for the ring with the oxygen ligands in equatorial positions. Structures have been reported for two further P-N-S ring compounds i.e. compounds (125)[328] and (126).[329] In the former the three chlorine atoms occupy axial positions, while in the latter, which is the major phenylation product of cis-$(NSOCl)_2NPCl_2$, the phenyl groups are trans to each other and the ring has a slight boat conformation.



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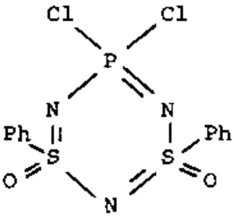


(126)

Quantum mechanical calculations for ring compounds in the two series $(NCMe)_{3-x}(NPMe_2)_x$ and $(NCNMe_2)_{3-x}(NPMe_2)_x$ have been used to assess the relationship between ring stability and anticancer activity.[330]

5.2.5 Bonds to Oxygen

Lower Oxidation States. Single crystals of P_4O_6 have been grown in situ on a diffractometer and the structure solved for data collected at -5°C.[331] The molecule contains a mirror plane but within the limits of the determination it belongs to the T_d point group. Reaction of P_4O_6 with alkali metal oxides leads to the next higher oxide P_4O_7 and two structure determinations[332,333] show the expected adamantane-type structure with one terminal P-O bond.

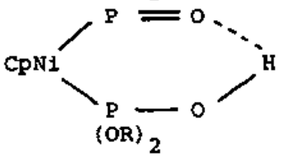
Oxidation of hypophosphorous acid by Ag^{2+} in perchloric acid solution follows the rate law:[334]

$$\frac{-d[Ag(II)]}{dt} = 2k_2[Ag(II)][H_3PO_2]/1 + K_5[Ag(I)]$$

k_2 has a value of $7.6 \times 10^2 M^{-1} sec^{-1}$ at 30°C and K_5, the formation constant of $AgH_3PO_2^+$, is 38 M^{-1} at 30°C.

The molecular adduct, $2KH_2PO_3.H_3PO_3$, contains a three dimensional network formed by strong hydrogen bonding (O...O 2.57Å) between the acid and the anion.[335] The double phosphites, $LiMHPO_3.xH_2O$ for M = K and x = 0 or 1, and M = Tl or NH_4 and x = 0, have been prepared and a full structure obtained for the anhydrous thallium compound.[336]

Dialkylphosphites, $HP(O)(OR)_2$ where R = Me or Et, react with dicyclopentadienyl nickel to give six-membered ring compounds (127), which most probably contain a symmetrical O-H-O bond.[337]



(127)

Sodium diethylphosphite and the etherate of boron trifluoride in acetonitrile solution liberate sodium fluoride to give tris(diethylphosphito)borane $[(EtO)_2PO]_3B$ as a high boiling liquid.[338] Its reactions with ethanol, water and sulphur have been investigated. On heating $VOCl_3$ with dialkylarylphosphites, HCl or alkyl/aryl chlorides are lost to yield polymeric products with formulae such as $VO[OP(O)R(OR)Cl_2]$ and $[VO\{O_2P(O)R\}Cl]$.[339]

Trifluoroethanol derivatives, $RP(OCH_2CF_3)_2$ where R = Me or Ph, are the products when the appropriate phosphorus chloride reacts with trifluoroethanol in the presence of a tertiary base;[340] these compounds can then be converted into phosphazeno derivatives $Me_3P{:}N{\cdot}PR(OCH_2CF_3)$ by reaction with $Me_3P{:}NSiMe_3$. Two trifluoroethoxy groups can be added to a range of P(III) species including $P(OCH_2CF_3)_3$, $PhP(OCH_2CF_3)_2$ and $Ph_2POCH_2CF_3$ on treatment with two mols of trifluoroethyl benzene sulphenate,[341] and the resulting P(V) compounds will all accept a further $CF_3CH_2O^-$ group to give hexacoordinate anions. As initially produced the phenyl groups in the $Ph_2P(OCH_2CF_3)_4^-$ anion occupy cis-positions but rapid isomerisation gives a mixture containing predominantly the trans form.

In contrast to the mechanism of the Arbuzov reaction, the first step in the reaction between a trialkylphosphite and trimethylsilyl iodide according to ^{31}P n.m.r. measurements is the formation of an iodophosphite, e.g. $(MeO)_2PI$, and Me_3SiOMe.[342] The final products are, however, O-trimethylsilyl esters of the alkylphosphonic acid.

The +5 Oxidation State. Di(t-butyl)phosphine oxide and mercury(II) acetate give the complex $[(t\text{-}Bu)_2P(O)]_2Hg$, a crystalline solid containing Hg-P bonds of high thermal stability.[343] On treatment with mercury(II) chloride, bromide, iodide, cyanide, acetate, etc., the compound is converted into $(t\text{-}Bu)_2P(O)HgX$.

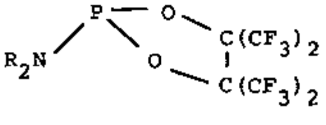
Crystallisation of triphenylphosphine oxide from a solution of oxalic acid in methanol gives the centrosymmetric complex $2Ph_3PO.(COOH)_2$, in which the phosphine oxide molecules are attached by short hydrogen bonds (O...H-O 2.550Å).[344] Short, symmetrical hydrogen bonds are also present in the dimeric structure of di(p-methylphenyl)phosphoric acid.[345]

Protonation, followed by sulphonation, condensation or solvolysis is observed according to ^{31}P n.m.r. measurements when $PhPO(OH)_2$ and the corresponding chloride are dissolved in 100%

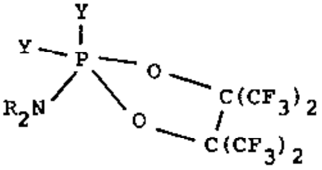
sulphuric acid, oleum or chlorosulphuric acid.[346]

Distorted octahedral coordination by oxygen atoms has been observed in the structure of the tris complex of ytterbium(III) with the tetraphenyl ester of imidodiphosphoric acid.[347]

Dioxaphospholanes (128), which can be obtained by treatment of a halogenoaminophosphine with the dilithium salt of perfluoropinacol can be oxidised by chlorine[348] or hydrogen fluoride[349] to respectively (129, X = Y = Cl or X = H, Y = F). The former (R = H) on further treatment with the pinacol salt yields the dichelated compound (130), for which an X-ray structure shows almost ideal trigonal bipyramidal geometry about phosphorus.[348]



(128, R = H, Me or Et)



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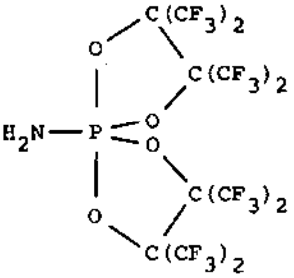

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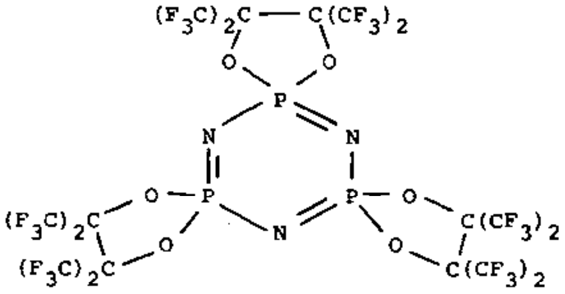
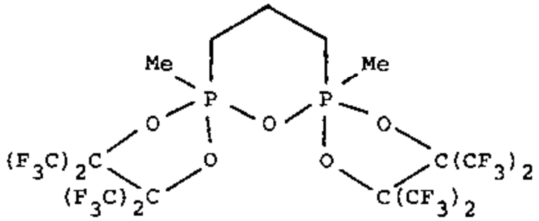


(131)

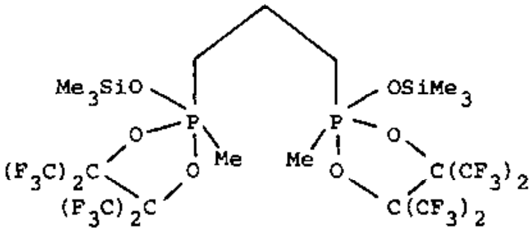
On reaction with ammonia, one of the fluorine atoms in (129, R = H, X = Y = F) can be replaced by an amino group but use of $LiNH_2$ is necessary to substitute the second fluorine.[350] The resulting tri-amino derivative is however unstable and undergoes slow loss of ammonia to give the cyclotriphosphazene (131). Reactions of a number of phosphorus(III) species with both $ClS[OCH(CF_3)_2]_3$ and $S[OCH(CF_3)_2]_2$ have been described.[351]

A novel oxyphosphorane (132) containing a λ^5P-O - λ^5P system is the product when the perfluoropinacolyl-trimethylsilyl phosphorane

(<u>133</u>) reacts with thionyl chloride.[352] The six-membered ring



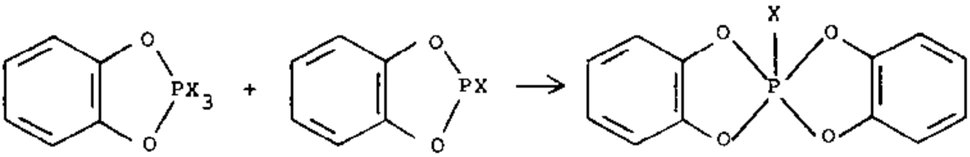
(<u>132</u>)



(<u>133</u>)

system has a boat conformation and the methyl groups are cis with respect to the ring.

Ligand exchange occurs when P-halogeno-catechyl derivatives and a range of phosphorus(III) halides interact at room temperature; two examples are given in equations (52) and (53).[353]



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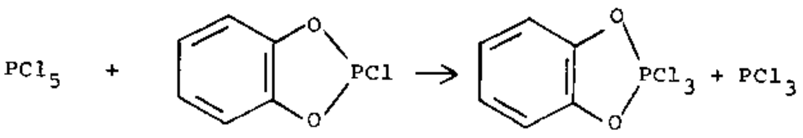


...(53)

Formation of perfluoroalkyl phosphonates can now be carried out much more readily than in the past by using the reaction between a perfluoroalkyl iodide and tetraethyldiphosphite, outlined in equation (54).[354]

$$R_fI + [(EtO)_2P]_2O \xrightarrow{(t\text{-}BuO)_2} R_fP(OEt)_2 \xrightarrow{t\text{-}BuOOH} R_fP(O)(OEt)_2 \qquad ...(54)$$

The α-form of (phenylphosphonato)trimethyl tin, which is obtained from Me_3SnCl and $PhP(O)(OH)_2$ in aqueous solution, contains a novel, infinite chain structure.[355] Further reactions leading to polymeric complexes have been reported between metal halides and organophosphorus compounds such as $(RO)_3PO$,[356] $(RO)_2PHO$,[356] $PhPO(OH)_2$,[356] triethylphosphonoformate,[357] diethylacetyl- or diethylbenzoyl-phosphonate,[358] methyl methylphenylphosphinate[359,360] and triethylthiophosphate.[361,362] The reactions were generally carried out at elevated temperatures to promote loss of an alkyl halide, the organophosphorus residues then behave as bridging groups between metal centres.

Matrix isolation studies in N_2 at 12K confirm the presence of monomeric $NaPO_3$ in the vapour phase above heated Na_3PO_4.[363] With $Na_5P_3O_{10}$ it is probable that both $NaPO_2$ and NaPO are produced in addition to $NaPO_3$.[363] Ab initio calculations for the isolated $LiPO_3$ molecule point to an energy difference of only ca. 4 kcal mol^{-1} between the lowest unidentate and lowest bidentate structure and the molecule should perhaps be considered as non-rigid with respect to migration of the cation about the anion.[364]

Solid state ^{31}P n.m.r. spectra have been obtained for $NH_4H_2PO_4$, $AlPO_4$, the minerals hydroxyapatite and crandallite and a soil sample.[365] A structural study has been reported for the pseudo-trisodium phosphate, $Na_3PO_4.11H_2O.^1/5NaCl$,[366] and a new form of aluminium dihydrogen phosphate, crystallising in pseudo-pentagonal dodecahedra has been isolated.[367] Its structure consists of a three dimensional network of AlO_6 octahedra linked by $O_2P(OH)_2$ tetrahedra. Compounds isolated from the H_3PO_4-$Al_2(SO_4)_3$-NH_4F-H_2O system at 80°C have compositions close to $Al(HPO_4)F.2H_2O$, and i.r. spectra and the results of thermolysis reactions are reported.[367]

Recent measurements indicate that $Ti_2O(HPO_4)$ is the major species in an aqueous HCl-NaCl solution of Ti(IV) to which an excess of phosphate has been added.[368] In the Mn^{3+}-PO_4^{3-} system there is evidence for $Mn(H_2PO_4)^{2+}$, $Mn(H_2PO_4)_2^{+}$ and a hydrolysed species such as $Mn(OH)H_2PO_4^{+}$.[369]

A series of salts formulated as $M[PO_4(VOOH)]$, where M = K, Rb, Cs or NH_4, has been isolated and characterised.[370] The recently prepared cobalt-acetylphosphate complex $[Co(NH_3)_5OPO_3COMe]^{+}$ undergoes base hydrolysis exclusively via C-O bond fision and new data suggest that hydrolysis of the acetyl-phenylphosphonate anion, $PhOPO_2OCOMe^{-}$, is significantly catalysed by the hydroxo-complex $[(NH_3)_5CoOH]^{2+}$.[371]

Among the structures determined in 1981 are the following which contain monophosphate groups: $Pb(H_2PO_4)_2$;[372] $Hg(HPO_4)$;[373] $CePO_4$, a synthetic analogue of monazite;[374] $VOPO_4.2H_2O$;[375] the double salts $NaMPO_4$, where M = Cu, Pb or Ba;[376] $K_4UO_2(PO_4)_2$, obtained by a high temperature reaction between $K_4P_2O_7$ and $(UO_2)_2P_2O_7$;[377] and $Co_2(PO_4)Cl$, which is isostructural with $Fe_2(PO_4)Cl$.[378] The phosphate-diphosphate, $K_2H_5(PO_4,P_2O_7)$ obtained by evaporation of an aqueous solution of K_2HPO_4 and diphosphoric acid, has also been examined by single crystal X-ray diffraction.[379]

Metal ions, including alkali, alkaline earth, Al^{3+} and some transition metal ions, retard the hydrolysis of di- and triphosphates in acid solution, while in alkaline solution alkali metal cations accelerate the hydrolysis.[380] Catalytic effectiveness decreases with increase in ionic radius.

The triphosphate complex $[Co(NH_3)_4(H_2P_3O_{10})].H_2O$, see Figure 8, shows a boat conformation for the eight-membered ring formed by the ligand behaving as an αγ-chelating group.[381] Two intramolecular NH...O hydrogen bonds from axial ammine groups stabilise the structure.

Five crystalline phases have been isolated from the $K_4P_2O_7$-$Mg(NO_3)_2$-H_2O system at 20°C,[382] and the triphosphate, $Sc_5(P_3O_{10})_3.23H_2O$ has been prepared and characterised.[383] The double salts $(Na,NH_4)_5P_3O_{10}.xH_2O$,[384] $(NH_4)_3CaP_3O_{10}.2H_2O$[385] and $(NH_4)Ca_2P_3O_{10}.2.5H_2O$,[385] have also been investigated.

The macromolecular anion in the new uranium ultraphosphate, $(UO_2)_2P_6O_{17}$, contains corrugated 24-membered rings condensed further into a three dimensional structure.[386]

Crystals of the compounds $2Ag_2HPO_4.Te(OH)_6$,[387] $2Na_3P_3O_9.Te(OH)_6.6H_2O$,[388,389] and $K_3P_3O_9.Te(OH)_6.2H_2O$[388,389] do

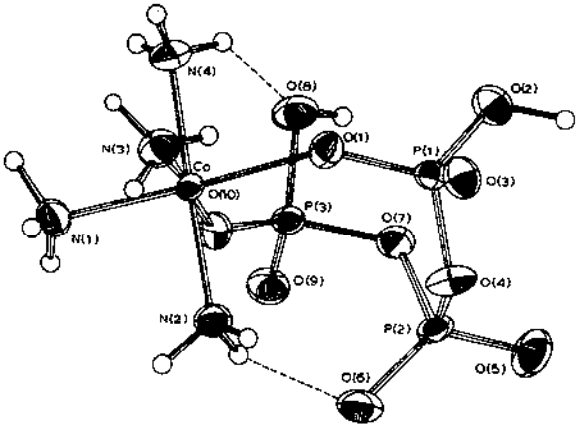


Figure 8. Structure of $[Co(NH_3)_4(H_2P_3O_{10})]$ (reproduced by permission from Acta Crystallogr., B37(1981)657).

not contain condensed phospho-tellurate anions but consist of isolated TeO_6 octahedra and the appropriate phosphate anion.

