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Chapter 3

ELEMENTS OF GROUP 3

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3.1 BORON

3.1.1 Boranes

Empirical rules have been derived for predicting the ^{11}B n.m.r. spectra of *closo*-boranes and -heteroboranes.[1]

The electron affinity for BH has been calculated using a variety of orbital basis sets. The best value, including zero-point corrections, was +0.07eV.[2] The microwave spectrum of HBF^+ showed that $r_s BH = 117.347(2)$pm, and $r_s BF = 121.028(2)$pm.[3] Calculations have been reported on optimised structures and energies for B_2H_4 at the HF/6-31G and MP2/6-31G** levels. The latter gave an optimised BB distance of 165.3pm, for the orthogonal 0012 D_{2d} structure, 153.7pm for the 1011 C_s structure (with BH_2 perpendicular to the BHBH plane), and 146.2pm for the doubly-bridged 2010 C_{2v} structure. The last two structures are less stable than the first, with the energies in the sequence $D_{2d} < C_{2v} < C_s$.[4]

A simple preparation of B_2H_6 has been reported, i.e. treatment of $NaBH_4$ with I_2 in diglyme.[5] Coupled Hartree-Fock and equations-of-motion calculations have been carried out at the *ab initio* level for the B-B and B-H indirect nuclear spin-spin coupling constants for B_2H_6, B_2H_4, $B_2H_7^-$, $B_3H_8^-$, B_4H_{10} and B_5H_9. The B-H-B coupling constant is found to be variable in sign and magnitude, but the B-B coupling for two-centre two-electron bonds is always positive.[6]

Calculation suggests that in cleavage reactions of B_2H_6 electronic steering favours geminal (asymmetric) entry of a second Lewis base molecule, from the known structure $(LBH_2)H(BH_3)$ to $(L_2BH_2)^+BH_4^-$.[7] The rotational spectra of B_2H_6-HF and B_2H_6-DF complexes are consistent with a linear BB-H/DF equilibrium structure, with the H/D end of the H/DF attached axially to one of the terminal BH_2 groups.[8]

^{11}B-^{11}B two-dimensional correlated n.m.r. (COSY) spectra of boranes and their substituted derivatives show that coupling between ^{11}B nuclei linked by bridging hydrogens is more common than previously supposed. Examples included B_4H_{10}, $(Me_2N)_2B_4H_8$, 2-MeB_5H_8 and $B_{10}H_{14}$.[9] The kinetics of thermal decomposition of B_4H_{10} were investigated by mass spectrometry (40 - 78°C). The initial reaction can be interpreted in terms of the three steps

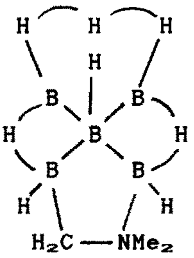
$$B_4H_{10} \rightleftharpoons \{B_4H_8\} + H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$\{B_4H_8\} + B_4H_{10} \longrightarrow B_5H_{11} + \{B_3H_7\} \quad \ldots\ldots\ldots\ldots(2)$$

$$\{B_3H_7\} + \{B_3H_7\} \longrightarrow \{\text{"}B_6H_{14-2m}\text{"}\}\ \text{(polymerises)} + mH_2 \quad \ldots\ldots(3)$$

(1)-(3) of which the first is rate-determining.[10] Calculations suggested that it may be possible to detect the bis(boranyl) form of B_4H_{10} as an intermediate in the formation of the normal "butterfly" geometry.[11]

Reactions of the iminium salt $[Me_2NCH_2]I$ with $1\text{-X-}B_5H_7^-$, where X = H, Et or Br, give the μ-((dimethylamino)methyl)pentaborane derivatives, $1\text{-X-}\mu\text{-}(Me_2NCH_2)\text{-}B_5H_7$. N.m.r. data suggest a structure in which a bridging hydrogen of B_5H_9 has been replaced by a -C-N- two-atom bridge, (1). The clusters are analogues of *arachno*-$B_5H_{10}^-$.[12] High field strength n.m.r. spectra show that samples



(1)

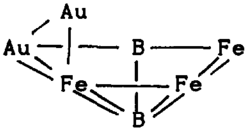
previously thought to be 2-Me- and 3-Me-B_5H_{10} are identical equilibrium mixtures of these two isomers.[13]

M.o. calculations have been reported on $B_{10}H_{10}$ and $B_{10}H_{10}^{2-}$ which shed light on the *hyper-closo* versus *iso-closo* controversy in metallaboranes. They support the former model, and reveal a topological transformation for generating polar deltahedra with 2n skeletal electrons.[14] $B_{10}H_{11}C_6H_{11}(SMe_2)$ and ^tBuNC produce $B_{10}H_{10}(C_6H_{11})SMe_2CNH^tBu$, which was characterised by ^{11}B n.m.r. and i.r. spectra. The isocyanide carbon has inserted into the open face of the starting material, without disturbing the relative positions of the original substituents.[15] The reaction of PMe_2Ph and *nido*-$B_{10}H_{14}$ gives the previously unsuspected *endo,exo*-isomer of *arachno*-$B_{10}H_{12}(PMe_2Ph)_2$, together with smaller amounts of the expected *exo,exo*-isomer. The species were readily identified by multiple resonance and difference n.m.r. spectra.[16]