Solid solution formation giving $Ca_5(OH)_{1-x}Cl_x(PO_4)_3$ has been investigated showing that the a axis expands linearly with chlorine content from 9.418Å in hydroxy-apatite to 9.635Å in chloroapatite.[390] A detailed crystallographic study of bromoapatite $Ca_5(PO_4)_3Br$ points to it being almost stoichiometric with Br...Br separations of 3.37Å, thus giving a new value of 1.68Å as the apparent radius of the bromide ion.[391] Mixed sulphate-phosphate fluoroapatites with the composition $Ca_{10-x}Na_x(PO_4)_{6-x}(SO_4)_4F_2$ have structures related to that of pure fluoroapatite by doubling the length of the b axis.[392]

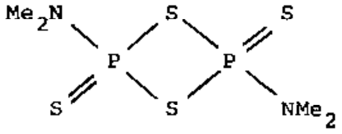
The lamellar structure of γ-zirconium phosphate can be modified by replacing a fraction of the interlayer HPO_4 groups by either phosphoric acid esters residues, $C_nH_{2n+1}OPO_3$ where n = 1 to 18,[393] or 2-glycerophosphate groups,[394] or phosphonic acid residues.[395,396] Organic derivatives can also be prepared using substituted epoxides yielding products with the formula $Zr(O_3POCH_2CHOHR)_n.xH_2O$ where $R = CH_2CCl_3$, CH_2Cl or CHO.[397]

A Zr-phosphate complex containing apparent monolayers of tris(bipyridyl)ruthenium(II) has also been isolated.[398] X-ray p.e.s. data for both the α- and γ-zirconium phosphates indicate binding energies higher than those for other zirconium and trivalent metal phosphates.[399]

Among the exchange processes investigated using α-zirconium phosphate and related species are the following: HCl-Na^+,[400] K^+-H^+,[401] Cd^{2+}-Pb^{2+},[402] Na^+-Cs^+-H^+,[403] and Co^{2+}, Ni^{2+} and Cu^{2+}.[404] Alkali metal ion exchange has also been followed on mixed zirconium-titanium phosphates with Zr:Ti ratios of 0.37 to 0.61,[405] and the intercalation of alcohols into both γ-zirconium and γ-titanium phosphates has been investigated.[406]

5.2.6 Bonds to Sulphur, Selenium or Tellurium

Reaction between P_4S_3 and $(Me_2N)_2S$ in benzene yields the thiophosphoric anhydride (134), whose structure shows a trans arrangement of ligands at phosphorus;[407] terminal and endocyclic P-S bond lengths are 1.926 and 2.122Å respectively with P-S-P and S-P-S angles 86.86 and 93.14°. A new series of cage compounds $P_{4-x}As_xS_3$, where x = 1 to 3, result from mixtures of P_4S_3 and As_4S_3 after heat treatment.[408] The most stable compound is PAs_3S_3 which, from ^{31}P n.m.r. spectroscopy, has structure (135). I.r. and Raman data for β-P_4S_5 and P_4S_7 have been assigned;[409] the former decomposes on melting to a mixture of P_4S_3, α-P_4S_7 and β-P_4S_6 while the latter dissociates to some extent to β-P_4S_6 and sulphur.



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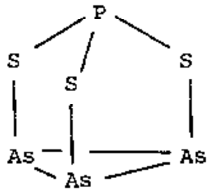

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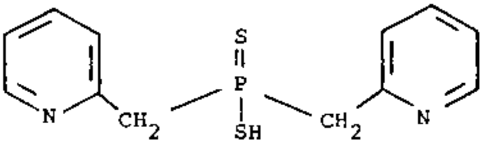
Hydrolysis of the products from reactions of P_4S_{10} with 2- or 4-methylpyridine gives respectively (136) and (137), but the



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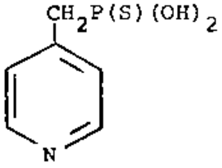
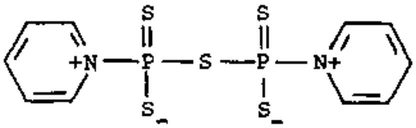
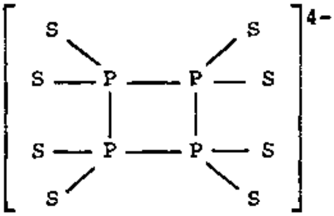


(137)

3-methyl derivatives yields a zwitterionic adduct (<u>138</u>), similar to that already observed in the P_4S_{10}-pyridine reaction.[410]



(<u>138</u>)



(<u>139</u>)

On reaction with polysulphides in non-aqueous media, white phosphorus yields a mixture of thiophosphates from which salts of the cyclic anion (<u>139</u>) can be isolated.[411] The ring is planar from crystallographic constraints; the P-P and P-S distances are 2.280, 2.287 and 1.976, 1.980Å respectively. Sulphur atoms in the hexathiodiphosphate anion $P_2S_6{}^{4-}$ are replaced in a stepwise manner on treatment with hydrogen peroxide in sodium hydroxide.[412] Of the members of the series $P_2O_nS_{6-n}{}^{4-}$ only two compounds, $Na_4P_2OS_5.7H_2O$ and $Na_4P_2O_2S_4.8H_2O$, can be isolated as pure compounds but n.m.r. data are available for all compounds with n = 1 to 5. By reaction with ammonia and hydrogen peroxide, it is possible to prepare the related amido-derivatives $K_3[P_2(NH_2)S_5].3H_2O$ and $(NH_4)_2[P_2(NH_2)_2S_4].H_2O$.

Organophosphorus dichlorides are converted to the corresponding fluorides by hydrogen fluoride in the presence of a tertiary base and on treatment with hydrogen sulphide they give fluorophosphinothioic acids, RPF(SH) where R = Me, Et or Ph.[413] Fluorothiophosphites are also obtained when PF_3 reacts with two mols of both H_2S and HF in the presence of an amine to yield compounds with the formulae $Et_2NH_2(PFHS_2)$ and $Et_3NH(PFHS_2)$.[414] With 3 mols of H_2S and 5 mols of diethylamine, phosphorus trifluoride is converted to the trithiophosphite, $(Et_2NH_2)_3(PHS_3)$.

The structures of the three sulphides, PF_2HS, $PClF_2S$ and $PBrF_2S$ have been determined by electron diffraction,[415] and HeI p.e.s. for Me_2PSMe, Me_2PSeMe and the two arsenic analogues have been assigned.[416]

Addition compounds of molecular iodine and a number of phosphine sulphides, including $2Ph_3PS.3I_2$, $Ph_3PS.2I_2$,

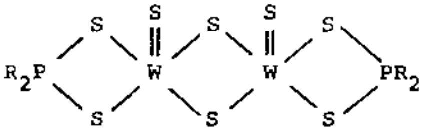
$(MeC_6H_4)_3PS.I_2$ and $(MeC_6H_4)_3PS.2I_2$, have been studied using Job's method in a range of solvents.[417]

^{31}P n.m.r. measurements on $(Ph_2P)_3CH$ and the sulphur oxidation products, $(Ph_2P)_{3-n}(Ph_2PS)_nCH$ where n = 1 to 3, point to unhindered but restricted rotation about the P-methine bond for n = 0 or 1.[418] For n = 2 and 3, rotation has activation energies of respectively 29 and 49 kJ mol^{-1}. An X-ray structure was determined for the trisubstituted compound $(Ph_2PS)_3CH$.

Among the compounds isolated in a study of complex formation with ligands of the type $(Me_2N)_nCl_{3-n}PS$ are $(Me_2N)_3PS.SnCl_4$; $2(Me_2N)_2ClPS.MCl_4$ for M = Sn, Zr or Hf; $(Me_2N)_2ClPS.SbCl_5$ and $(Me_2N)Cl_2PS.SbCl_5$.[419]

Reaction of a platinum bis(dithiocarbamate) with diphenylphosphine sulphide gives the complex anion $[Pt(S_2CNR_2)(Ph_2PS_2]^-$ in which the platinum is in square planar coordination to two sulphur atoms of the thiocarbamate and two phosphorus atoms.[420]

Molecules of $Ph_2P(S)SH$ in the solid state are linked into infinite helical chains by almost linear S-H...S bonds (S...S 3.790Å, S-H...S 169.5°),[421] and related dialkylthiophosphinic acids react with titanium tetrachloride to give the hydrolytically sensitive chelates $(R_2PS_2)_2TiCl_2$ where R = Me or Et.[422] Crystal structures, also showing bidentate character for dithiophosphinate groups, have been reported for $Me_2Sn(S_2PMe_2)_2$,[423] $I_2Sn(S_2PEt_2)_2$,[423] and for the molybdenum-sulphur cluster compound, $[Mo_3S_7(S_2PR_2)_3]^+R_2PS_2^-$ where R = Et or n-Pr,[424] obtained from a reaction between $Mo(CO)_6$ and a bis(diorganothiophosphoryl)disulphane $R_2P(S)S_2P(S)R_2$. $W(CO)_6$ on the other hand is thought to give a dinuclear compound (140). A series of arsolane and arsenane complexes with dialkyldithiophosphates of the type (141) has been isolated.[425]



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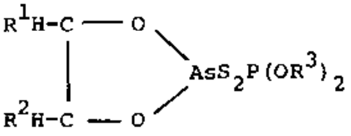


(141)

A centrosymmetric structure with a trans arrangement of substituents is found for $Ph_2P(S)P(S)Ph_2$, the P-P bond length

(2.263Å) is longer than that in related alkyl derivatives.[426] Nickel and cobalt complexes may be isolated using the difunctional dithiophosphinic acids, $^{-}S_2P(R)\cdot(CH_2)_n\cdot(R)PS_2^{-}$ where R = 4-methoxyphenyl and n = 4 to 10.[427]

Structural data are now available for Tl_3PS_4, which contains almost regular tetrahedral PS_4^{3-} anions (P-S 2.02 to 2.06Å).[428] New intercalation compounds based on $MnPS_3$ result when $Mn_{0.8}PS_3K_{0.4}.H_2O$ or $Mn_{0.5}PS_3Na.4H_2O$ are treated with $Cren_3Cl_3$, $Ru(bipy)_3Cl_2$, and $[CpFe(CO)diphos]BF_4$.[429]

I.r. and ^1H n.m.r. spectra have been measured for the potassium salt $(PhO)_2P(Se)SeK$ and data reported for its acid catalysed solvolysis in methanol and ethanol.[430] Trifluoromethylselenophosphoryl dichloride, $CF_3SeP(O)Cl_2$ has been synthesised in high yield from CF_3SeCl and $MeOPOCl_2$ in the presence of BCl_3 or $SbCl_5$.[431] Important parameters in the electron diffraction structure of F_2HPSe are : r(P=Se) 2.026, r(P-F) 1.557 and r(P-H) 1.422Å.[432]

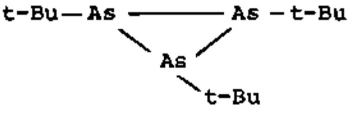
I.r. and Raman data for Me_3PTe and its deuterated analogue can be analysed on the basis of C_{3v} symmetry;[433] the P-Te force constant is assessed at 2.20 mdynes $Å^{-1}$, suggesting a weaker bond than that in related R_3AsSe species. ^{125}Te n.m.r. shifts for a range of phosphorus tellurides confirm the rapid migration of tellurium in $R_3P:Te-R_3P$ mixtures,[434] but the tellurophosphines, $R^1TePR^2_2$ and R_2PTePR_2, on the other hand give doublets and triplets respectively from Te-P coupling.

5.3 ARSENIC

5.3.1 Arsenic and Arsenides

U.v. p.e.s. data have been reported for As_4 and As_2.[435]

A cyclocondensation reaction between 1,2-dipotassium-1,2-di-t-butyldiarsenide and t-butylarsenic dichloride gives the cyclotriarsine (142), which is stable in the dark and absence of air at -30°C.[436] At room temperature, oligomerisation to $(t\text{-}BuAs)_4$ takes place. Depending on the mol ratio of reactants,



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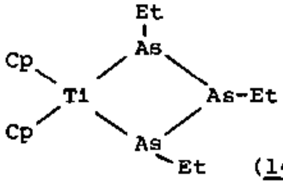


(143)

potassium in THF converts the cyclo-pentaarsine $(AsEt)_5$ to either $K_2As_5Et_5$ or $K_2As_2Et_2$.[437] With dicyclopentadienyl titanium dichloride each of these compounds reacts to give the triarsine chelate (143).

This year saw the report of a new series of Zintl phases, e.g. Ba_4SiAs_4 and Ba_4GeAs_4, which from X-ray diffractometry contain isolated $SiAs_4^{8-}$ or $GeAs_4^{8-}$ anions.[438,439] The compounds, which result when the elements are heated to 1000°C, follow the principle that the metalloid of lower electronegativity is saturated by covalent bonds and the electrons provided by ionisation of the alkaline earth metal are assigned to the more electronegative partner.

Structural data have also been gathered for the binary arsenides, Sc_7As_3[440] and Nb_5As_3,[441] and the calcium aluminium ternaries, Ca_3AlAs_3[442] and $Ca_3Al_2As_4$[443] together with $Ca_5Al_2Sb_6$. The first ternary contains $(AlAs_3)_n^{6-}$ chains, structurally similar to those in $(SiO_3)_n^{2-}$, polysilicate systems. Preparative and structural details are also available for KFe_2As_2, KCo_2As_2, KRh_2As_2 and KRh_2P_2,[444] which are isotypes of $ThCr_2Si_2$, and for K_2PdAs_2 and K_2PdP_2.

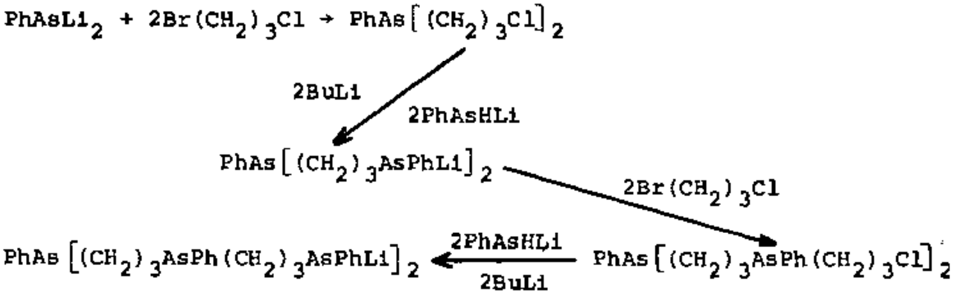
5.3.2 Bonds to Carbon

Considerably less is known about As(III)-C double bonds than for the phosphorus analogues but one such compound has been isolated.[446] The reaction of phenyl bis(trimethylsilyl)arsine and an excess of dimethyl formamide, see equation (55), like the related phosphorus reaction,[153] is catalysed by sodium hydroxide.

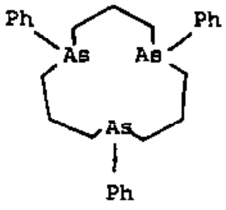
$$PhAs(SiMe_3)_2 + HCONMe_2 \longrightarrow PhAs{:}CHNMe_2 + (Me_3Si)_2O \qquad ...(55)$$

A series of ligands described as "crown arsines" has been synthesised from intermediates outlined in Scheme 5.[447] Two of the compounds isolated have structures (144) and (145); the related compound with six PhAs groups, i.e. $[PhAs(CH_2)_3]_6$, is also known.

Primary amine reactions with the tertiary arsine $MeC(CH_2AsI_2)_3$ lead to adamantane-type compounds (146, X = Ni-Pr, Nn-Bu, NPh etc.),[448] which can be converted to triarsathio-adamantanes (146, X = S) by reaction with carbon disulphide.[449] Noradamantane structures (147, X = $C(COOEt)_2$, $C(COOMe)_2$ or $C(COPh)_2$) are



Scheme 5.



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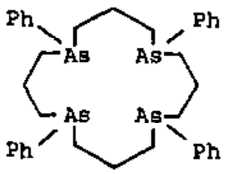

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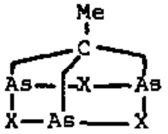

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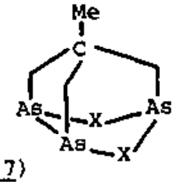

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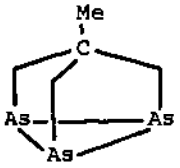


(148)

proposed for new cage compounds obtained when $MeC(CH_2AsI_2)_3$ reacts with either $H_2C(COOEt)_2$, $H_2C(COOMe)_2$ or $H_2C(COPh)_2$.[450] Chromium, molybdenum and tungsten carbonyl complexes have been prepared using a further adamantane-type ligand (146, X = O),[451] and a cationic complex $[CpFe(CS)(Me_2CO)L]^+$ has been isolated in which the ligand L is the cyclo-triarsine (148).[452]

Up to three $(Me_2As)_2O$ groups can be incorporated into the cobalt cluster compound $RCCo_3(CO)_9$, giving $RCCo_3(CO)_3[(Me_2As)_2O]_3$ for which an X-ray diffraction structure is available.[453] Derivatives of the tridentate ligand $Me_2AsOAsMeOAsMe_2$ have also been studied. Metal carbonyl complexes with methylarsine are generally unstable and it is possible to isolate pure only $MeAsH_2.W(CO)_5$.[454] In other cases both hydrogen and carbon monoxide are lost and, for example, with $Fe(CO)_5$ the cubane like oligomer $[MeAsFe(CO)_3]_4$ is obtained. Di-t-butyl-chloroarsine reacts in THF solution with $[W(CO)_3Cp]^-$ to give $Cp(CO)_3WAs(t\text{-}Bu)_2$ and this compound with sulphur yields $Cp(CO)_3WAs(S)(t\text{-}Bu)_2$.[455]

Boron trihalide complexes with trimethyl- and triphenylarsines have been prepared and characterised by vibrational and n.m.r. spectroscopy.[456] Normal coordinate analyses for the Me_3As series and potential energy distribution are also reported.

Ylidic species formulated as $(t\text{-}Bu)_3\overset{+}{A}s\text{-}\overset{-}{M}Cl_2$ result when tri-t-butyl arsine reacts with either $SnCl_2$ or $GeCl_2$, but when the mixed arsine $(t\text{-}Bu)_2(Me_3Si)As$ is used, the products are the chlorostannylene or chlorogermylene $t\text{-}Bu_2AsMCl$.[457]

Structures have been determined for triphenylarsines substituted in the para position by Cl, OMe, or Me[458] and for trimesitylarsine.[459] The para substituent has little effect on bond distances and angles but incorporation of methyl groups into the 2 and 6 positions increases the mean As-C distance from ca. 1.96 to 1.976Å and the C-As-C angle from ca. 99° to 107.6°.

Complexes with 2:1 and 2:2 stoichiometries are observed when triphenylarsine, and the antimony or bismuth analogues react with mercury(II) halides.[460] Slow diffusion of chlorine into an aqueous solution of Ph_4AsCl gives the trichloride, Ph_4AsCl_3.[461]

5.3.3 Bonds to Halogens

A new type of fluoroarsonium salt, $Ph_2AsF_2^+AsF_6^-$ can be obtained either by treating arsenic pentafluoride with benzene in SO_2ClF solution or by a reaction of AsF_5 with Ph_2AsF_3.[462] The compound, which is an "isomer" of $PhAsF_4$, is converted to a mixture of Ph_2AsF_3 and $CsAsF_6$ by CsF. Divalent metal fluorides on reaction with AsF_5 in anhydrous hydrogen fluoride give adducts $MF_2.2AsF_5$, where M = Mg, Ca, Sr, Ba, Mn, Co, Ni, Cd, Hg or Pb.[463] From i.r. and X-ray powder data they belong to one of three different structural types depending on the fluoride ion donor ability of MF_2.

Practical details have been given for the conversion of arsenic trichloride to R_2AsI, where R = Me, Et, n-Pr or n-Bu, via R_3As and R_3AsI_2.[464]

Further experiments of the oxidation of ferrocene by Group 5 halides in the presence of oxygen has led to the isolation of small amounts of $(Cp_2Fe)_2As_4Cl_{10}O_2$.[465] The compound contains an unusual anion, shown in Figure 9, which is derived from two neutral $Cl_2AsOAsCl_2$ molecules and two chloride ions.

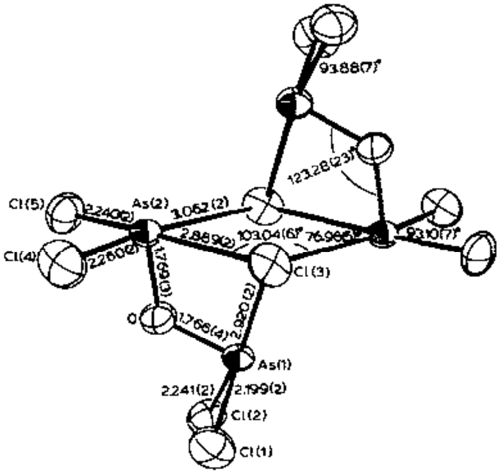
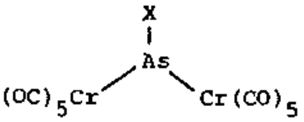


Figure 9. Structure of $As_4Cl_{10}O_2^{2-}$ reproduced by permission from Inorg. Chem., 20(1981)849).

A number of reactions have been reported for the chloroarsinidene complex (149, X = Cl). With a range of nucleophiles, the chlorine atom is replaced to give derivatives in which X = Br, I, OMe, OEt, SEt or SePh.[466] Structures for (149, X = Cl or Ph) point to trigonal planar coordination about arsenic. Anionic complexes, $R_4N^+[(OC)_5CrAsClXCr(CO)_5]$, can be isolated from reactions of (149, X = Cl) with substituted ammonium halides or pseudo-halides,[467] and finally, with chelating ligands, e.g. 2,4-pentanedione or 1,3-diphenyl-1,3-propanedione, compounds such as (150) are obtained.[468]



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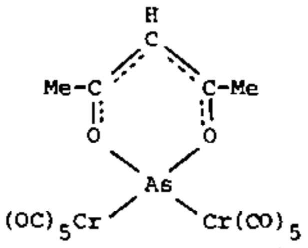
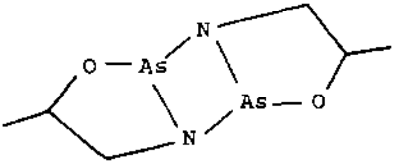


(150)

5.3.4 Bonds to Nitrogen

Evolution of dimethylamine occurs when $As(NMe_2)_3$ is treated with norephedrines and, among other oligomers, diazadiarsacyclobutanes such as (<u>151</u>) are obtained.[469]



(<u>151</u>)

5.3.5 Bonds to Oxygen

Reaction between $As(NMe_2)_3$ or Me_2AsNMe_2 and either substituted polyethylene glycols such as $HO(CH_2CH_2O)_nCH_2CH_2OAsMe_2$, where n = 0 to 4,[470] or α,ω-diols[471] lead to new molecules with formulae such as $M\text{-}As[O(CH_2CH_2O)_nCH_2CH_2OAsMe_2]_2$. Similar compounds incorporating silicon or phosphorus atoms have also been isolated.

The structure of $Ph_3AsO.H_2O$ has been redetermined showing a centrosymmetric dimer in which each molecule is hydrogen bonded to two water molecules (As-O 1.644, O...O 2.800Å).[472] The anhydrous oxide, $(MeOOCC_6H_4)Et_2AsO$, on the other hand, contains discrete molecules with an As-O distance of 1.651Å. When Ph_3AsO reacts with aqueous hydrogen fluoride in glass apparatus the product is a tetrafluoroborate salt $[(Ph_3PO)_2H]^+BF_4^-$, with a short hydrogen bridge (O...O 2.44Å) in the cation.[473] In the absence of glass the product is Ph_3AsF_2.

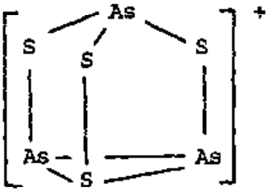
The first step in the hydrolysis of trimethyl arsenate is first order in ester and water with $k_1(25^\circ C) = 73M^{-1}sec^{-1}$, the second step is fast and the third step is unobservable.[474] Data are also available for the ethyl, n-pentyl and i-propyl derivatives.

Examples of a new structure type are provided by $AgCo_3H_2(AsO_4)_3$ and the corresponding zinc compound which are obtained on heating aqueous mixtures of As_2O_5, $AgNO_3$ and either $CoSO_4.7H_2O$ or $ZnSO_4.7H_2O$.[475] Arsenic pentoxide and ammonium dichromate yield the new arsenato-chromate $(NH_4)_3AsCr_4O_{16}$ while the corresponding potassium salt can be obtained from K_2CO_3 and As_2O_5.[476] The structures contain a central AsO_4 tetrahedron, each oxygen of which is shared with a CrO_4 group, and are thus isotypes of $K_3PCr_4O_{16}$. The structure of $Fe(H_2AsO_4)_3.5H_2O$ has also been determined.[477]

Two new microcrystalline forms of thorium arsenate, $Th(HAsO_4)_2.4H_2O$ and $Th(HAsO_4)_2.2\frac{1}{2}H_2O$ have been synthesised and characterised.[478] They are less stable chemically and thermally than the previously reported monohydrate, as shown by the extensive hydrolysis which occurs during Na-K exchange on the 2½-hydrate.[479]

5.3.6 Bonds to Sulphur, Selenium or Tellurium

Salts of two novel cations, i.e. $As_3S_4^+$ and $As_3Se_4^+$, have been prepared in liquid sulphur dioxide solution by the oxidation of α- or β-As_4S_4 and an As-Se melt with either AsF_5 or SbF_5.[480] Structures for both species show mirror symmetry in the cation, see (152), and there are significant interactions with the MF_6^- anions.

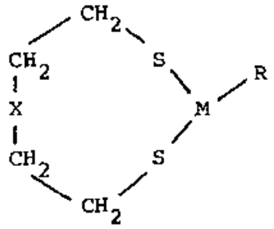


(152)

Tertiary arsines are not oxidised by sulphur in benzene solution, but under more forcing conditions, i.e. at 150°C for 8h in o-dichlorobenzene, Ph_3AsS, Ph_2MeAsS and $Ph_2As(S)CH_2AsPh_2$ can be obtained.[481] The triphenylarsine sulphide structure shows the presence of two almost identical independent molecules in the asymmetric unit, but because of different orientations of the phenyl groups, C_{3v} symmetry is not achieved.[482]

High yields of tri-(t-butylthio)arsine can be obtained when AsF_3 reacts with t-butylthiotrimethylsilane, and similar reactions take place with SbF_3 and BiF_3.[483] HeI p.e.s. and dipole moments have been measured for $As(SPh)_3$ and Me_2AsSPh.[484]

Arsenic, antimony and bismuth derivatives of O,O-diethylphosphoryldithiocarbamate, $M[S_2CNHP(O)(OEt)_2]_3$, have been isolated and shown to be non-electrolytes.[485] High resolution ^1H and ^{13}C n.m.r. data for the arsocanes and stibocanes (153) have been analysed and assigned; they show that in solution there is an equilibrium between a chair-chair conformer and two enantiomers



(153, M = As or Sb,
X = O or S,
R = Cl or Br)

with a boat-chair conformation.[486]

Triangular pyramidal coordination about arsenic (As-S 2,246, 2.303, 2.347Å) is found in the structure of $La_4O_3(AsS_3)_2$.[487] The Tl_3AsS_3-Tl_3SbS_3 system shows a complete series of solid solutions while that between $TlAsS_2$ and $TlSbS_2$ shows only a eutectic.[488]

GdAsSe and NdAsSe crystallise with a CeAsS-type structure,[489] and X-ray data are reported for crystals of AsSI, α- and β- AsSeI, and α- and β-AsTeI.[490]

5.4 ANTIMONY

5.4.1 Antimony and Antimonides

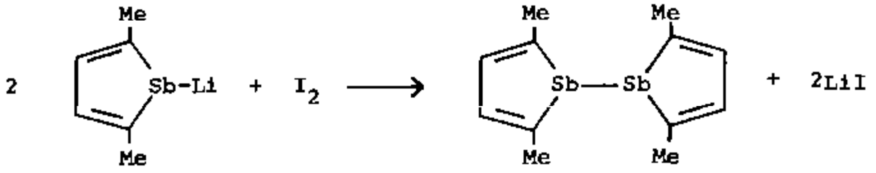
The change in antimony structure with pressure from a rhombohedral type (space group $R\bar{3}m$) to primitive simple cubic could not be confirmed, although the structure approaches the latter.[491] It is noted however that at 86 x 10^2MPa, there is a transition to a structure as yet unidentified. The compounds Ba_5Sb_4[492] and $Ba_2Mn_2M_2O$, where M = Sb or Bi,[493] have been synthesised. The former has a Gd_5Si_4 structure and in the latter Mn and Sb(Bi) form corrugated hexagonal nets with oxygen bridging between manganese atoms.

5.4.2 Bonds to Carbon

New preparations for Me_2SbCl and $MeSbCl_2$ from $(Me_2Sb)_2$ give pure compounds, but the dichloride decomposes on standing even in the dark.[494] Remeasured Mössbauer isomer shifts for the series Me_nSbCl_{3-n}, where n = 0 to 3, indicate a decrease in s-electron density at the antimony atom with increase in the value of n, a trend ascribed to an increase in p character of the lone pair orbital.

The anhydride and thioanhydride, $(t\text{-}Bu_2Sb)_2X$ where X = O or S, are produced on treatment of the monochloride with sodium hydroxide or sodium sulphide, but analogous reactions with $t\text{-}BuSbCl_2$ leads to the cyclic species $(t\text{-}BuSbO)_{3 \text{ and } 4}$ and $(t\text{-}BuSbS)_{2-4}$.[495]

The distibine (154) is obtained following equation (56), and in



(154) ...(56)

contrast to other distibines it is stable in air.[496] An X-ray structure shows a trans conformation about the Sb-Sb bond, with the rings in almost parallel planes perpendicular to this bond.

On reaction with metal carbonyls, distibines can yield either singly bridged distibine products, as in $(OC)_5Mo(SbR_2SbR_2)Mo(CO)_5$ where R = Me or Et, or species bridged by two R_2Sb groups, as in $(OC)_4Mo(SbR_2)_2Mo(CO)_4$ where R = Me, Et or Ph.[497] With $Fe_2(CO)_9$, among the products are $(OC)_4Fe(SbR_2SbR_2)$, where R = Et or t-Bu, and $(OC)_3Fe(SbR_2)_2Fe(CO)_3$, where R = Et or Ph.[498] Nickel carbonyl with tetramethyldistibine gives the distibine bridged product $(OC)_3Ni(SbMe_2SbMe_2)Ni(CO)_3$,[498] and CO is displaced from $M(CO)_6$, where M = Cr, Mo or W, by tris(trimethylsilyl)stibine to give the complexes $M(CO)_5Sb(SiMe_3)_3$ which are initiators for the polymerisation of THF.[499]

A number of new tetradentate ligands with Sb_2N_2, Sb_2S_2 and Sb_2O_2 donor sets has been synthesised, with formulae such as $R_2Sb(CH_2)_3.X.(CH_2)_2.X.(CH_2)_3SbR_2$, where X = NMe or S and R = Me or Ph, and $Me_2Sb(CH_2)_2O(CH_2)_2O(CH_2)_2SbMe_2$.[500]

In contrast to the unusual square pyramidal structure of pentaphenylantimony, the compound in which two phenyl groups are replaced by a biphenyl group, i.e. $Ph_3Sb(C_6H_4.C_6H_4)$, has a trigonal bipyramidal structure.[501] The biphenyl group spans equatorial and axial positions; the mean Sb-C distances are 2.146 and 2.206Å respectively to the equatorial and axial sites. Pentapropynyl antimony, obtained from $(MeC\vdots C)_3SbCl_2$ and $MeC\vdots CNa$, also has a trigonal bipyramidal structure, but the pentamethoxide in the solid state is a centrosymmetric dimer with two bridging methoxy groups.[502] Bridging Sb-O distances are 2.095 and 2.105Å while those to terminal methoxide groups have a mean value of 1.939Å; the angle at the bridging oxygen atom is 107.0°.

HeI p.e.s. have been measured and assigned for Me_3SbX_2, where X = Cl, Br or I, $SbCl_5$ and $SbMe_5$.[503]

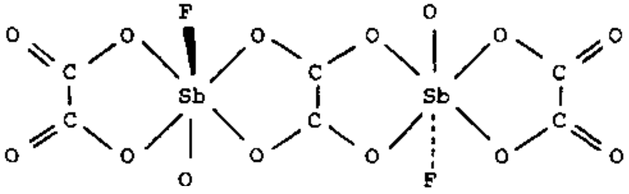
1:1 addition compounds can be isolated from mixtures of Me_3SbCl_2 and $SbCl_3$ and Me_3SbBr_2 and $SbBr_3$ in dichloromethane solution.[504] X-ray data show that five-fold coordination about antimony in Me_3SbCl_2 is maintained while with $SbCl_3$ there are three further contacts at distances between 3.154 and 3.308Å with chlorine atoms of different Me_3SbCl_2 molecules.

Dioximate, $R^1_3Sb(ON{:}CR^2R^3)_2$,[505] and dicarboxylate complexes, such as $Me_3Sb(O_2CR)_2$ for R = CH_2Ph and $CH{:}CHPh$[506] have been prepared from the appropriate trisubstituted antimony dihalide, and titanium(IV) chloride has been shown to yield $Ph_4SbTiCl_5$, $Ph_3SbCl_2.TiCl_3$ and $Ph_3SbCl_2.TiCl_4$ on reaction with Ph_4SbCl, Ph_3Sb and Ph_3SbCl_2 respectively.[507]

^1H n.m.r. spectra for the 8-quinolinate complex, Me_2SbCl_2(oxime), in a variety of solvents suggest the presence of isomeric forms in which the methyl and chlorine groups are repsectively cis and trans in an octahedral arrangement about antimony.[508] Dianions(L) derived from, for example, 2,2'-(methylidynenitrilo)diphenol behave as tridentate ligands and complex compounds such as $SbCl_3L$ and $PhSbCl_2L$ have been isolated.[509] Sulphur dioxide can be inserted into one of the Ph-Sb bonds in the complex compounds Ph_3SbL_2, where HL = salicylaldehyde, 8-hydroxyquinoline, acetylacetone etc.[510]

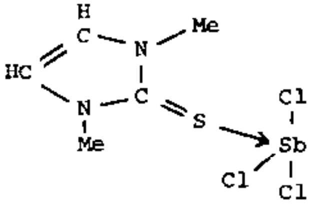
5.4.3 Bonds to Halogens

A new antimony(III) fluoride oxalate, obtained from $(NH_4)_2C_2O_4$ and SbF_3, has the formula $(NH_4)_4H_2(C_2O_4)_3(SbOF)_2.H_2O$ and contains the complex anion shown in (155).[511] The antimony atoms are in pseudo-pentagonal bipyramidal coordination by five oxygen atoms from two oxalate groups and a terminal atom; the axial positions are occupied by the fluorine atom and the antimony lone pair of electrons.