Nido-2-$XB_{10}H_{13}$, where X = Cl, Br or I, and SMe_2 react to form *arachno*-2-X-6,9-$(SMe_2)_2$-$B_{10}H_{11}$. These, on heating under reflux with ROH (R = Me or Et) yield *arachno*-1-X-4-$(SMe_2)_2B_9H_{12}$ and *arachno*-4-(SMe_2)-7-$(OR)B_9H_{12}$. Related complexes also gave, with *cis*-$PtCl_2(PMe_2Ph)_2$ (among other products) *conjuncto*-Pt_2-$(PMe_2Ph)_2(B_2H_5)(B_6H_9)$.[17] $(Et_4N)_2B_{10}H_{10}$ and hydrated $AlCl_3$ form 6-$B_{10}H_{13}Cl$ by addition of two protons and HCl to the $B_{10}H_{10}^{2-}$ cage, with the $AlCl_3$ playing a significant role.[18] A single-crystal structure determination for 1:2'-$[B_5H_8]_2$ confirms the coupled cage structure, with two pentaborane units joined apex to base by a two-centre, two-electron B-B bond. The compound can undergo coupled-cage to single cage condensations to e.g. $B_9H_{14}^-$, $B_{12}H_{12}^{2-}$ etc.[19]

3.1.2 Borane Anions and Metallo-derivatives.

$Fe_4(CO)_{12}(AuPPh_3)_2BH$ can be prepared from $Au(PPh_3)Cl$ and $[HFe_4(CO)_{12}BH]^-$. The structure contains the unit (2).[20] The butterfly anionic cluster $[(\mu\text{-}H)Fe_4(CO)_{12}BH]^-$ is prepared from $[(\mu\text{-}H)Fe_3(CO)_9BH_3]^-$ via H_2 elimination,[21], by deprotonation of $HFe_4(CO)_{12}BH_2$ or by reaction of $[HFe_3(CO)_9BH_3]^-$ with $Fe_2(CO)_9$. The hydrogen mobility on the cluster framework is greater than for the hydrocarbon analogue. EHMO calculations were used to rationalise the B^-/C changes.[22] A second report on $Fe_4(CO)_{12}(AuPPh_3)_2BH$



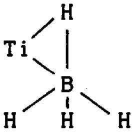
(2)

suggests that it is related to the known $Fe_4(CO)_{12}BH_3$ with two *endo*-hydrogen atoms replaced by $AuPPh_3$ units. This causes migration of hydrogen from the metal framework to the boron, causing the latter to be associated with 6 metal atoms.[23]

The new polypyrazolylborate ligands $[H_nB(3\text{-}Rpz)_{4-n}]^-$, where R = ^tBu or Ph; n = 0, 1 or 2, have been prepared. Series of transition metal complexes of these ligands were also reported. Appropriate selection of the 3-R group in the ligands with n = 1 allows the construction of custom-sized pockets around the metal ions.

[24,25] The five-coordinate $Me_nCl_{3-n}Sn[(pz)_2BH_2]$ and six-coordinate $Me_nCl_{3-n}Sn[(pz)_3BH]$, where Pz = 1-pyrazolyl; n = 0 - 3, are prepared from the appropriate methyltin chlorides and $K[(pz)_2BH_2]$ or $K[(pz)_3BH]$.[26]

Absorption spectra of one-electron oxidised intermediates ($H_4B^\cdot$ $Ph_4B^\cdot$ radicals) are observed on the oxidation of H_4B^- or Ph_4B^- by $N_3^\cdot$, $Br_2^{\cdot -}$ or $(SCN)_2^{\cdot -}$ in pulse-irradiated solutions.[27] M.o. calculations (self-consistent electron pairs method, using two-exponent basis sets with polarisation) for $HMBH_4$ and MBH_4^+, where M = Be or Mg, show that in many cases there are very small differences between different possible geometries.[28]



(3)

The X-ray crystal structure of $Ti(BH_4)_3(PMe_3)_2$ shows that two of the BH_4^- groups have unusual geometries, involving interaction of Ti with one B-H bond in a "side-on" manner, (3).[29] $TiCl_4$ and $NaBH_4$ in THF or dimethoxyethane (DME) form $Ti(BH_4)_3(THF)_2$, $NaTi(BH_4)_4(DME)_3$ respectively. The latter decomposes on heating to give $Ti(BH_4)_3(DME)$. This contains eight-coordinate titanium, with the BH_4 groups and DME all bidentate.[30] $Cp_2Zr(H)BH_3CH_3$ contains a bidentate BH_3Me ligand, characterised by X-ray diffraction, i.r., ^{11}B and ^1H n.m.r. spectra.[31] Quasi-relativistic SCF-Xα-SW calculations have been performed on $M(BH_4)_4$, where M = Zr, Hf, Th or U. The d-block conpounds are tetrahedral, with strong covalent contributions from π-bonding ligand group orbitals. In the lanthanide complexes, the 5f metal orbitals are significant in the metal-ligand covalent bonding.[32] The HeI and HeII photo-electron spectra of $M(BH_3Me)_4$, where M = Zr, Hf, Th or U, and of $Th(BH_4)_4$ were assigned on the basis of these calculations.[33]