(155)

The solubility of antimony metal in molten mixtures of antimony trichloride and aluminium trichloride reaches a maximum at ca. 0.6 mol fraction $AlCl_3$ then decreases to zero in pure $AlCl_3$.[512] This solubility is considered due to a reaction in which species with oxidation states <3 are formed and which are stabilised in the high pCl conditions of the $AlCl_3$ systems. Similar solubility is found in $SbCl_3$-CsCl mixtures; here the low oxidation state species formed are stabilised in low pCl conditions. Addition compounds between $SbCl_3$ and amides such as dimethyl formamide, dimethylacetamide and tetramethylurea have been characterised[513] and a crystal structure reported for the 1:1 adduct with tetramethylthiourea.[514] Here the central atom is in distorted pseudo-trigonal bipyramidal coordination with equatorial positions occupied by a chlorine atom (2.428Å), the sulphur of the donor and the antimony lone pair; the remaining chlorine atoms occupy axial positions (2.527 and 2.687Å). Similar coordination is found in the 1:1 adduct with 1,3-dimethyl-2-(3H)-imidazolethione (156), but here intermolecular interactions



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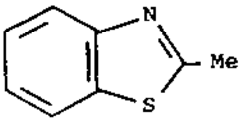


(157)

increase the antimony coordination number to six giving polymeric, zig-zag chains.[515]

Complexes of 2-methyl-benzothiazole(L) (157) with antimony and bismuth halides have the formulae $SbCl_3L$ or $3MX_3.2L$ where M = Sb and X = Br or I, M = Bi and X = Cl, Br or I, and although $SbCl_3.L$ is considered to be a monomer the 3:2 complexes are polymeric.[516]

The ternary adduct, $SbCl_3.I_2$(1,4-dithian), has been prepared and a structure determined.[517]

^{121}Mössbauer data are available for adducts of $SbCl_3$ with a number of substituted ureas.[518]

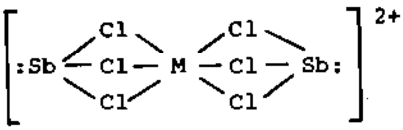
Single crystal X-ray studies of the 1:1 adduct of $SbCl_3$ and $GaCl_3$ show there is strong chlorine bridging between the $SbCl_2^+$ and $GaCl_4^-$ ions giving infinite chains parallel to the b axis.[519] The antimony environment consists of two short bonds to chlorine (2.295 and 2.299Å), two longer contacts (2.713 and 2.772Å) and, completing trigonal bipyramidal coordination, the antimony lone pair.

Antimony halide anions continue to attract attention and a series of mixed species including $SbCl_3F^-$, $SbBr_3F^-$, $SbCl_3F_2^{2-}$, $SbCl_3F_3^{3-}$,[520] $SbCl_2Br_3^{2-}$, $SbCl_3Br_2^{2-}$, $SbCl_3I_2^{2-}$, $SbBr_3I_2^{2-}$,[521] $SbCl_3Br_3^{3-}$, $SbBr_3I_3^{3-}$, $SbF_3Cl_3^{3-}$ and $SbFCl_5^{3-}$ [522] have been prepared from the appropriate antimony trihalide and an amine hydrohalide. 4-Benzylpiperidinium and N-benzylpiperazinium salts for $Sb(Bi)Cl_5^{2-}$ and the corresponding bromides have been prepared and characterised, the cations being chosen to show the effect of hydrogen bonding.[523] A partial structure for (N-benzylpiperazinium)$_2SbCl_5$ was determined.

Investigation of the i.r. spectrum of the mixed oxidation state species Cs_2SbCl_6 shows no bands assignable to the $Sb(III)Cl_6^{3-}$ ion when conventional spectrometers are used at room temperature but bands at 256, 214, 170 and 118 cm^{-1} do appear in the Fourier transform spectra at 77K.[524] The intensities decrease dramatically on raising the temperature, an effect ascribed to thermal charge transfer dynamics within the lattice.

Absorption spectra of a range of 3d metal chlorides in molten $SbCl_3$ or $SbCl_3$-KCl mixtures are interpreted in terms of the formation of octahedral and tetrahedral species with structures similar to those in (<u>158</u>) and (<u>159</u>).[525]

^{81}Br and ^{121}Sb n.q.r. spectra for the addition compound $SbBr_3(POBr_3)_2$ are interpreted in terms of a dinuclear species with an asymmetric bromine bridge,[526] while ^{81}Br data point to a dramatic change in structure for $pyHSbBr_4$ from a pseudo-trigonal



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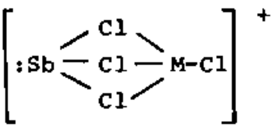


(159)

bipyramidal arrangement at room temperature to one more reasonably described as $SbBr_3.Br^-$ at 77K.[527]

Treatment of SbF_5 with $B(OTeF_5)_3$ leads to fluorine substitution and the mono- and di-substitution products $SbF_{5-n}(OTeF_5)_n$ can be isolated.[528] With MOF_4, where M = Mo, W or Re, antimony pentafluoride gives 1:1 addition compounds.[529] Structural studies show that the molybdenum compound consists of a polymeric zig-zag chain of alternate Mo and Sb atoms bridged by single fluorine atoms, while in the rhenium analogue there are essentially covalent eight-membered $Sb_2Re_2F_4$ rings.

Arsenic and antimony pentafluorides have been used in the oxidation of S_4N_4 to give the dipositive cation and although the normal AsF_6^- and SbF_6^- counter ions occur, there is evidence for the novel $Sb_3F_{14}^-$ anion.[530] As shown in Figure 10, this mixed oxidation state species consists of an angular SbF_2^+ cation linked

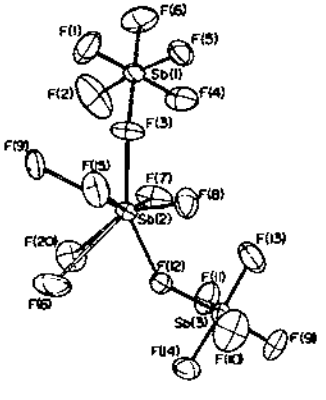
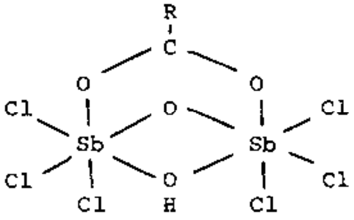


Figure 10. Structure of the $Sb_3F_{14}^-$ anion (reproduced by permission from Inorg. Chem., 20(1981)3799).

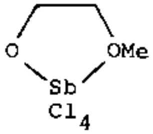
to two SbF_6^- anions by asymmetric fluorine bridges.

Interesting bridged carboxylato-antimony chlorides (160) can be isolated from reactions between $SbCl_5.H_2O$ and carboxylic acids or between $H_5O_2SbCl_6$ and $RCOOSbCl_4$, where R = CF_3, CCl_3, $CHCl_2$, Et, Me,



(160)

i-Pr or H;[531] the structure of the trichloroacetate has been determined. The $SbCl_5.H_2O$ addition compound on reaction with oxalic acid gives $(SbCl_4)_2C_2O_4$, and this compound is also obtained via a redox reaction between $SbCl_5.H_2O$ and squaric acid.[532] Although 1-methoxyethanol gives initially a 1:1 adduct with $SbCl_5$, it readily decomposes to the cyclic stibolanate (161); with dimethoxyethane, on the other hand, the product is a 1:2 adduct



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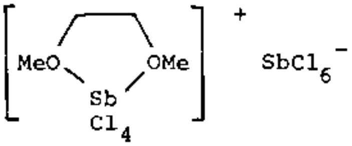


(162)

formulated as (162).[533] Dimethylphosphinic acid reactions with $SbCl_5$ lead to $(Cl_4SbO_2PMe_2)_2$, in which bridging O_2PMe_2 groups give an eight-membered ring system with approximately C_{2h} symmetry.[534]

When $SbCl_5$ reacts with $Ru_3(CO)_{12}$, the product is the molecular complex $[Ru(CO)_3Cl_2]_2.SbCl_3$ in which the antimony trichloride molecule is coordinated to a chlorine atom attached to ruthenium.[535]

^{121}Sb n.m.r. data for the seven hexahaloantimonates in the series $(SbCl_nBr_{6-n})^-$ have been analysed to show that for n = 2 to 4 only the cis isomeric forms are present in acetonitrile solutions.[536] Substitution of chlorine by bromine leads to upfield shifts with $SbBr_6^-$ occurring some 2430 ppm from $SbCl_6^-$.

5.4.4 Bonds to Oxygen

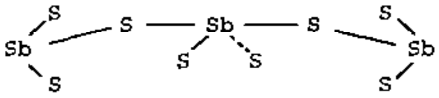
The chlorocatechol complex, $pyH[Sb(C_6Cl_4O_2)Cl_2]$, has a structure containing chlorine bridged anion chains where antimony is attached to the oxygen atoms (2.051 and 2.065Å) and three chlorine atoms (2.469, 2.873 and 3.001Å).[537]

Species identified in the $SbCl_3$-Sb_2O_3 and $SbBr_3$-Sb_2O_3 systems are SbOCl (m.p. 280°C), $Sb_4O_5Cl_2$ (m.p. 595°C), $Sb_8O_{11}Cl_2$ (m.p. 585°C) and $Sb_4O_5Br_2$ (m.p. 610°C) and $Sb_8O_{11}Br_2$ (m.p. 635°C).[538] Only one compound, $VSbO_4$, in which vanadium and antimony are in the +3 and +5 oxidation states respectively, is observed in the Sb_2O_3-V_2O_5 system.[539] The $BaSb_3O_5(OH)$ structure contains $(Sb_3O_6)_n^{3n-}$ chains in which each antimony has four associated oxygen atoms at distances between 1.93 and 2.27Å.[540] In the phosphite, $Sb_2(HPO_3)_3$, obtained from a reaction between Sb_2O_3 and aqueous H_3PO_3, the central atom is in pseudo-trigonal bipyramidal coordination and eight of the nine phosphite oxygen atoms are relatively strongly coordinated to two antimony atoms.[541]

Exchange of the alkaline earth ions together with Pb^{2+} on crystalline antimonic acid has been investigated[542] and the following selectivity order for the +3 cations $Al \ll Ga \lesssim Yb < Fe < La < In$ has been established.[543] Selectivity coefficients have also been measured for the Group 2 cations on ferric antimonate.[544] Mixed tin-antimony oxides are formed when the gel produced in the alkaline hydrolysis of a mixture of $SnCl_4$ and $SbCl_5$ is calcined at 600°C.[545] Investigation by powder neutron diffraction points to a rutile type lattice in which some of the interstitial positions in the tin(IV) oxide structure are occupied by Sb(III).[546]

5.4.5 Bonds to Sulphur

Two new thioantimonites, $Cs_4Sb_{14}S_{23}$[547] and $Ba_8Sb_6S_{17}$,[548] have been prepared, the former by hydrothermal synthesis and the latter by fusion from the appropriate binary sulphides. The $Sb_{14}S_{23}^{4-}$ anion has a complex polymeric structure containing both SbS_3 and SbS_4 units while in $Sb_6S_{17}^{16-}$, in addition to the well known pseudo-tetrahedral SbS_3^{3-} group, there is the previously unknown $Sb_3S_8^{7-}$ unit. As shown in (<u>163</u>), this species consists of a central pseudo-trigonal bipyramidal SbS_4 unit in which the axial atoms are shared with terminal SbS_3 groups.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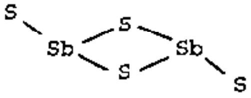
(164)

Heating Ca metal with Sb_2S_3 and elemental sulphur leads to the new sulphide $Ca_2Sb_2S_5$,[549] whose structure contains SbS_3^{3-} and $Sb_2S_4^{2-}$ (164) units, and a new compound $Li_{3x}Sb_{6-x}S_9$ where x = 0.33, has been isolated when a 3:17 mixture of Li_2S and Sb_2S_3 is heated.[550] The structure has been determined for this compound and for $Eu_3Sb_4S_9$,[551] isolated in an investigation into the $EuS-Sb_2S_3$ system.

Complex formation has been observed between a number of transition metal ions and antimony hydrogen bis(thioglycollate).[552]

Iodine bridging is a major feature in the structure of the substituted dithiocarbamate $[Sb(S_2CNEt_2)_2I].CHCl_3$.[553]

5.5 BISMUTH

Extended Hückel calculations with relativistic parameterisation have been reported for a number of Main Group element clusters, including Bi_9^{5+} and Bi_9^{7+}.[554] Stepwise liberation of hydrogen is observed in the LiH-Bi reaction leading to the successive formation of LiBi and Li_3Bi.[555] The ternary bismuthides, $Ca_9Cd_4Bi_9$, $Sr_9Cd_4Bi_9$ and $Ca_9Zn_4Bi_9$, recently synthesised from the elements have the same structure as $Ca_9Mn_4Bi_9$.[556]

All three Ph-Bi bonds in Ph_3Bi can be cleaved by mercaptocarboxylic acids in chloroform solution as shown in equation (57) but

$$Ph_3Bi + 2HSCH_2COOH \longrightarrow 3PhH + Bi(SCH_2COO)(HSCH_2COO) \qquad ...(57)$$

only two groups are removed in acetone with mercaptopropionic and -benzoic acids.[557] The first chiral organo-bismuth compound, $(4\text{-}Me\text{-}C_6H_4)(2\text{-}Me_2NCH_2C_6H_4)BiBr$, has been synthesised.[558]

Two bismuth chloride complexes with 1-alkyl-3-(2-pyridyl)-thiourea (L), i.e. $(BiCl_3L_2)_2$ and $(BiL_6)(NO_3)_3$, have been isolated.[559] The former has a binuclear centrosymmetric structure with bismuth in distorted octahedral coordination from three terminal chlorines (2.503-2.894Å), a bridging chlorine (3.073Å) and sulphurs from two ligands (2.786 and 2.735Å). In the cationic complex, bismuth lies on a centre of symmetry and is again in octahedral coordination with bonds to three independent sulphur atoms of 2.792, 2.798 and 2.808Å.

^{209}Bi n.q.r. measurements suggest an α-UF_5 structure for BiF_5 and data for $ClF_2^+ BiF_6^-$ point to the presence of two crystallographically non-equivalent bismuth atoms.[560]

Complex formation has been studied in aqueous solution between Bi(III) and oxy- and thio-diacetic acids, $X(CH_2COOH)_2$ where X = O or S.[561] The $Bi_2(SO_4)_3$-K_2SO_4 system provides evidence for $KBi(SO_4)_2$ and $K_3Bi(SO_4)_3$.[562]

An extensive series of papers deals with the crystallography of a range of dithiocarbamato-bismuth derivatives. Polymeric structures with bridging halogen atoms are found for the mixed complexes, $Bi(S_2CNEt_2)_2I$,[563] $Bi(S_2CNEt_2)_2Br$,[563] and $Bi(S_2CNEt_2)I_2$.[564] The latter compound reacts with one molecule of either bipyridyl or terpyridyl to give for the former a binuclear species with seven-fold coordination about bismuth but a monomeric structure for the latter.[565] Treatment of the diiodo compound with Et_4NI in DMF, yields an iodine bridged anionic species, $(Et_4N)_2[I_2(Et_2NCS_2)BiI_2BiS_2CNEt_2)I_2]$.[566] The dihalides, $Bi(S_2CNEt_2)X_2$ where X = Cl, Br or I, on recrystallisation from a DMF-n-butanol mixture are converted to species with the stoichiometry $Bi_5(S_2CNEt_2)_8X_7$ which contain four $[Bi(S_2CNEt_2)_2]^+$ cations, a BiX_6^{3-} anion and, for neutrality a halide ion.[567] Recrystallisation of the bromide from pyridine-n-butanol gives solvated $(pyH)_2[Bi_4(S_2CNEt_2)_4Br_{10}]$, but with pyridine alone the dihalides yield tetrapyridine adducts containing $Bi(S_2CNEt_2)X_2(py_3)$ units with a molecule of lattice pyridine.[568] A small amount of a second compound, shown by X-ray crystallography to be $(C_5H_5NCSNEt_2)_2(BiCl_5py)$, was also obtained from the dichloride reaction with pyridine.[569]

In addition to confirming the presence of $RbBiS_2$, $RbBi_3S_5$ and $CsBiS_2$ in the $Rb(Cs)_2S$-Bi_2S_3 systems, the new compounds Rb_3BiS_3 and $CsBi_3S_5$ were also identified.[570]

REFERENCES

1 D.G.Ott, "Syntheses with Stable Isotopes of Carbon, Nitrogen and Oxygen." John Wiley and Sons, New York, 1981 (reviewed in J. Am. Chem. Soc., 103(1981)6271).