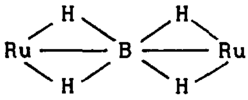
$Cp^*_2NbBH_4$ can be prepared from $NbCl_5$, LiC_5Me_5 and $NaBH_4$ in 1,2-dimethoxyethane. This compound has an exceptionally large barrier to bridge/terminal hydrogen exchange, and it is a useful precursor to many Cp^*_2Nb species.[34] The borohydride complexes $(dmpe)_2CrH(\eta^2\text{-}BH_4)$, where dmpe = $Ph_2CH_2CH_2PPh_2$, $(Me_3P)_3WH_3(\eta^2\text{-}BH_4)$ and $(Me_2PhP)_3ReH(\eta^1\text{-}BH_4)(\eta^2\text{-}BH_4)$ have been prepared. ^1H and ^{31}P

n.m.r. data show that the molecules are non-rigid, with metal hydride exchanges occurring.[35] Crystal and molecular structures were determined for $CpMo(CO)_2\{P(Ph)[N(SiMe_3)_3]_2\}(\mu\text{-}H\text{-}BH_2)$, prepared from $CpMo(CO)_2\{P(Ph)[N(SiMe_3)_3]_2$ and B_2H_6. It contains the unusual four-membered ring $\overline{Mo\text{-}P\text{-}B(H_2)\text{-}(\mu\text{-}H)}$.[36]

The crystal structure of $FeH(dmpe)_2(BH_4)$ shows the presence of a singly-bridged BH_4 ligand - with a bent Fe-H-B linkage, Fe-H-B angle 161.7°.[37] Reactions of $(\mu\text{-}H)Fe_3(CO)_9BH_4$ with Lewis bases can lead to either cluster substitution or degradation, with the former occurring via H_2 rather than CO elimination.[38] The ferraboranes $(\mu\text{-}H)Fe_3(CO)_9BH_3R$, where R = H or Me, and their conjugate bases $[(\mu\text{-}H)Fe_3(CO)_9BH_2R]^-$ have been prepared. The crystal structure of $(\mu\text{-}H)Fe_3(CO)_9BH_4$ shows that there is $\eta^3\text{-}BH_4$ coordination.[39] The reactions of $[(\mu\text{-}H)Fe_3(CO)_9BH_2R]^-$, where R = H or Me, with Lewis bases (CO, $PhMe_2P$, Et_3N or H_2O) have been explored. Several possible pathways were identified.[40]

The new complexes $MH(\eta^2\text{-}BH_4)(CO)(PR_3)$, where M = Ru or Os, R_3 = $^iPr_3$ or Me^tBu_2, were reported. Above -30°C these are fluxional, with exchange of the M-H-B and B-H_t hydrogens.[41] $[L(H)Ru(\mu,\eta^2\text{-}BH_4)Ru(H)L]^+BPh_4^-$, where L = $MeC(CH_2PPh_2)_3$, is the first bimetallic Group 8 tetrahydroborate complex containing an $(\mu,\eta^2\text{-}BH_4)$ group. The Ru-B distances (near 210pm) are close to the sum of the covalent radii for Ru and B, suggesting direct Ru-B bonding, i.e. (4).[42]

The i.r. and Raman spectra of $(Ph_3P)_2CuBH_4$ and its BD_4 analogue gave assignments for at least 7 of the 12 fundamental vibrational



(4)

wavenumbers for the bidentate bridge unit CuH_2BH_2, including the Cu-B stretch, at 359 cm^{-1} (BH_4), 329 cm^{-1} (BD_4).[43] The solution usually described as "copper(I) borohydride" contains Cl^- ions associated with the Cu(I). The species was identified tentatively as $(LiCl)_xCuBH_4$.[44] A 1/1 mixture of CuCl and $NaBH_4$ in THF, in the presence of alkenes, produces copper(I) alkylborohydrides.[45]

Thermal desolvation is possible for $La(BH_4)_3.nTHF$, where n = 3 or 3.6. Thermodynamic characteristics were calculated for non-solvated $La(BH_4)_3$.[46] The complexes $Ln(BH_4)_3.DME$, where Ln = Gd-Tm, Lu; DME = dimethoxyethane, were obtained by the thermal decomposition of $NaLn(BH_4)_4.xDME$.[47] UH_3 and B_2H_6 in THF form $U(BH_4)_3(THF)_3$. The U-B distances in this were consistent with μ_3-H bonding by the BH_4^- ligands.[48] Cp_3UCl and Na(HBBN), where BBN = 9-borabicyclo[3.3.1]nonane react to give $Cp_3U(HBBN)$. This is the first complex having an HBBN ligand attached to a d- or f-block element. X-ray diffraction shows the presence of a UH_2B bridge unit.[49]

The structure of $B_2H_7^-$ has been determined more accurately, using neutron diffraction. The ion has C_s symmetry, with bent geometry (B-H-B angle 127(2)°) and staggered terminal B-H bonds. The average terminal and bridging B-H bond lengths are 118(2) and 127(6)pm respectively, with B...B 227(1)pm. The B-H-B bridge is slightly asymmetric, with B(1)-H 132(2), B(2)-H 121(2)pm.[50]

A series of cyanide-bridged derivatives of $B_3H_8^-$ and $B_9H_{14}^-$ has been prepared, e.g. $[B_3H_7(NC)B_3H_7]^-$ and $[B_3H_7(NC)BH_2(NC)BH_3]^-$.[51] Two-dimensional ^{11}B-^{11}B correlation (COSY) spectra have been obtained for $B_3H_7X^-$, where X = Cl, NCS, NCSe, $NCBH_3$, $NCBH_2Cl$, $NCBPh_3$, $NCBH_2CN$, NCB_3H_7 or CNB_3H_6Cl, and $B_3H_6(Cl)X$, where X = Cl, NCS, $NCBH_2Cl$ or NCB_3H_7. All of the monosubstituted derivatives and $B_3H_6Cl_2^-$ show a coupling correlation between substituted and unsubstituted borons. Unsymmetrically disubstituted derivatives show only one coupling correlation, between the boron atoms carrying the substituents.[52]

Treatment of the diglyme-adduct of $Mg(B_3H_8)_2$ with ammonia yields $[Mg(NH_3)_6](B_3H_8)_2$, which is stable below about 100°C.[53] N.m.r. and i.r. data were reported for $[Fe_2(CO)_6B_3H_6]^-$, together with m.o. calculations which rationalise the deprotonation of $Fe_2(CO)_6B_3H_7$ via loss of an Fe-H-B, and not a B-H-B proton.[54] Many polyhedral metalloborane structural types are accessible by reactions of $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ with polyhedral borane anions. Thus, with $B_3H_8^-$, the *arachno*-4-vertex $2\text{-}(C_6Me_6)ClRuB_3H_8$ and the *arachno*-5-vertex $1\text{-}(C_6Me_6)RuHB_4H_9$ are both formed.[55]

Bond indices have been calculated by a C.N.D.O.-based m.o. bond index method, for real and hypothetical *closo*-borane species $B_nH_n^{c-}$, where n = 5-12; c = 0, 2 or 4.[56] The reduction of $B_5H_9^-$ by $M^+(naphthalene)^-$, where M = Na, K, Rb or Cs, gives $B_5H_9^{2-}$. $M_2B_5H_9$ compounds are stable in the absence of air for several days. N.m.r. data suggested that the anion is fluxional at room temperature. The new compounds react with two molecules of HX, where X = Cl or Br, to give B_5H_{11} and 2MX. This is the safest and simplest route yet to B_5H_{11}.[57] A relationship has been derived between bond length and bond order for B-B two-centre bonds in boron cluster compounds, especially $B_nH_n^{2-}$, where n = 6, 8, 9, 10 or 12.[58]

Carefully controlled treatment of $Na_2B_6H_6$ with halogens in aqueous alkaline solution gave mixtures of the halogeno-derivatives $X_nB_6H_{6-n}^{2-}$, where X = Cl, Br or I; n = 1-6. For X = Cl or Br, n = 2-4, both stereoisomers are formed simultaneously, while for X = I only the trans- or mer-compounds were formed. All were separated by ion-exchange chromatography on diethylaminoethyl cellulose.[59] For all of the above compounds, where n = 1-5, ^{11}B and $^{11}B\{^1H\}$ n.m.r. spectra were recorded and assigned.[60] Their i.r. and Raman spectra were assigned according to the appropriate point groups. The positions of the B_6 modes were almost invariant to substitution, while those of the B_6-X modes do shift to lower wavenumbers on increasing the mass of X.[61]

The ^{11}B and ^1H n.m.r. spectra of $B_6H_7^-$ gave values for the lifetimes of the migrating proton on one of the faces of the octahedral boron skeleton of the anion. The temperature dependence of the lifetimes was used to determine the kinetic parameters of the proton migration. This migration is believed to involve anion/cation interaction.[62] The i.r. spectra were reported, with no detailed assignments, for $[NiL_3][B_6H_7]_2$, where L = bipy or phen.[63]