2 K.Dehnicke and J.Strähle, Angew. Chem. Int. Ed. Engl., 20(1981)413.

3 M.R.Churchill and H.J.Wasserman, Inorg. Chem., 20(1981)2899.

4 S.Martinengo, G.Ciani, A.Sironi, B.T.Heaton and J.J.Mason, J. Am. Chem. Soc., 101(1979)7095.

5 D.E.Fjare and W.L.Gladfelter, J. Am. Chem. Soc., 103(1981) 1572.

6 P.Sobota and Z.Janas, Inorg. Chim. Acta, 53(1981)L11.

7 D.L.Thorn, W.A.Nugent and R.L.Harlow, J. Am. Chem. Soc., 103(1981)357).

8 P.B.Shevlin, D.W.McPherson and P.Melius, J. Am. Chem. Soc., 103(1981)7006.

9 U.Schindewolf and H.Schwab, J. Phys. Chem., 85(1981)2707.

10 G.Silvestri, S.Gambino, G.Filardo, C.Cuccia and E.Guarino, Angew. Chem. Inr. Ed. Engl., 20(1981)101.

11 M.S.Thompson and T.J.Meyer, J. Am. Chem. Soc., 103(1981)5577.

12 R.J.Cotter and A.L.Yergey, J. Am. Chem. Soc., 103(1981)1596.

13 M.Ohashi, R.P.Barron and W.R.Benson, J. Am. Chem. Soc., 103(1981)3943.

14 T.D.Lee, W.R.Anderson and G.D.Daves, Anal. Chem., 53(1981)304.

15 G.Zingler, H.Kelling and E.Popowski, Z. Anorg. Allg. Chem., 476(1981)41.

16 L.S.Khaikin, A.V.Belyakov, G.S.Koptev, A.V.Golubinskii, L.V.Vilkov, N.V.Girbasova, E.T.Bogoradovskii and V.S.Zavgorodnii, J. Mol. Struct., 66(1980)191.

17 S.Yamamoto, M.Yasunobu and N.Nishimura, Bull. Chem. Soc. Japan., 54(1981)3677.

18 F.P.Lossing, Y.-T.Lam and A.Maccoll, J. Inorg. Nucl. Chem., 59(1981)2228.

19 R.N.McDonald, A.K.Chowdhury, M.J.Pellerite and J.I.Brauman, J. Am. Chem. Soc., 103(1981)674, 676.

20 R.Sutcliffe, D.Griller, J.Lessard and K.W.Ingold, J. Am. Chem. Soc., 103(1981)624.

21 H.Schachner and W.Sundermeyer, J. Fluorine Chem., 18(1981)259.

22 R.E.Banks and N.Dickinson, J. Fluorine Chem., 19(1981)97.

23 A.Sekiya and D.D.DesMarteau, J. Fluorine Chem., 17(1981)463.

24 W.Y.Lam and D.D.DesMarteau, J. Fluorine Chem., 18(1981)441.

25 E.-U.Würthwein, Angew. Chem. Int. Ed. Engl., 20(1981)99.

26 W.C.Fultz, J.L.Burmeister, C.P.Cheng and T.L.Brown, Inorg. Chem., 20(1981)1734.

27 K.Ogawa, Y.Takeuchi, H.Suzuki and Y.Nomura, J. Chem. Soc. Chem. Commun., (1981)1015.

28 A.T.Hutton and H.M.N.H.Irving, J. Chem. Soc. Chem. Commun., (1981)735.

29 G.V.Schustov, N.B.Tavakalyan and R.G.Kostyanovsky, Angew. Chem. Int. Ed. Engl., 20(1981)200.

30 P.B.Dervan, M.E.Squillacote, P.M.Lahti, A.P.Sylwester and J.D.Roberts, J. Am. Chem. Soc., 103(1981)1120.

31 P.G.Schultz and P.B.Dervan, J. Am. Chem. Soc., 103(1981)1563.

32 M.N.Hughes, M.Okolow-Zukowska and H.L.Wallis, J. Chem. Soc. Dalton, (1981)2009.

33 P.Glavic and J.Zupan, J. Inorg. Nucl. Chem., 43(1981)1565.

34 S.F.Nelsen, P.J.Kinlen and D.H.Evans, J. Am. Chem. Soc., 103(1981)7045.

35 M.A.Mathur and H.H.Sisler, Inorg. Chem., 20(1981)426.

36 S.Arya, W.U.Malik, P.Vasudevan and H.S.Nalwa, J. Inorg. Nucl. Chem., 43(1981)3381.

37 S.F.Nelsen and P.M.Gannett, J. Am. Chem. Soc., 103(1981)3300.

38 H.Delalu, A.Marchand, M.Ferriol and R.Cohen-Adad, J. Chim. Phys., 78(1981)247.

39 K.Schlosser, Z. Naturforsch., 36b(1981)1544.

40 K.G.Phelan and G.Stedman, J. Chem. Soc. Chem. Commun., (1981)299.

41 M.J.Pellerite, R.L.Jackson and J.I.Brauman, J. Phys. Chem., 85(1981)1624.

42 R.L.Jackson, M.J.Pellerite and J.I.Brauman, J. Am. Chem. Soc., 103(1981)1802.

43 C.Casewit and J.D.Roberts, J. Am. Chem. Soc., 102(1980)2364.

44 C.Casewit, J.Wenninger and J.D.Roberts, J. Am. Chem. Soc., 103(1981)6248.

45 K.O.Christe and C.J.Schack, Inorg. Chem., 20(1981)2566.

46 D.H.Sieh and C.J.Michejda, J. Am. Chem. Soc., 103(1981)442.

47 M.E.Gross, W.C.Trogler and J.A.Ibers, J. Am. Chem. Soc., 103(1981)192.

48 T.G.Back, J. Chem. Soc. Chem. Commun., (1981)530.

49 H.H.Nelson and H.S.Johnston, J. Phys. Chem., 85(1981)3891.

50 H.Frei and G.C.Pimentel, J. Phys. Chem., 85(1981)3355.

51 G.W.Ray and R.T.Watson, J. Phys. Chem., 85(1981)1673.

52 B.K.Balbach, F.Helus, F.Oberdorfer and M.L.Ziegler, Angew. Chem. Int. Ed. Engl., 20(1981)470.

53 P.Felder, T.-K.Ha, A.M.Dwivedi and Hs.H.Günthard, Spectrochim. Acta, 37A(1981)337.

54 R.E.Stevens, T.J.Yanta and W.L.Gladfelter, J. Am. Chem. Soc., 103(1981)4981.

55 R.L.Van Ettenrand and J.M.Risley, J. Am. Chem. Soc., 103(1981)5633.

56 M.S.Garley and G.Stedman, J. Inorg. Nucl. Chem., 43(1981)2863.

57 S.B.Oblath, S.S.Markowitz, T.Novakov and S.G.Chang, J. Chem. Phys., 85(1981)1017.

58 Y.-N.Lee, S.E.Schwartz, J. Phys. Chem., 85(1981)840.

59 S.A.McDonald and L.Andrews, J. Mol. Spectrosc., 82(1980)459.

60 G.Y.Markovits, S.E.Schwartz and L.Newman, Inorg. Chem., 20(1981)445.

61 K.C.Jain, K.K.Pandey and U.C.Agarwala, Z. Anorg. Allg. Chem., 472(1981)217.

62 D.W.H.Rankin, M.R.Todd, F.G.Riddell and E.S.Turner, J. Mol. Struct., 71(1981)171.

63 S.Gomiscek, R.Clem, T.Novakov and S.G.Chang, J. Phys. Chem., 85(1981)2567.

64 R.J.Gowland and G.Stedman, J. Inorg. Nucl. Chem., 43(1981)2859

65 F.T.Bonner, M.J.Akhtar, T.-V.King, L.-H.Chen and T.Ishida, J. Phys. Chem., 85(1981)4051.

66 F.T.Bonner, H.Degani and M.J.Akhtar, J. Am. Chem. Soc., 103(1981)3739.

67 R.T.Barber, J. Am. Chem. Soc., 103(1981)1307.

68 G.Poulet, J.-L.Jourdain and G.Le Bras, Compt. Rend., 293 II (1981)899.

69 K.Aurivillius and C.Stalhandske, Acta Chem. Scand., A35(1981)537.

70 R.A.Kenly, P.L.Trevor and B.Y.Lan, J. Am. Chem. Soc., 103(1981)2203.

71 E.W.Colvin, A.D.Robertson, D.Seebach and A.K.Beck, J. Chem. Soc. Chem. Commun., (1981)952.

72 R.Gleiter, Angew. Chem. Int. Ed. Engl., 20(1981)444.

73 T.Chivers, R.T.Oakley, O.J.Scherer and G.Wolmershäuser, Inorg. Chem., 20(1981)914.
74 T.Chivers, P.W.Codding and R.T.Oakley, J. Chem. Soc. Chem. Commun., (1981)584.
75 H.W.Roesky, M.N.S.Rao, C.Graf, A.Giereo and E.Hädicke, Angew. Chem. Int. Ed. Engl., 20(1981)592.
76 H.W.Roesky, R.Emmert, W.Clegg, W.Isenberg and G.M.Sheldrick, Angew. Chem. Int. Ed. Engl., 20(1981)591.
77 W.Clegg, O.Glemser, K.Harms, G.Hartmann, R.Mews, M.Noltemeyer and G.M.Sheldrick, Acta Cryst., B37(1981)548.
78 J.W.Lown and S.M.S.Chauhan, J. Chem. Soc. Chem. Commun., (1981)675.
79 D.M.Byler and H.Susi, J. Mol. Struct., 77(1981)25.
80 F.-M.Schnepel and O.Glemser, Spectrochim. Acta, 37A(1981)257.
81 T.Bechtold and A.Engelbrecht, J. Fluorine Chem., 19(1982)379.
82 R.C.Kumar and J.M.Shreeve, J. Am. Chem. Soc., 103(1981)1951.
83 T.Abe and J.M.Shreeve, Inorg. Chem., 20(1981)2894; J. Chem. Soc. Chem. Commun., (1981)242.
84 A.Waterfeld and R.Mews, Angew. Chem. Int. Ed. Engl., 20(1981)1017.
85 D.D.DesMarteau, R.D.LeBlond, S.F.Hossain and D.Nothe, J. Am. Chem. Soc. 103(1981)7734.
86 A.Hasegawa, R.L.Hudson, O.Kikuchi, K.Nishikida and F. Williams J. Am. Chem. Soc., 103(1981)3436.
87 W.W.Wilson, R.D.Wilson and K.O.Christe, J. Inorg. Nucl. Chem., 43(1981)1551.
88 W.W.Wilson and K.O.Christe, Inorg. Chem., 20(1981)4139.
89 W.W.Wilson and K.O.Christe, J. Fluorine Chem., 19(1982)253.
90 P.Charpin, M.Lance, T.Bui Huy and R.Bougon, J. Fluorine Chem. 17(1981)479.
91 R.Bougon and T.Bui Huy, J. Fluorine Chem., 18(1981)87.
92 C.J.Schack and K.O.Christe, J. Fluorine Chem., 18(1981)363.
93 H.Bürger, G.Pawelke, R.Dammel and H.Bock, J. Fluorine Chem., 19(1982)565.
94 C.J.Schack, J. Fluorine Chem., 18(1981)583.
95 A.Sekiya and D.D.DesMarteau, Inorg. Chem., 20(1981)1.
96 N.Thiel, W.Schwarz and A.Schmidt, Z. Naturforsch., 36b(1981)775.
97 M.Soulard, F.Bloc and A.Hatterer, J. Chem. Soc. Dalton, (1981)2300.
98 M.Plewa and K.F.Tebbe, Z. Anorg. Allg. Chem., 477(1981)7.
99 H.Handel, P.Labbe, R.LeGoaller and J.-L.Pierre, J. Chim. Phys., 78(1981)421.
100 F.Jeanneaux, A.Grand and J.G.Riess, J. Am. Chem. Soc., 103(1981)4272.
101 E.Niecke, K.Schwichtenhövel, H.-G.Schäfer and B.Krebs, Angew. Chem. Int. Ed. Engl., 20(1981)963.
102 E.Niecke, R.Rüger and W.W.Schoeller, Angew. Chem. Int. Ed. Engl., 20(1981)1034.
103 H.Nöth and V.Thorn, Z. Naturforsch., 36b(1981)659.
104 W.Leidinger and W.Sundermeyer, J. Fluorine Chem., 19(1981)85.
105 U.Müller, R.Dübgen and K.Dehnicke, Z. Anorg. Allg. Chem., 473(1981)115.
106 C.Bianchini, M.DiVaira, A.Meli and L.Sacconi, J. Am. Chem. Soc., 103(1981)1448.
107 P.Dapporto, L.Sacconi, P.Stoppioni and F.Zanobini, Inorg. Chem., 20(1981)3834.
108 C.Bianchini, M.DiVaira, A.Meli and L.Sacconi, Inorg. Chem., 20(1981)1169.