Electron-counting considerations suggest that the *iso-closo* species $H(PMe_3)_2Ir(B_8H_7Cl)$ and $H(PPh_3)(Ph_2P\overline{C_6H_4)Ir(B}_9H_8)$ in fact contain two skeletal electrons fewer than their *closo*-analogues, and are thus best regarded as *hyper-closo*-metalloboranes.[64] One product of the reaction of *arachno*-$B_6H_{11}^-$ and $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ is the novel *arachno*-9-vertex ruthenaborane $(\eta^6\text{-}C_6Me_6)RuB_8H_{14}$. This is unique among metallaboranes in having the same skeletal configuration as *n*-B_9H_{15}.[65]

It has been shown that isomerisation of $B_9H_9^{2-}$ and $C_2B_7H_9$ by a single diamond-square-diamond mechanism is forbidden, while a double-DSD process is allowed. The barriers between the 3 carbaborane isomers of lowest energy are seen to be high enough for the isomers to be separated.[66] B_5H_9 reacts with NaH or KH in THF or diglyme, or with NaI, to form $B_9H_{14}^-$. This anion can then be used *in situ* as an intermediate in the synthesis of other higher borane systems.[67]

$B_{10}H_{14}$ and $NaNO_2$/THF form $Na[B_9H_{12}NH]$. $Na[B_9H_{14}]$ and $Na[B_{10}H_{15}]$ as major products. $B_9H_{11}NH.CNCy$ has an *arachno*- open cage structure like that of 9-NEt_3-6-SB_9H_{11}. $B_9H_{11}NH$ at 400°C forms *closo*-B_9H_9NH, the first *closo*-azaborane to be reported.[68]

Several new 10-vertex, *nido*-metallaborane clusters have been reported and characterised, e.g. 6,6,6,6-$(CO)_2(PPh_3)_2$-6-MoB_9H_{13} and related species. The fluxional properties of the exopolyhedral ligands were followed by multinuclear n.m.r.[69] $WH_6(PMe_2Ph)_3$ and $(NEt_4)(B_9H_{14})$ give the first wolfraborane, 6,6,6,6,6-$(PMe_2Ph)H_2$-*nido*-6-WB_9H_{13}. The structure is similar to that of *nido*-B_9H_{14}, with B(6)H replaced by the tungsten centre. *Mer*-$OsCl_3(PMe_2Ph)_3$ gives 6,6,6-$(PMe_2Ph)_3$-*nido*-OsB_9H_{13}, and several other related species were reported.[70] $[Cp^*RhCl_2]_2$ and *arachno*-$B_9H_{14}^-$ form 6-Cp^*-*nido*-6-RhB_9H_{13}. The crystal structure and n.m.r. spectra of this show that it is a *nido*-decaborane analogue, with B(6)H unit replaced by the isolobal and isoelectronic Cp^*Rh centre.[71] This complex reacts with excess PMe_2Ph to give a range of phosphine-substituted derivatives.[72]

Pure $(Et_4N)_2B_nH_n$, where n = 10 or 12, can be obtained by pyrolysis of Et_4NBH_4.[73] Phase equilibria were studied for the systems $Cs_2B_nH_n$-$CsNO_3$-H_2O, where n = 10 or 12. The double salts $Cs_2B_nH_n.CsNO_3$ were formed in each case.[74] $[PMePh_3][B_{10}H_{13}(PPh_2)]$ forms orthorhombic crystals, belonging to the space group $Pca2_1$. The anion structure is like that of $B_{10}H_{14}^{2-}$, but with the bridging PPh_2 between B(6) and B(9), instead of *endo*-terminal hydrogen atoms.[75]

$[Cp^*RuCl_2]_2$ and $[NEt_4]_2[B_{10}H_{14}]$ in MeCN produce $[Ru(NCMe)_6]$-[7-Cp^*-*nido*-7-$RuB_{10}H_{13}]_2$. The anions are *nido*-7-metallaundecaboranyl open-faced clusters, with two Ru(7)-H-B and one B(9)-H-B(10) bridges, which exchange very readily in solution.[76] The reaction between $OsCl_3(PMe_2Ph)_3$ and *closo*-$B_{10}H_{10}^{2-}$ in ethanol gives $(PMe_2Ph)_2OsB_{10}H_8(OEt)_2$. $OsCl_2(PPh_3)_3$, however, gives the P-phenylene *ortho*-cycloboronated $(PPh_3)(Ph_2P\overline{C_6H_4)OsB}_{10}H_7(OEt)_2$. Both have closed 11-vertex 1-metallaundecaborane geometries of *iso*-*closo* type.[77] $RuCl_3(PMe_2Ph)_3$ and *closo*-$B_{10}H_{10}^{2-}$ in refluxing methanol produce 1,1-$(PMe_2Ph)_2$-1,2-μ-H-2,5-$(OMe)_2$-*isocloso*-1-Rh-