109 M.Dräger and B.Mathiasch, Angew. Chem. Int. Ed. Engl., 20(1981)1029.

110 M.Yoshifuji, I.Shima, N.Inamoto, K.Hirotsu and T.Higuchi, J. Am. Chem. Soc., 103(1981)4587.

111 A.B.Burg, Inorg. Chem., 20(1981)3731.

112 R.Appel and W.Paulen, Angew. Chem. Int. Ed. Engl., 20(1981)869.

113 P.Dehnert, J. Grobe and Duc Le Van, Z. Naturforsch., 36b(1981)48.

114 M.Bauder and J.Hellmann, Z. Naturforsch., 36b(1981)266.

115 M.Baudler and J.Hellmann, Z. Anorg. Allg. Chem., 480(1981)129.

116 H.Köpf and R.Voigtländer, Chem. Ber., 114(1981)2731.

117 M.Baudler and A.Marx, Z. Anorg. Allg. Chem., 474(1981)18.

118 M.Feher, R.Fröhlich and K.-F.Tebbe, Z. Anorg. Allg. Chem., 474(1981)31.

119 M.Baudler and S.Klautke, Z. Naturforsch., 36b(1981)527.

120 M.Baudler, H.Suchomel, G.Fürstenberg and U.Schings, Angew. Chem. Int. Ed. Engl., 20(1981)1044.

121 R.Gleiter, M.C.Böhm and M.Baudler, Chem. Ber., 114(1981)1004.

122 W.Weigand, A.W.Cordes and P.N.Swepston, Acta Crystallogr., B37(1981)1631.

123 G.Fritz and J.Härer, Z. Anorg. Allg. Chem., 481(1981)185.

124 M.Baudler, G.Reuschenbach and J.Hahn, Z. Anorg. Allg. Chem., 482(1981)27.

125 M.Baudler and P.Lütkecosmann, Z. Anorg. Allg. Chem., 472(1981)38.

126 M.Baudler, Y.Aktalay, K.-F.Tebbe and T.Heinlein, Angew. Chem. Int. Ed. Engl., 20(1981)967.

127 M.Baudler, Y.Aktalay, J.Hahn and E.Därr, Z. Anorg. Allg. Chem., 473(1981)20.

128 M.C.Böhm and R.Gleiter, Z. Naturforsch., 36b(1981)498.

129 M.Baudler, J.Hellmann, P.Backmann, K.-F.Tebbe, R.Fröhlich and M.Feher, Angew. Chem. Int. Ed. Engl., 20(1981)406.

130 H.G. von Schnering, V.Manriquez and W.Hönle, Angew. Chem. Int. Ed. Engl., 20(1981)594.

131 H.G. von Schnering and G.Menge, Z. Anorg. Allg. Chem., 481(1981)33.

132 H.G. von Schnering, Angew. Chem. Int. Ed. Engl., 20(1981)33.

133 R.Berger, Acta Chem. Scand., A35(1981)635.

134 L.-E.Tergenius, B.I.Nolång and T.Lundström, Acta Chem. Scand., A35(1981)693.

135 R.Rühl and W.Jeitschko, Acta Crystallogr., B37(1981)39.

136 M.H.Möller and W.Jeitschko, Inorg. Chem., 20(1981)828.

137 B.Eisenmann and H.Schäfer, Z. Naturforsch., 36b(1981)415.

138 K.E.Mironov and R.V.Abdullin, Russ. J. Inorg. Chem., 25(1980)1142.

139 G.Achenbach and H.-U.Schuster, Z. Anorg. Allg. Chem., 475(1981)9.

140 W.Carrillo-Cabrera and T.Lundström, Acta Chem. Scand., A35(1981)545.

141 A.Harsta and E.Wennebo, Acta Chem. Scand., A35(1981)227.

142 A.Rebbah, J.Yazbeck and A.Deschanvres, Rev. Chim. Min., 18(1981)43.

143 A.Rebbah and A.Deschanvres, Rev. Chim. Min., 18(1981)125.

144 A.Rebbah and A.Deschanvres, Rev. Chim. Min., 18(1981)173.

145 A.Rebbah and A.Deschanvres, Ann. Chim. (Paris), 6(1981)585.

146 R.Appel, F.Knoll and I.Ruppert, Angew. Chem. Int. Ed. Engl., 20(1981)731.

147 R.D.Brown, P.D.Godfrey and D.McNaughton, Aust. J. Chem., 34(1981)465.

148 A.B.Burg, Inorg. Chem., 20(1981)3734.
149 R.H.Neilson, Inorg. Chem., 20(1981)1679.
150 K.Issleib, H.Schmidt and C.Wirkner, Z. Anorg. Allg. Chem., 473(1981)85.
151 K.Issleib, H.Schmidt and C.Wirkner, Z. Chem., 21(1981)357.
152 E.Niecke and D.-A.Wildbredt, J. Chem. Soc. Chem. Commun., (1981)72.
153 G.Becker, W.Uhl and H.-J.Wessely, Z. Anorg. Allg. Chem., 479(1981)41.
154 G.Becker, M.Rössler and W.Uhl, Z. Anorg. Allg. Chem., 473(1981)7.
155 G.Becker and W.Uhl, Z. Anorg. Allg. Chem., 475(1981)35.
156 B.Eshtiagh-Hosseini, H.W.Kroto, J.F.Nixon, M.J.Maah and M.J.Taylor, J. Chem. Soc. Chem. Commun., (1981)199.
157 T.C.Klebach, R.Lourens, F.Bickelhaup, C.H.Stam and A. van Herk, J. Organomet. Chem., 210(1981)211.
158 G.Becker, G.Gresser and W.Uhl, Z. Naturforsch., 36b(1981)16.
159 R.Appel, G.Maier, H.P.Reisenauer and A.Weiterhaus, Angew. Chem. Int. Ed. Engl., 20(1981)197.
160 H.Oberhammer, G.Becker and G.Gresser, J. Mol. Struct., 75(1981)283.
161 J.C.T.R.Burckett-St. Laurent, P.B.Hitchcock, H.W.Kroto and J.F.Nixon, J. Chem. Soc. Chem. Commun., (1981)1141.
162 H.-P.Abicht and K.Issleib, Z. Chem., 21(1981)341.
163 A.H.Cowley, M.Lattman and J.C.Wilburn, Inorg. Chem., 20(1981)2916.
164 S.G.Baxter, R.L.Collins, A.H.Cowley and S.F.Sena, J. Am. Chem. Soc., 103(1981)714.
165 S.G.Baxter, A.H.Cowley and S.K.Mehrotra, J. Am. Chem. Soc., 103(1981)5572.
166 G.D.Fong and R.L.Kuczkowski, Inorg. Chem., 20(1981)2342.
167 D.E.Cabelli, A.H.Cowley and M.J.S.Dewar, J. Am. Chem. Soc., 103(1981)3286.
168 D.E.Cabelli, A.H.Cowley and M.J.S.Dewar, J. Am. Chem. Soc., 103(1981)3290.
169 E.Niecke, W.W.Schoeller and D.-A.Wildbredt, Angew. Chem. Int. Ed. Engl., 20(1981)131.
170 P.W.Clark and B.J.Mulraney, J. Organomet. Chem., 217(1981)51.
171 S.G.Baxter, A.H.Cowley, R.E.Davis and P.E.Riley, J. Am. Chem. Soc., 103(1981)1699.
172 R.Appel, J.Peters and R.Schmitz, Z. Anorg. Allg. Chem., 475(1981)18.
173 K.Iijima, E.Koshimizu and S.Shibata, Bull. Chem. Soc. Japan, 54(1981)2255.
174 J.E.Drake, J.L.Hencher and L.N.Khasrou, Can. J. Chem., 59(1981)2898.
175 H.Schmidbaur and E.Weiss, Angew. Chem. Int. Ed. Engl., 20(1981)283.
176 I.J.Galpin, G.W.Kenner, A.Marston and O.S.Mills, J. Chem. Soc. Chem. Commun., (1981)789.
177 R.L.Beddoes and O.S.Mills, J. Chem. Research(S), (1981)233.
178 U.Müller, R.Dübgen and K.Dehnicke, Z. Anorg. Allg. Chem., 473(1981)115.
179 H.J.Becker, D.Fenske and M.Heymann, Z. Anorg. Allg. Chem., 475(1981)27.
180 A.Tzschach and W.Uhlig, Z. Anorg. Allg. Chem., 475(1981)251.
181 M.Baacke, S.Hietkamp, S.Morton and O.Stelzer, Chem. Ber., 114(1981)2568.
182 M.Baacke , S.Heitkamp, S.Morton and O.Stelzer, Chem. Ber., 114(1981)3691.

183 E.P.Kyba, R.E.Davis, C.W.Hudson, A.M.John, S.B.Brown, M.J.McPhaul, L.K.Liu and A.C.Glover, J. Am. Chem. Soc., 103(1981)3868.
184 M.D.Fryzuk and P.A.MacNeil, J. Am. Chem. Soc., 103(1981)3592.
185 P.A.W.Dean, D.D.Phillips and L.Polensek, Can. J. Chem., 59(1981)50.
186 G.Becker, Z. Anorg. Allg. Chem., 480(1981)21.
187 G.Becker, Z. Anorg. Allg. Chem., 480(1981)38.
188 E.Lindner and J.C.Wuhrmann, Chem. Ber., 114(1981)2272.
189 E.Lindner and J.C.Wuhrmann, Z. Naturforsch., 36b(1981)297.
190 R.Thamm and E.Fluck, Z. Naturforsch., 36b(1981)910.
191 G.Borch, O.Dahl, P.Klaeboe and P.H.Nielsen, Acta Chem. Scand., A34(1981)497.
192 P.Braunstein, D.Matt, Y.Dusausoy, J.Fischer, A.Mitschler and L.Ricard, J. Am. Chem. Soc., 103(1981)5115.
193 R.M.K.Deng and K.B.Dillon, J. Chem. Soc. Chem. Commun., (1981)1170.
194 W.S.Sheldrick, A.Schmidpeter, F.Zwaschka, K.B.Dillon, A.W.G.Platt and T.C.Waddington, J. Chem. Soc. Dalton Trans., (1981)413.
195 R.Appel and K.Waid, Z. Naturforsch., 36b(1981)127.
196 R.Appel and K.Waid, Z. Naturforsch., 36b(1981)131.
197 H.Schmidbaur and T.Costa, Chem. Ber., 114(1981)3063.
198 U.Schubert, C.Kappenstein, B.Milewski-Mahrla and H.Schmidbaur, Chem. Ber., 114(1981)3070.
199 H.Schmidbaur and U.Deschler, Chem. Ber., 114(1981)2491.
200 G.E.Hardy, W.C.Kaska, B.P.Chandra and J.I.Zink, J. Am. Chem. Soc., 103(1981)1074.
201 J.Weiss and B.Nuber, Z. Anorg. Allg. Chem., 473(1981)101.
202 G.Fritz, U.Braun, W.Schick, W.Hönle and H.G.Von Schnering, Z. Anorg. Allg. Chem., 472(1981)45.
203 H.Schmidbaur, U.Deschler and B.Milewski-Mahrla, Angew. Chem. Int. Ed. Engl., 20(1981)586.
204 O.J.Scherer and H.Jungmann, Z. Naturforsch., 36b(1981)1663.
205 H.J.Hecht and G.Ruban, Cryst. Struct. Commun., 10(1981)495.
206 G.Ruban and V.Zabel, Cryst. Struct. Commun., 10(1981)499.
207 H.Schmidbaur and A.Schier, Chem. Ber., 114(1981)3385.
208 H.Schmidbaur, U.Deschler, B.Milewski-Mahrla and B.Zimmer-Gasser, Chem. Ber., 114(1981)608.
209 H.Schmidbaur, T.Costa and B.Milewski-Mahrla, Chem. Ber., 114(1981)1428.
210 H.Schmidbaur and C.E.Zybill, Chem. Ber., 114(1981)3589.
211 R.Appel and V.I.Gläsel, Z. Naturforsch., 36b(1981)447.
212 A.J.Blake, R.A.Howie and G.P.McQuillan, Acta Crystallogr., B37(1981)997.
213 A.J.Blake, R.A.Howie and G.P.McQuillan, Acta Crystallogr., B37(1981)1959.
214 P.Wermer and B.S.Ault, Inorg. Chem., 20(1981)970.
215 A.P.Hagen and D.L.Terrell, Inorg. Chem., 20(1981)1325.
216 S.Cradock, G.S.Laurenson and D.W.H.Rankin, J. Chem. Soc. Dalton Trans., (1981)187.
217 G.S.Laurenson and D.W.H.Rankin, J. Chem. Soc. Dalton Trans., (1981)425.
218 G.S.Laurenson and D.W.H.Rankin, J. Chem. Soc. Dalton Trans., (1981)1047.
219 E.A.V.Ebsworth, D.J.Hutchison, E.K.Macdonald and D.W.H. Rankin, Inorg. Nucl. Chem. Lett., 17(1981)19.
220 E.A.V.Ebsworth, D.W.H.Rankin and J.D.Whitelock, J. Chem. Soc. Dalton Trans., (1981)840.

221 J.A.S.Duncan, E.A.V.Ebsworth, R.O.Gould, C.L.Jones, D.W.H.Rankin and J.D.Whitelock, J. Chem. Soc. Dalton Trans., (1981)1028.
222 G.M.Brown, J.E.Finholt, R.B.King and T.W.Lee, J. Am. Chem. Soc., 103(1981)5249.
223 R.G.Kalbandkeri, D.K.Padma and A.R.V.Murthy, Indian J. Chem., 20A(1981)83.
224 J.Neeman and U.Klingebiel, Chem. Ber., 114(1981)527.
225 K.Weissermel, H.-J.Kleiner, M.Finke and U.-H.Felcht, Angew. Chem. Int. Ed. Engl., 20(1981)223.
226 A.Hinke, W.Kuchen and J.Kulter, Angew. Chem. Int. Ed. Engl., 20(1981)1060.
227 M.Gouterman, P.Sayer, E.Shankland and J.P.Smith, Inorg. Chem., 20(1981)87.
228 K.B.Dillon, A.W.G.Platt and T.C.Waddington, Inorg. Nucl. Chem. Lett., 17(1981)201.
229 H.W.Roesky, K.-L.Weber and J.Schimkowiak, Angew. Chem. Int. Ed. Engl., 20(1981)973.
230 D.W.Davidson, L.D.Calvert, F.Lee and J.A.Ripmeester, Inorg. Chem., 20(1981)2013.
231 P.Behmel, W.Clegg, G.M.Sheldrick, G.Weber and M.Ziegler, J. Mol. Struct., 74(1981)19.
232 R.Bartsch, O.Stelzer and R.Schmutzler, Z. Naturforsch., 36b(1981)1349.
233 I.Ruppert, Z. Anorg. Allg. Chem., 477(1981)59.
234 W.Althoff, M.Fild and R.Schmutzler, Chem. Ber., 114(1981)1082.
235 A.Addou and P.Vast, Rev. Chim. Min., 18(1981)184.
236 K.B.Dillon, A.W.G.Platt and T.C.Waddington, J. Chem. Soc. Dalton Trans., (1981)2292.
237 W.Kuchen, H.Somberg and U.Tobolla, Chem. Ber., 114(1981)3485.
238 D.Mootz, W.Poll, H.Wunderlich and H.-G.Wussow, Chem. Ber., 114(1981)3499.
239 K.B.Dillon, T.C.Waddington and D.Younger, J. Inorg. Nucl. Chem., 43(1981)2665.
240 G.Sonnek, H.Reinheckel and K.-G.Baumgarten, Z. Chem., 21(1981)268.
241 T.Abouchaccra, M.Helioui, E.Puckaric, R. de Jaeger and J.Heubel, J. Chem. Reserch(S), (1981)230.
242 G.Beyendorff-G ulba, J.Strähle, A.Liebelt and K.Dehnicke, Z. Anorg. Allg. Chem., 483(1981)26.
243 A.Yu Tsivadze, T.L.Novoderezhkina, O.N.Gilyarov and B.N.Kulikovskii, Russ. J. Inorg. Chem., 25(1980)2434.
244 C.Friebel and A.Saavedra, Z. Anorg. Allg. Chem., 473(1981)42.
245 A.Finch, P.N.Gates and A.S.Muir, J. Chem. Soc. Chem. Commun., (1981)812.
246 G.P.Dudchik and O.G.Polyachenok, Russ. J. Inorg. Chem., 25(1980)1436.
247 O.J.Scherer and H.Conrad, Z. Naturforsch., 36b(1981)515.
248 E.Niecke, R.Rüger and W.W.Schoeller, Angew. Chem. Int. Ed. Engl., 20(1981)1034.
249 A.H.Cowley, J.E.Kilduff and J.C.Wilburn, J. Am. Chem. Soc., 103(1981)1575.
250 A.Schmidpeter and K.Karaghiosoff, Z. Naturforsch., 36b(1981)1273.
251 A.Schmidpeter, H.Tautz, J. von Seyerl and G.Huttner, Angew. Chem. Int. Ed. Engl., 20(1981)408.
252 H.Tautz and A. Schmidpeter, Chem. Ber., 114(1981)825.

253 E.Niecke, A.Seyer and D.-A.Wildbredt, Angew. Chem. Int. Ed. Engl., 20(1981)675.
254 A.B.Burg, Inorg. Chem., 20(1981)2739.
255 J.Febvay, D.Grec and J.G.Riess, Inorg. Chem., 20(1981)4285.
256 A.H.Cowley, R.A.Kemp and J.C.Wilburn, Inorg. Chem., 20(1981)4289.
257 A.H.Cowley, S.K.Mehrotra and H.W.Roesky, Inorg. Chem., 20(1981)712.
258 R.Keat, L.Manojlovic-Muir, K.C.Muir and D.S.Rycroft, J. Chem. Soc. Dalton Trans., (1981)2192.
259 H.Binder and R.Fischer, Z. Anorg. Allg. Chem., 474(1981)43.
260 E.Niecke, K.Schwichtenhövel, H.-G.Schäfer and B.Krebs, Angew. Chem. Int. Ed. Engl., 20(1981)963.
261 E.Niecke, A.Nickloweit-Lüke and R.Rüger, Angew. Chem. Int. Ed. Engl., 20(1981)385.
262 E.Niecke, A.Nickloweit-Lüke, R.Rüger, B.Krebs and H.Grewe, Z. Naturforsch., 36b(1981)1566.
263 M.Wieber, O.Mulfinger and H.Wunderlich, Z. Anorg. Allg. Chem., 477(1981)108.
264 H.Wunderlich, Acta Crystallogr., B37(1981)995.
265 S.D.Worley, J.H.Hargis, L.Chang and W.B.Jennings, Inorg. Chem., 20(1982)2339.
266 A.H.Cowley, R.E.Davis and K.Remadna, Inorg. Chem., 20(1981)2146.
267 K.Bergesen, B.Pedersen and J.Songstad, Acta Chem. Scand., A35(1981)147.
268 D.Gonbeau, M.Sanchez and G.Pfister-Guillouzo, Inorg. Chem., 20(1981)1966.
269 R.G.Cavell, K.I.The and L.Vande Griend, Inorg. Chem., 20(1981)3813.
270 H.Nöth and V.Thorn, Z. Naturforsch., 36b(1981)1424.
271 H.Nöth and V.Thorn, Z. Naturforsch., 36b(1981)659.
272 S.Kleeman, E.Fluck and W.Schwarz, Z. Anorg. Allg. Chem., 475(1981)137.
273 H.W.Roesky, H.Zamankhan, W.S.Sheldrick, A.H.Cowley and S.K.Mehrotra, Inorg. Chem., 20(1981)2910.
274 W.S.Sheldrick, S.Pohl, H.Zamankhan, M.Banek, D.Amirzadel-Asl and H.W.Roesky, Chem. Ber., 114(1981)2132.
275 D.Schomburg, N.Weferling and R.Schmutzler, J. Chem. Soc. Chem. Commun., (1981)609.
276 W.Keim, R.Appel, A.Storek, C.Krüger and R.Goddard, Angew. Chem. Int. Ed. Engl., 20(1981)116.
277 E.Fluck, R.Hösle and A.-K.Zischka, Z. Anorg. Allg. Chem., 474(1981)105.
278 C.Glidewell, R.Keat and D.S.Rycroft, Inorg. Chim. Acta, 53(1981)L231.
279 F.Jeanneaux, A.Grand and J.G.Riess, J. Am. Chem. Soc., 103(1981)4272.
280 R.Appel, U.Gläsel and V.I.Gläsel, Chem. Ber., 114(1981)1542.
281 A.F.Cameron and L.F.D.Duncanson, Acta Crystallogr., B37(1981)1604.
282 G.Oliva, E.E.Castellano and L.R.Franco de Carvalho, Acta Crystallogr., B37(1981)474.
283 U.Engelhardt, B.Friedrich and I.Kirner, Z. Naturforsch., 36b(1981)791.
284 J.E.Richman, R.O.Day and R.R.Holmes, Inorg. Chem., 20(1981) 3378.
285 J.E.Richman, O.D.Gupta and R.B.Flay, J. Am. Chem. Soc., 103(1981)1291.
286 J.E.Richman and R.B.Flay, J. Am. Chem. Soc., 103(1981)5265.

287 H.W.Roesky, H.Djarrah, D.Amirzadeh-Asl and W.S.Sheldrick, Chem. Ber., 114(1981)1554.

288 A.Schmidpeter, H.Tautz and F.Schreiber, Z. Anorg. Allg. Chem., 475(1981)211.

289 R.O.Day, R.R.Holmes, H.Tautz, J.H.Weinmaier and A.Schmidpeter, Inorg. Chem., 20(1981)1222.

290 M.L.Thompson, A.Tarassoli, R.C.Haltiwanger and A.D.Norman, J. Am. Chem. Soc., 103(1981)6770.

291 W.Zeiss, A.Pointner, C.Engelhardt and H.Khehr, Z. Anorg. Allg. Chem., 475(1981)256.

292 W.Zeiss, T.Kuhn, D.Lux, W.Schwarz and H.Hess, Z. Naturforsch., 36b(1981)561.

293 M.Kubjacek and K.Utvary, Monatsh., 112(1981)305.

294 M.Kubjacek and K.Utvary, Monatsh., 112(1981)1353.

295 P.J.Argent, D.Parker, R.A.Shaw and M.Woods, Inorg. Nucl. Chem. Lett., 17(1981)11.

296 C.W.Allen and P.L.Toch, Inorg. Chem., 20(1981)8.

297 H.R.Allcock, P.P.Greigger, L.J.Wagner and M.Y.Bernheim, Inorg. Chem., 20(1981)716.

298 P.Clare and D.B.Sowerby, J. Inorg. Nucl. Chem., 43(1981)467.

299 P.Clare and D.B.Sowerby, J. Inorg. Nucl. Chem., 43(1981)477.

300 A.W.Cordes, P.N.Swepston, R.T.Oakley, N.L.Paddock and T.N.Ranganathan, Can. J. Chem., 59(1981)2364.

301 B.Thomas, G.Grossmann and D.Scheller, Z. Anorg. Allg. Chem., 480(1981)163.

302 H.R.Allcock, P.J.Harris and M.S.Connolly, Inorg. Chem., 20(1981)11.

303 H.R.Allcock, P.J.Harris and R.A.Nissan, J. Am. Chem. Soc., 103(1981)2256.

304 H.R.Allcock and P.J.Harris, Inorg. Chem., 20(1981)2844.

305 P.J.Harris, J.L.Desorcie and H.R.Allcock, J. Chem. Soc. Chem. Commun., (1981)852.

306 J.M.E.Goldschmidt and E.Licht, J. Chem. Soc. Dalton Trans., (1981)107.

307 J.M.E.Goldschmidt and R.Goldstein, J. Chem. Soc. Dalton Trans., (1981)1283.

308 Z.Gabay and J.M.E.Goldschmidt, J. Chem. Soc. Dalton Trans., (1981)1456.

309 N.Friedman, J.M.E.Goldschmidt, U.Sadeh and M.Segev, J. Chem. Soc. Dalton Trans., (1981)103.

310 T.T.Bamgboye and D.B.Sowerby, J. Inorg. Nucl. Chem., 43(1981)2253.

311 V.Chandrasekhar, S.S.Krishnamurthy, A.R.V.Murthy, R.A.Shaw and M.Woods, Inorg. Nucl. Chem. Lett., 17(1981)181.

312 H.Prakash, Indian J. Chem., 20A(1981)170.

313 H.R.Allcock and T.J.Fuller, J. Am. Chem. Soc., 103(1981)2250.

314 M.Manfait, A.J.P.Alix, J.-L.Butour, J.-F.Labarre and F.Sournies, J. Mol. Struct., 71(1981)39.

315 A.A. van der Huizen, A.P.Jekel, J.Rusch and J.C. van de Grampel, Rec. Trav. Chim., 100(1981)343.

316 M.Krishnaiah, L.Ramamurthy, P.Ramabrahmam and H.Manohar, Z. Naturforsch., 36b(1981)765.

317 Y.S.Babu, H.Manohar and R.A.Shaw, J. Chem. Soc. Dalton Trans., (1981)599.

318 K.D.Gallicano, R.T.Oakley, N.L.Paddock and R.D.Sharma, Can. J. Chem., 59(1981)2654.

319 P.Ramabrahmam, S.S.Krishnamurthy and M.Woods, Z. Naturforsch., 36b(1981)894.

320 B.Thomas and G.Grossmann, Z. Chem., 21(1981)152.

321 K.S.Dhathathreyan, S.S.Krishnamurthy, A.R.V.Murthy, R.S R.A.Shaw and M.Woods, J. Chem. Soc. Dalton Trans., (1981)1928.

322 G.J.Bullen, S.J.Williams, N.L.Paddock and D.J.Patmore, Acta Crystallogr., B37(1981)607.

323 N.L.Paddock, T.N.Ranganathan, S.J.Rettig, R.D.Sharma and J.Trotter, Can. J. Chem., 59(1981)2429.

324 K.D.Gallicano, N.L.Paddock, S.J.Rettig and J.Trotter, Can. J. Chem., 59(1981)2435.

325 J.C. van de Grampel, A.A. van der Huizen, A.P.Jekel, D.Wiedijk, J.-F.Labarre and F.Sournies, Inorg. Chim. Acta, 53(1981)L169.

326 J.Galy, R.Enjalbert, A.A. van der Huizen, J.C. van de Grampel and J.-F.Labarre, Acta Crystallogr., B37(1981)2205.

327 F. van Bolhuis, B. de Ruiter and J.C. van de Grampel, J. Chem. Soc. Chem. Commun., (1981)1065.

328 F. van Bolhuis,C.Cnossen-Voswijk and J.C. van de Grampel, Cryst. Struct. Commun., 10(1981)69.

329 F. van Bolhuis, J.B. van den Berg and J. C. van de Grampel, Cryst. Struct. Commun., 10(1981)1031.

330 J.-P.Faucher, F.Crasnier and J.-F.Labarre, J. Mol. Struct., 76(1981)165.

331 M.Jansen, M.Voss and H.-J.Deiseroth, Angew. Chem. Int. Ed. Engl., 20(1981)965.

332 M.Jansen and M.Voss, Angew. Chem. Int. Ed. Engl., 20(1981)100.

333 K.H.Jost and M.Schneider, Acta Crystallogr., B37(1981)222.

334 A.K.Indrayan, S.K.Mishra and Y.K.Gupta, Inorg. Chem., 20(1981)450.

335 J.Loub and H.Paulus, Acta Crystallogr., B37(1981)2058.

336 M.Rafiq, J.Durand and L.Cot, Rev. Chim. Min., 18(1981)1.

337 H.Werner and Tri Ngo Khac, Z. Anorg. Allg. Chem., 475(1981)241.

338 H.Binder and J.Palmtag, Z. Naturforsch., 36b(1981)45.

339 S.Singh and D.M.Puri, Indian J. Chem., 20A(1981)375.

340 E.-P.Flindt, Z. Anorg. Allg. Chem., 479(1981)57.

341 D.B.Denney, D.Z.Denney, P.J.Hammond and Y.-P.Wang, J. Am. Chem. Soc., 103(1981)1785.

342 J.Chojnowski, M.Cypryk and J.Michalski, J. Organomet. Chem., 215(1981)355.

343 P.Peringer and J.Eichbichler, J. Inorg. Nucl. Chem., 43(1981)2033.

344 D.Thierbach and F.Huber, Z.Anorg. Allg. Chem., 477(1981)101.

345 E.Gebert,A.H.Reis, S.W.Peterson, L.I.Katzin, G.W.Mason and D.F.Peppard, J. Inorg. Nucl. Chem., 43(1981)1451.

346 K.B.Dillon, M.P.Nisbet and T.C.Waddington, J. Chem. Soc. Dalton Trans., (1981)212.

347 S.Kulpe, I.Seidel and E.Herrmann, Z. Chem., 21(1981)333.

348 W.Storzer, D.Schomburg and G.-V.Röschenthaler, Z. Naturforsch., 36b(1981)1071.

349 W.Storzer, G.-V.Röschenthaler, R.Schmutzler and W.S.Sheldrick, Chem. Ber., 114(1981)3609.

350 G.-V.Röschenthaler, W.Storzer and R.Schmutzler, J. Fluorine Chem., 19(1982)579.

351 G.-V.Röschenthaler, Z. Anorg. Allg. Chem., 479(1981)158.

352 D.Schomburg, N.Weferling and R.Schmutzler, J. Chem. Soc. Chem. Commun., (1981)810.

353 J.Gloede and B.Hellmann, Z. Anorg. Allg. Chem., 480(1981)142.

354 M.Kato and M.Yamabe, J. Chem. Soc. Chem. Commun., (1981)1173.

355 K.C.Molloy, M.B.Hossain, D. van der Helm, D.Cunningham and J.J.Zuckerman, Inorg. Chem., 20(1981)2402.

356 C.Miyake, Y.Hinatsu and S.Imoto, J. Inorg. Nucl. Chem., 43(1981)2407.

357 C.M.Mikulski, D.Tuttle, B.Marks, N.Harris, P.Sanford, R.Rabin and N.M.Karayannis, Inorg. Chim. Acta, 53(1981)L165.

358 C.M.Mikulski, N.Harris, P.Sanford, F.J.Iaconianni, L.L.Pytlewski and N.M.Karayannis, J. Inorg. Nucl. Chem., 43(1981)2753.

359 C.M.Mikulski, J.Unruh, R.Rabin, F.J.Iaconianni, L.L.Pytlewski and N.M.Karayannis, J. Inorg. Nucl. Chem., 43(1981)225.

360 C.M.Mikulski,J.Unruh,D.F.Delacato,F.J.Iaconianni,L.L.Pytlewski and N.M.Karayannis, J. Inorg. Nucl. Chem., 43(1981)1751.

361 C.M.Mikulski, S.Chauhan, R.Rabin and N.M.Karayannis, Inorg. Nucl. Chem. Lett., 17(1981)195.

362 C.M.Mikulski, S.Chauhan, R.Rabin and N.M.Karayannis, J. Inorg. Nucl. Chem., 43(1981)2017.

363 R.Teghil, L.Bencivenni, S.N.Cesaro, A.Szabo, M.Spoliti and M.Maltese, J. Mol. Struct., 73(1981)15.

364 V.G.Zakzhevskii, A.I.Boldyrev and O.P.Charkin, Russ. J. Inorg. Chem., 25(1980)2614.

365 R.J.P.Williams, R.C.F.Giles and A.M.Posner, J. Chem. Soc. Chem. Commun., (1981)1051.

366 A.Larbot, J.Durand and L.Cot, Cryst. Struct. Commun., 10(1981)55.

367 D.Brodalla, R.Kniep and D.Mootz, Z. Naturforsch., 36b(1981) 907.

368 V.V.Pechkovskii, N.I.Gavrilyuk and R.Ya.Mel'nikova, Russ. J. Inorg. Chem., 25(1980)997.

368 H.Einaga and Y.Komatsu, J. Inorg. Nucl. Chem., 43(1981)2449.

369 L.Ciavatti, R.Palombari and E.Belli, J. Inorg. Nucl. Chem., 43(1981)2485.

370 S.Pulvin, E.Bordes, M.Ronis and P.Courtine, J. Chem. Research(S), (1981)29.

371 D.A.Buckingham and C.R.Clark, Aust. J. Chem., 34(1981)1769.

372 P.Vasic, B.Prelesnik, R.Herak and M.Curic, Acta Crystallogr., B37(1981)660.

373 E.Dubler, L.Beck, L.Linowsky and G.B.Jameson, Acta Crystallogr., B37(1981)2214.

374 G.W.Beall, L.A.Boatner, D.F.Mullica and W.O.Milligan, J. Inorg. Nucl. Chem., 43(1981)101.

375 H.R.Tietze, Aust. J. Chem., 34(1981)2035.

376 A.W.Kolsi, M.Quarton and W.Freundlich, Ann. Chim. (Paris), 6(1981)411.

377 S.A.Linde, Yu.E.Gorbunova and A.V.Lavrov, Russ. J. Inorg. Chem., 25(1980)1105.

378 A.G.Nord and T.Stefanidis, Cryst. Struct. Commun., 10(1981) 1251.

379 A.Larbot, J.Durand, S.Vilminot and A.Norbert, Acta Crystallogr., B37(1981)1023.

380 M.Watanabe, M.Matsuura and T.Yamada, Bull. Chem. Soc. Japan, 54(1981)738.

381 E.A.Merritt, M.Sundaralingam and R.D.Cornelius, Acta Crystallogr., B37(1981)657.

382 V.V.Kokhanouskii, Z.N.Zemtsova and S.G.Tereshkova, Russ. J. Inorg. Chem., 25(1980)1305.

383 L.I.Prodan, I.E.Yaskevich, I.V.Batyi, A.F.Selevich and A.N.Antsipovich, Russ. J. Inorg. Chem., 26(1981)668.

384 E.A.Prodan, L.I.Petrovskaya and V.N.Korzhuev, Russ. J. Inorg. Chem., 25(1980)1013.

385 T.N.Galkova, E.A.Prodan and M.M.Pavlyuchenko, Russ. J. Inorg. Chem., 25(1980)1195.
386 Yu.E.Gorbunova, S.A.Linde and A.V.Lavrov, Russ. J. Inorg. Chem., 26(1981)383.
387 A.Durif and M.T.Averbuch-Pouchot, Z. Anorg. Allg. Chem., 472(1981)129.
388 N.Boudjada, Z. Anorg. Allg. Chem., 477(1981)225.
389 N.Boudjada, M.T.Averbuch-Pouchot and A.Durif, Acta Crystallogr., B37(1981)645,647.
390 G.C.Maiti and F.Freund, J. Inorg. Nucl. Chem., 43(1981)2633.
391 J.C.Elliot, E.Dykes and P.E.Mackie, Acta Crystallogr., B37(1981)435.
392 M.C.Apella and E.J.Baran, Z. Naturforsch., 36b(1981)644.
393 S.Yamanaka, M.Matsunaga and M.Hattori, J. Inorg. Nucl. Chem., 43(1981)1343.
394 S.Yamanaka, K.Yamasaka and M.Hattori, J. Inorg. Nucl. Chem., 43(1981)1659.
395 M.B.Dines and P.M.DiGiacomo, Inorg. Chem., 20(1981)92.
396 S.Yamanaka and M.Hattori, Inorg. Chem., 20(1981)1929.
397 B.W.Levitt, J. Chem. Research(S), (1981)24.
398 R.C.Yeates, S.M.Kuznicki, L.B.Lloyd and E.M.Eyring, J. Inorg. Nucl. Chem., 43(1981)2355.
399 G.Alberti, U.Costantino, G.Marletta, O.Puglisi and S.Pignataro, J. Inorg. Nucl. Chem., 43(1981)3329.
400 P.Jerus and A.Clearfield, J. Inorg. Nucl. Chem., 43(1981) 2117.
401 A.Clearfield, G.A.Day, A.Ruvarac and S.Milorijic, J. Inorg. Nucl. Chem., 43(1981)165.
402 J.P.Gupta and D.V.Nowell, J. Chem. Soc. Dalton Trans., (1981)385.
403 L.Kullberg and A.Clearfield, J. Inorg. Nucl. Chem., 43(1981)2543.
404 L.Alagna, A.A.G.Tomlinson, C.Ferragina and A.LaGinestra, J. Chem. Soc. Dalton Trans., (1981)2376.
405 I.Tomita, K.Iwase, K.Saito and Y.Sugiyama, Bull. Chem. Soc. Japan, 54(1981)749.
406 U.Costantino, J. Inorg. Nucl. Chem., 43(1981)1895.
407 E.Fluck, G.Gonzalez, K.Peters and H.G. von Schnering, Z. Anorg. Allg. Chem., 473(1981)51.
408 R.Blachnik, A.Hoppe, U.Rabe and U.Wickel, Z. Naturforsch., 36b(1981)1493.
409 W.Bues, M.Somer and W.Brockner, Z. Anorg. Allg. Chem., 476(1981)153.
410 E.Bunel, J.Manzur and J.Retuert, J. Chem. Research(S), (1981)285.
411 H.Falius, W.Krause and W.S.Sheldrick, Angew. Chem. Int. Ed. Engl., 20(1981)103.
412 H.Falius and W.Krause, Z. Anorg. Allg. Chem., 477(1981)21.
413 U.Ahrens and H.Falius, Z. Anorg. Allg. Chem., 480(1981)90.
414 U.Ahrens and H.Falius, Z. Anorg. Allg. Chem., 480(1981)95.
415 L.Acha, E.R.Cromie and D.W.H.Rankin, J. Mol. Struct., 73(1981)111.
416 M.C.Böhm, M.Eckert-Maksic, R.Gleiter, J. Grobe and D. LeVan, Chem. Ber., 114(1981)2300.
417 S.Kaur and T.S.Lobana, J. Inorg. Nucl. Chem., 43(1981)2439.
418 I.J.Colquhoun, W.McFarlane, J.-M.Bassett and S.O.Grim, J. Chem. Soc. Dalton Trans., (1981)1645.
419 S.R.Wade and G.R.Willey, J. Inorg. Nucl. Chem., 43(1981)1465.
420 D.M.Anderson, E.A.V.Ebsworth, T.A.Stephenson and M.D. Walkinshaw, Angew. Chem. Int. Ed. Engl., 20(1981)290.