$B_{10}H_8$. The RhB_{10} cluster is a closed 11-vertex deltahedron, the *hexahapto* borane-Rh link being via one Rh-H-B and 5 Rh-B connectivities. The presence of a Rh-H-B bridge in a closed polyhedral cluster is remarkable.[78]

EHMO-FMO calculations on $B_{11}H_{13}^{2-}$ suggest asymmetry in occupation of the formerly degenerate cluster orbitals on protonation. Such calculations for $B_3H_8^-$ show that B-B edge-shortening is strongly correlated with the asymmetric nature of the H-bridges.[79] A new synthesis has been reported for $B_{11}H_{14}^-$ - from treatment of $NaBH_4$ with CH_3I in diglyme solvent. The yield was about 20· based on $NaBH_4$.[80]

MS-Xα molecular orbital calculations have been reported for $B_{12}H_{12}^{2-}$ and $B_9C_2H_{11}^{2-}$. For the latter, the calculated electron distribution indicates that the most probable site for electrophilic attack is at the B atom opposite to the C-C bond, on the pentagonal face.[81] Normal coordinate analyses have been carried out on $B_{12}Y_{12}^{2-}$, where Y = H, D, F, Cl, Br or I. This is a rare example of such calculations for icosahedral molecules.[82]

$[NMe_4][Et_3NB_{12}H_{11}]$ forms monoclinic crystals, space group $P2_1/c$. The B_{12} fragment is not distorted significantly from icosahedral symmetry, and the B-N distance is 163.2(11)pm.[83] 1,12-$B_{12}H_{10}(CO)_2$ reacts with $LiAlH_4$ in diglyme to form 1,12-$B_{12}H_{10}(CH_2OH)_2^{2-}$, from which 1,12-$B_{12}H_{10}(CH_2X)_2^{2-}$, where X = I, SCN, N_3 etc., can be prepared.[84] *Closo*-$B_{12}H_{12}^{2-}$ and $RuCl_3(PMe_2Ph)_3$ yield the new complex $(PMe_2Ph)_3RuB_{12}H_{12}$, while with $RuCl_2(PPh_3)_3$ the product is $(PPh_3)_2ClRuB_{12}H_{11}(NEt_3)$. Both could be regarded either as Ru(III) complexes of *closo*-dodecaboranyl ligands bound in an η^3-, tridentate mode to octahedral metal centres via 3 two-electron, three-centre B-H-Ru bridge bonds, or as 13-vertex, *pileo* 2n-electron metallaborane cluster species with capped, closed deltahedral cluster geometries.[85]

Thermolysis of 4-(PMe_2Ph)-*arachno*-4-PtB_8H_{12} in toluene forms, among other products, two new 17-vertex cluster compounds, i.e. $(PMe_2Ph)_4Pt_3B_{14}H_{16}$ and $(PMe_2Ph)PtB_{16}H_{18}(PMe_2Ph)$.[86] The novel *conjuncto* macropolyhedral species $(PMe_2Ph)_2Pt_2B_{16}H_{15}(C_6H_4Me)$-$(PMe_2Ph)$ has been isolated in low yield from the brief thermolysis of $(PMe_2Ph)_2PtB_8H_{12}$ in boiling toluene. It comprises a *closo*-Pt_2B_{10} subcluster and a *nido*-Pt_2B_7 subcluster fused together *via* a common Pt_2B triangular face.[87] $(Cp^*RuCl_2)_2$ and *anti*-$B_{18}H_{22}$ in the presence of base undergo B-vertex loss, with formation of a

19-vertex dirhodanonadecaborane, $Cp^*{}_2Rh_2B_{17}H_{19}$. This contains 12-vertex, *nido*-RhB_{11}, and 10-vertex, *nido*-5-RhB_9 subclusters, joined by a common B_3 face to give an effectively *syn*-configuration.[88]

3.1.3 Carba- and Other Non-metal Heteroboranes.

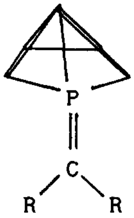
There is evidence that B and B_2 react spontaneously with CH_4 in Ar matrices. I.r. bands due to νBH (terminal and bridging) and δBH were seen. Aluminium also reacts with CH_4 under such conditions, but Ga and In do not.[89] A topological charge stabilisation criterion was used to predict the qualitative ordering of stabilities of positional isomers among the various classes of *closo*-carbaboranes, $C_2B_{n-2}H_n$, where $5 < n < 12$. Calculated orders agree with experimental data and the results of more detailed calculations.[90]

A theoretical study of trigonal-bipyramidal $C_2B_3H_5$ shows that diamond-square-diamond rearrangements are blocked by crossings of filled and vacant m.o.'s. This leads to very high activation barriers for such processes, and suggests that the trigonal-bipyramidal isomers of $C_2B_3H_5$ should be stereochemically rigid, in agreement with available experimental data.[91]

Competition experiments were used to determine the relative reactivities of the *closo*-carbaboranes $C_2B_nH_{n+2}$, where n = 4, 5 or 8, and some of their derivatives, towards electrophilic reagents such as $RX/AlCl_3$, where RX = MeCl, EtCl, Cl_2 or Br_2. *Closo*-2,4-$C_2B_5H_7$ was the most reactive, and reactivity to electophilic attack was increased by alkyl, but decreased by halogen, substitution. For *closo*-1,6-$C_2B_4H_6$, however, substitution at the 2-position by chlorine led to increased electrophilic reactivity.[92] Solid $NaHF_2$ and *nido*-$(Me_3Si)_2C_2B_4H_6$ react at 413K to give *nido*-$(Me_3Si)C_2B_4H_7$. The structure of the gas-phase product was determined by electron diffraction, giving the following bond lengths: C-C 146.0(11), C-B 154.4(8), B-B 175.8(16) pm (in the basal plane of the carbaborane cage). The distances involving the apical boron atom were: C-B 183.2(17), B-B 176.1(12) and 168.7(19) pm.[93]

$(Ph_2PCH_2)_2NiX_2$, where X = Cl or Br, and $K[C_2B_4H_7]$ both give $(dppe)NiC_2B_4H_6$ at higher temperatures (ca. -35°C), i.e. the *closo*-species. For X = Cl, at -80°C there was n.m.r. evidence for the intermediate formatiom of a *nido*-species, $(dppe)Ni(Cl)C_2B_4H_7$. This lost HCl on warming, producing the *closo*-compound. A mechanism was suggested which could be general for the insertion of ligated metal fragments into *nido*-borane cages to form *closo*-metallaboranes.[94] *Nido*-2,3-$Et_2C_2B_4H_6$, together with 2-butyne/NaH/$NiCl_2$, undergoes 2-carbon insertion into the cage system, leading to the tetracarbon carbaborane *nido*-4,5,7,8-$Me_2Et_2C_4B_4H_4$.[95]

A new class of heteroborane clusters, $R_2CPB_5H_8$, (5), has been prepared from the phospha-alkene $(Me_3Si)_2C=PCl$ and $B_5H_8^-$ (R = Me_3Si) or by dehydrochlorination of (μ-R_2CHPCl)B_5H_8, where R = Me_3Si or Ph.[96]



(5)

5-Me-6-Cl-*closo*-2,4-$C_2B_5H_5$ rearranges at 295°C to an equilibrium mixture of all 8 B-Me-B'-Cl-*closo*-2,4-$C_2B_5H_5$. The isomers appear in the order 1-Me-5-Cl-, then 3-Me-5-Cl-, 5-Me-1-Cl-, 5-Me-3-Cl-, 3-Me-1-Cl-, 1-Me-3-Cl and 1-Me-7-Cl-. The results are consistent with a diamond-square-diamond rearrangement mechanism.[97] *Closo*-2,4-$C_2B_5H_7$ and BX_3, where X = Cl, Br, I or Ph, react at elevated temperatures with X-substitution, primarily at the 3-position of the carbaborane, i.e. giving 3-X-*closo*-2,4-$C_2B_5H_7$. The reaction between BBr_3 and *closo*-1,6-$C_2B_4H_6$ at 265°C produces a *closo*-carbaborane with trigonal boron σ-bonded to a cage fragment, i.e. 2-Br_2B-*closo*-1,6-$C_2B_4H_5$.[98] *Nido*-2,3-$Et_2C_2B_4H_6$ and $H_3B.NEt_3$ at 140°C react with capping of the open face of the carbaborane, giving a good yield of *closo*-2,3-$Et_2C_2B_5H_5$. Subsequent heating of this to 320°C results in isomerisation to *closo*-2,4-$Et_2C_2B_5H_5$.[99]

Substitution of the 4,6-$C_2B_7H_{13}$ cluster led to the formation of 3-X-4,6-$C_2B_7H_{12}$, where X = Cl, Br, I or HS; 5-X-4,6-$C_2B_7H_{12}$, where X = Br, I, HS or Bu; and 3,5-X_2-4,6-$C_2B_7H_{11}$, where X = D, Cl, Br or I. All were characterised by ^1H and ^{11}B n.m.r.[100]

Two-dimensional ^{11}B-^{11}B n.m.r. spectra show that the thermal decomposition product of 4-CB_8H_{14} is 7-CB_8H_{12}. The latter was shown to have a similar structure to that of $B_9H_{12}^-$.[101] A new method of preparing *arachno*-6,9-$C_2B_8H_{14}$ has been reported, i.e.

reduction of *nido*-5,6-$C_2B_8H_{12}$ with $NaBH_4$ in EtOH/NaOH. Electrophilic halogenation of 6,9-$C_2B_8H_{14}$ produces 1-X-6,9-$C_2B_8H_{13}$, where X = Cl, Br or I.[102]