421 B.Krebs and G.Henkel, Z. Anorg. Allg. Chem., 475(1981)143.
422 W.Kuchen, A.Mamsch, D.Mootz and M.Steffen, Z. Anorg. Allg. Chem., 472(1981)133.
423 K.C.Molloy, M.B.Hossain, D. van der Helm, J.J.Zuckerman and F.P.Mullins, Inorg. Chem., 20(1981)2172.
424 H.Keck, W.Kuchen, J.Mathow, B.Meyer, D.Mootz and H. Wunderlich, Angew. Chem. Int. Ed. Engl., 20(1981)975.
425 H.P.S.Chauhan, G.Srivastava and R.C.Mehrotra, Synth. React. Inorg. Metal-Org. Chem., 11(1981)565.
426 A.J.Blake, R.A.Howie and G.P.McQuillan, Acta Crystallogr., B37(1981)966.
427 K.Diemert, P.Haas and W.Kuchen, Z. Anorg. Allg. Chem., 480(1981)65.
428 P.Toffoli, P.Khodadad and N.Rodier, Bull. Soc. Chim. Fr., (1981)I-429.
429 R.Clement, J. Am. Chem. Soc., 103(1981)6998.
430 N.T.Yatsimirskaya and R.Arain, J. Inorg. Nucl. Chem., 43(1981)1569.
431 A.Haas and J.Mikolajczak, Chem. Ber., 114(1981)829.
432 A.S.F.Boyd, G.S.Laurenson and D.W.H.Rankin, J. Mol. Struct., 71(1981)217.
433 F.Watari, Inorg. Chem., 20(1981)1776.
434 W.-W.du Mont and H.-J.Kroth, Z. Naturforsch., 36b(1981)332.
435 S.Ebel, H.Tom Dieck, H.Walther and J.Krizek, Inorg. Chim. Acta, 53(1981)L101.
436 M.Baudler and P.Bachmann, Angew. Chem. Int. Ed. Engl., 20(1981)123.
437 H.Köpf and U.Görges, Z. Naturforsch., 36b(1981)1205.
438 B.Eisenmann, H.Jordan and H.Schäfer, Angew. Chem. Int. Ed. Engl., 20(1981)197.
439 B.Eisenmann, H.Jordan and H.Schäfer, Z. Anorg. Allg. Chem., 475(1981)74.
440 R.Berger, B.I.Noläng and L.-E.Tergenius, Acta Chem. Scand., A35(1981)679.
441 S.Laohavanich, S.Thanomkul and S.Pramatus, Acta Crystallogr., B37(1981)229.
442 G.Cordier and H.Schäfer, Angew. Chem. Int. Ed. Engl., 20(1981)466.
443 G.Cordier, E.Czech, M.Jakowski and H.Schäfer,Rev. Chim. Min., 18(1981)9.
444 S.Rozsa and H.-U.Schuster, Z. Naturforsch., 36b(1981)1668.
445 S.Rozsa and H.-U.Schuster, Z. Naturforsch., 36b(1981)1666.
446 G.Becker, A.Münch and H.-J.Wessely, Z. Naturforsch., 36b(1981)1080.
447 J.Ennen and T.Kauffmann, Angew. Chem. Int. Ed. Engl., 20(1981)118.
448 J.Ellermann and M.Lietz, J. Organomet. Chem., 215(1981)165.
449 J.Ellermann and M.Lietz, J. Organomet. Chem., 218(1981)C45.
450 J.Ellermann and M.Lietz, Z. Naturforsch., 36b(1981)1532.
451 J.Ellermann, S.P.Ang, M.Lietz and M.Moll, J. Organomet. Chem., 222(1981)105.
452 J.Ellermann and M.Lietz, J. Organomet. Chem., 213(1981)C4.
453 H.Beurich and H.Vahrenkamp, Chem. Ber., 114(1981)2542.
454 E.Rottinger and H.Vahrenkamp, J. Organomet. Chem., 213(1981)1.
455 W.Malisch, M.Luksza and W.S.Sheldrick, Z. Naturforsch., 36b(1981)1580.
456 J.E.Drake, L.N.Khasrou and A.Majid, Can. J. Chem., 59(1981)2417.

457 W.-W.duMont and G.Rudolph, Z. Naturforsch., 36b(1981)1215.
458 A.N.Sobolev and V.K.Belsky, J. Organomet. Chem., 214(1981)41.
459 A.N.Sobolev, I.P.Romm, N.Yu Chernikova, V.K.Belsky and E.N.Guryanova, J. Organomet. Chem., 219(1981)35.
460 J.P. van Linthoudt, L.Verdonck and G.P. van der Kelen, J. Mol. Struct., 74(1981)255.
461 M.P.Bogaard, J. Peterson and A.D.Rae, Acta Crystallogr., B37(1981)1357.
462 F.L.Tanzella and N.Bartlett, Z. Naturforsch., 36b(1981)1461.
463 B.Frlec, D.Gantar and J.H.Holloway, J. Fluorine Chem., 19(1982)485.
464 C.R.Mitchell and R.A.Zingaro, Synth. React. Inorg. Metal-Org. Chem., 11(1981)1.
465 M.R.Churchill, A.G.Landers and A.L.Rheingold, Inorg. Chem., 20(1981)849.
466 J. von Seyerl, B.Sigwarth, H.-G.Schmid, G.Mohr, A. Frank, M.Marsili and G.Huttner, Chem. Ber., 114(1981)1392.
467 J. von Seyerl, B.Sigwarth and G.Huttner, Chem. Ber., 114 (1981)727.
468 J. von Seyerl, B.Sigwarth and G.Huttner, Chem. Ber., 114(1981)1407.
469 P.Marconi, Y.Madaule and J.-G.Wolf, J. Chem. Research(S), (1981)176.
470 H.T.Phung, P.B.Chi and F.Kober, Z. Anorg. Allg. Chem., 472(1981)75.
471 H.T.Phung, P.B.Chi and F.Kober, Z. Anorg. Allg. Chem., 482(1981) 81.
472 V.K.Belsky, J. Organomet. Chem., 213(1981)435.
473 C.Glidewell, G.S.Harris, H.D.Holden, D.C.Liles and J.S.McKechnie,J. Fluorine Chem., 18(1981)143.
474 C.D.Baer, J.O.Edwards and P.H.Rieger, Inorg. Chem., 20(1981)905.
475 P.Keller, H.Riffel, F.Zettler and H.Hess, Z. Anorg. Allg. Chem., 474(1981)123.
476 M.T.Averbuch-Pouchot and A.Durif, Z. Anorg. Allg. Chem., 476(1981)237.
477 A.Boudjada and J.C.Guitel, Acta Crystallogr., B37(1981)1402.
478 S.K.Sarpal and A.R.Gupta, J. Inorg. Nucl. Chem., 43(1981)2043
479 S.K.Sarpal and A.R.Gupta, J. Inorg. Nucl. Chem., 43(1981)1347
480 B.H.Christian, R.J.Gillespie and J.F.Sawyer, Inorg. Chem., 20(1981)3410.
481 D.H.Brown, A.F.Cameron, R.J.Cross and M.McLaren, J. Chem. Soc. Dalton Trans., (1981)1459.
482 S.V.L.Narayana and H.N.Shrivastava, Acta Crystallogr., B37(1981)1186.
483 A.F.Tanzen, O.C.Vaidya and C.J.Willis, J. Inorg. Nucl. Chem., 43(1981)1469.
484 G.Distefano, A.Modelli, A.Grassi, G.C.Pappalardo, K.J.Irgolic and R.A.Pyles, J. Organomet. Chem., 220(1981)31.
485 G.S.Sodhi and N.K.Kaushik, Indian J. Chem., 20A(1981)922.
486 M.Dräger, Z. Anorg. Allg. Chem., 482(1981)7.
487 M.Palazzi and S.Jaulmes, Acta Crystallogr., B37(1981)1340.
488 R.Sobott, Monatsh., 112(1981)411.
489 R.Schmelczer and D.Schwarzenbach, Z. Naturforsch., 36b(1981)463.
490 R.Kniep and H.D.Reski, Angew. Chem. Int. Ed. Engl., 20(1981)212.
491 D.Schiferl, D.T.Cromer and J.C.Jamieson, Acta Crystallogr., B37(1981)807.

492 E.Brechtel, G.Cordier and H.Schäfer, Z. Naturforsch., 36b(1981)1341.
493 E.Brechtel, G.Cordier and H.Schäfer, Z. Naturforsch., 36b(1981)27.
494 J.G.Stevens, J.M.Trooster, H.A.Meinema and J.G.Noltes, Inorg. Chem., 20(1981)801.
495 H.-J.Breunig and H.Kischkel, Z. Naturforsch., 36b(1981)1105.
496 A.J.Ashe, W.Butler and T.R.Diephouse, J. Am. Chem. Soc., 103(1981)207.
497 H.-J.Breunig and W.Fichtner, Z.Anorg. Allg. Chem., 477(1981) 119.
498 H.-J.Breunig, W.Fichtner and T.P.Knoblock, Z. Anorg. Allg. Chem., 477(1981)126.
499 H.-J.Breunig and W.Fichtner, J. Organomet. Chem., 222(1981) 97.
500 W.Levason, B.Sheikh and W.E.Hill, J. Organomet. Chem., 219(1981)163.
501 P.L.Millington and D.B.Sowerby, J. Chem. Soc. Dalton Trans., (1981)2011.
502 N.Tempel, W.Schwarz and J.Weidlein, Z. Anorg. Allg. Chem., 474(1981)157.
503 S.Elbel and H. tom Dieck, Z. Anorg. Allg. Chem., 483(1981)33.
504 J.Werner, W.Schwarz and A.Schmidt, Z. Naturforsch., 36b(1981)556.
505 K.Bajpai and R.C.Srivastava, Synth. React. Inorg. Metal-Org. Chem., 11(1981)7.
506 K.Bajbai, M.Srivastava and R.C.Srivastava, Indian J. Chem., 20A(1981)736.
507 H.K.Sharma,S.N.Dubey and D.M.Puri, Indian J. Chem., 20A(1981)620.
508 Y.Kawasaki and M.Kinoshita, Bull. Chem. Soc. Japan, 54(1981)929.
509 F.Di Bianca, G.Alonzo, M.T.Lo Guidice, G.Ruisi and N.Bertazzi, J. Inorg. Nucl. Chem., 43(1981)3001.
510 A.Y.Sonsale, A.K.Chatterkee, S.Gopinathan and C.Gopinathan, Indian J. Chem., 20A(1981)1121.
511 D.Coudreau-Ducourant, B.Ducourant, R.Fourcade and G.Mascherpa, Z. Anorg. Allg. Chem., 476(1981)229.
512 M.Sørlie and G.P.Smith, J. Inorg. Nucl. Chem., 43(1981)931.
513 C.Airoldi, Inorg. Chem., 20(1981)998.
514 E.Hough and D.G.Nicholson, J. Chem. Soc. Dalton Trans., (1981)2083.
515 B.Rubin, F.J.Heldrich, W.K.Dean, D.J.Williams and A.Viehbeck, Inorg. Chem., 20(1981)4434.
516 A.Giusti and G.Peyronel, J. Inorg. Nucl. Chem., 43(1981)2675.
517 G.Kiel, Z. Naturforsch., 36b(1981)55.
518 S.Calogero, U.Russo, J.D.Donaldson, P.W.C.Barnard and J.A.Barker, Inorg. Chim. Acta, 53(1981)L227.
519 C.Peylhard, P.Teulon and A.Potier, Z. Anorg. Allg. Chem., 483(1981)236.
520 N.K.Jha, A.Kumari and R.S.Prasad, J. Inorg. Nucl. Chem., 43(1981)1759.
521 N.K.Jha, A.Kumari and R.S.Prasad, J. Inorg. Nucl. Chem., 43(1981)3095.
522 N.K.Jha, A.Kumari and R.S.Prasad, J. Inorg. Nucl. Chem., 43(1981)3016.
523 F.Cariati, A.Panzanelli, L.Antolini, L.Menabue, G.C.Pellacani and G.Marcotrigiano, J. Chem. Soc. Dalton Trans., (1981)909.
524 H.W.Clark and B.I.Swanson, J. Am. Chem. Soc., 103(1981)2928.
525 P.J.Iredale and A.Thompson, J. Inorg. Nucl. Chem.,43(1981)2667

526 T.Okuda, H.Ishihara, K.Yamada, M.Hiura and H.Negita, J. Mol. Struct., 74(1981)347.

527 T.Okuda, K.Yamada, H.Ishihara, M.Hiura, S.Gima and H.Negita, J. Chem. Soc. Chem. Commun., (1981)979.

528 O.Leirzke and F.Sladky, Z. Naturforsch., 36b(1981)268.

529 J.Fawcett, J.H.Holloway and D.R.Russell, J.Chem. Soc. Dalton Trans., (1981)1212.

530 R.J.Gillespie, J.P.Kent, J.F.Sawyer, D.R.Slim and J.D.Tyrer, Inorg. Chem., 20(1981)3799.

531 S.Blösl, W.Schwarz and A.Schmidt, Z. Anorg. Allg. Chem., 474(1981)51.

532 W.Schwarz, A.Schmidt and S.Blösl, Z. Anorg. Allg. Chem., 477(1981)113.

533 G.E.Binder and A.Schmidt, Z. Anorg. Allg. Chem., 482(1981)73.

534 A.-F.Shihada, F.Weller, Z. Anorg. Allg. Chem., 472(1981)102.

535 P.Teulon and J.Roziere, J. Organomet. Chem., 214(1981)391.

536 R.G.Kidd and H.G.Spinney, Can. J. Chem., 59(1981)2940.

537 M.Alamgir, N.Allen, P.W.C.Barnard, J.D.Donaldson and J. Silver, Acta Crystallogr., B37(1981)1284.

538 B.Z.Nurgaliev, B.A.Popovkin and A.V.Novoselova, Russ. J. Inorg. Chem., 26(1981)1043.

539 G.Duquenoy, F.-A.Josien, J.Livage and M.Michaud, Rev. Chim. Min., 18(1981)344.

540 F.Thuillier-Chevin, P.Maraine and G.Pérez, Acta Crystallogr., B37(1981)11.

541 J.Loub and H.Paulus, Acta Crystallogr., B37(1981)1106.

542 M.Abe and K.Sudoh, J. Inorg. Nucl. Chem., 43(1981)2537.

543 M.Abe, M.Tsuji and M.Kimura, Bull. Chem. Soc. Japan, 54(1981)130.

544 J.P.Rawat and K.P.S.Muktawat, J. Inorg. Nucl. Chem., 43(1981)2121.

545 F.J.Berry and B.J.Laundy, J. Chem. Soc. Dalton Trans., (1981)1442.

546 F.J.Berry and C.Greaves, J. Chem. Soc. Dalton Trans., (1981)2447.

547 A.S.Kanishcheva, V.G.Kuznetsov, Yu.N.Mikhailov, V.N.Batog and V.M.Skorikov, J. Struct. Chem., 21(1980)672.

548 W.Dorrscheidt and H.Schäfer, Z. Naturforsch., 36b(1981)410.

549 G.Cordier and H.Schäfer, Rev. Chim. Min., 18(1981)218.

550 J.Olivier-Fourcade, L.Izghouti and E.Philippot, Rev. Chim. Min., 18(1981)207.

551 P.Lemoine, D.Carré and M.Guittard, Acta Crystallogr., B37(1981)1281.

552 H.K.Sharma, S.Lata, S.N.Dubey and D.M.Puri, Indian J. Chem., 20A(1981)1031.

553 G.McKie, C.L.Raston, G.L.Rowbottom and A.H.White, J. Chem. Soc. Dalton Trans., (1981)1360.

554 L.L.Lohr, Inorg. Chem., 20(1981)4229.

555 Yu.M.Dergachev, N.A.Grechanaya and T.N.Dymova, Russ. J. Inorg. Chem., 25(1980)966.

556 E.Brechtel, G.Cordier and H.Schäfer, Z. Naturforsch., 36b(1981)1099.

557 U.Praeckel and F.Huber, Z. Naturforsch., 36b(1981)70.

558 P.Bras, H.Herwijer and J.Wolters, J. Organomet. Chem., 212(1981)C7.

559 L.P.Battaglia and A.B.Corradi, J. Chem. Soc. Dalton Trans., (1981)23.

560 A.I.Kuzmin, V.F.Sukhoverkhov and A.V.Sharabarin, Russ. J. Inorg. Chem., 26(1981)440.

561 A.Napoli and M.Paolillo, J. Inorg. Nucl. Chem., 43(1981)2435.
562 L.A.Kochubei, E.V.Margulis and F.I.Vershinina, Russ. J. Inorg. Chem., 25(1980)1544.
563 C.L.Raston, G.L.Rowbottom and A.H.White, J. Chem. Soc. Dalton Trans., (1981)1352.
564 C.L.Raston, G.L.Rowbottom and A.H.White, J. Chem. Soc. Dalton Trans., (1981)1366.
565 C.L.Raston, G.L.Rowbottom and A.H.White, J. Chem. Soc. Dalton Trans., (1981)1383.
566 C.L.Raston, G.L.Rowbottom and A.H.White, J. Chem. Soc. Dalton Trans., (1981)1369.
567 C.L.Raston, G.L.Rowbottom and A.H.White, J. Chem. Soc. Dalton Trans., (1981)1372.
568 C.L.Raston, G.L.Rowbottom and A.H.White, J. Chem. Soc. Dalton Trans., (1981)1379.
569 C.L.Raston, G.L.Rowbottom and A.H.White, J. Chem. Soc. Dalton Trans., (1981)1389.
570 V.B.Lazarev, A.F.Trippul and S.I.Berul, Russ. J. Inorg. Chem., 25(1980)1694.