Nido-6-H_3N-6-CB_9H_{11} has been prepared by an improved route. Its reactions leading to 6-L-CB_9H_{11} were also reported, where L = H, $Me_2C{=}NH$ or Me_2S, together with formation of 2-L-1-Cp-2,1-$CCoB_9H_9$, where L = H_3N, H_2N^- or Me_2NH.[103] B(3) of 1,2-dimercapto-o-carbaborane is removed by refluxing with NaI in ethanol, giving 7,8-dimercapto-7,8-dicarbaundecaborate(10). This has an 11-apex structure derived from an icosahedron. The carbon atoms are *ortho*-, in the open face, with two exocyclic sulphur atoms.[104] The reaction of $B_{10}H_{14}$ with Me_2S and bis(trimethylsilyl)acetylene forms the new monocarbon carbaborane 9-Me_2S-7-[$(Me_3Si)_2CH$]-$CB_{10}H_{11}$. The cluster geometry of this is based on an icosahedron, missing one vertex, with the exopolyhedral $(Me_3Si)_2CH$ group bonded to the cage carbon atom. This compound reacts with NaH, involving loss of H_2, dissociation of the Me_2S and cage closure, forming the anion 2-$(Me_3Si)_2CHCB_{10}H_{10}^-$.[105]

Line splittings in the ^{10}B and ^{11}B n.m.r. spectra of o-carbaborane-d_2 in the presence of a very strong electric field were used to derive the components of the boron quadrupole coupling tensors.[106] ^{13}C, ^{10}B and ^{11}B n.m.r. data on o-carbaborane were used to probe its molecular dynamics.[107] The synthesis of carbon-to-boron bridged o-carbaboranes has been reported.[108] The esters ROOC-C≡C-COOR and $(ROOC)_3CH$ react with o-carbaboranes at 275°C to give reasonable yields of 9-alkyl-o-carbaboranes, and if R is larger than methyl there is significant polyalkylation.[109]

Several routes have been established for the preparation of $[1\text{-}H_3B\text{-}1,2\text{-}C_2B_{10}H_{11}]^-$, a useful precursor to 1-L-H_2B-1,2-$C_2B_{10}H_{11}$, where L = Me_2S, py, Me_3N or Et_3N. All of these species were characterised by ^{11}B, ^1H and ^{13}C n.m.r.[110] RMgBr, where R = 2-Me-1,2-$C_2B_{10}H_{10}$, undergoes dioxan-induced disproportionation to MgR_2.2(dioxan). The crystal structure of this shows that it is monomeric.[111]

The structure of $[Fe(TPP)]^+(B_{11}CH_{12})^-$ indicates very weak coordination by the anion, and it is suggested that $B_{11}CH_{12}^-$ is the least-coordinating anion known to date.[112] Several compounds have been reported which contain the 1-carba-*closo*-dodecaborane cage, including 1L-1-$CB_{11}H_{11}$ (L = H_3N, Me_2S), 12-L-1-$CB_{11}H_{11}$ (L =

Me_2S, $MeSCH_2SMe$). Direct halogenation of $[1\text{-}CB_{11}H_{12}]^-$ produces $[7,8,9,10,12\text{-}Cl_5\text{-}1\text{-}CB_{11}H_7]^-$ and $[7,8,9,10,11,12\text{-}X_6\text{-}1\text{-}CB_{11}H_6]^-$, for X = Cl or Br; $[12\text{-}I\text{-}CB_{11}H_{11}]^-$ and $[7,12\text{-}I_2\text{-}1\text{-}CB_{11}H_{10}]^-$.[113]

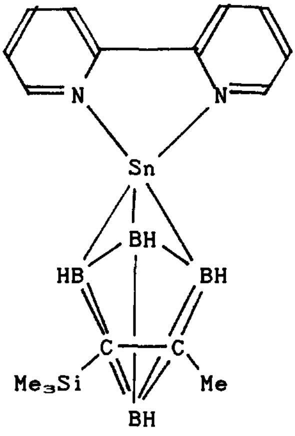
3.1.4 Metalla-heteroboranes.

The reaction of $[N(PPh_3)_2]^+[W(\equiv CR)(CO)2(\eta^5\text{-}1,2\text{-}C_2B_9H_9Me_2)]$ with [*trans*-PtH(acetone)$(PEt_3)_2$][BF_4] gives $PtW(CO)_2(PEt3)2\{\eta^6\text{-}C_2B_9H_8\text{-}(CH_2R)Me_2)$. This in turn reacts with PMe_3 or CO to give $PtW(\mu\text{-}H)\text{-}\{\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_7(CH_2R)Me_2\}(CO)_2(L)(PEt_3)_2$, where R = C_6H_4Me-4, and L = CO or PMe_3.[114]

$(PhCH_2)_2C_2B_4H_6$ is prepared on a large scale from dibenzylacetylene with B_5H_9/NMe_3. It is a good precursor for mixed iron-carbaborane-polyarene complexes such as $(\eta^6\text{-}C_8H_{10})Fe[(PhCH_2)_2\text{-}C_2B_4H_4]$.[115] *Nido*-2,3-$Et_2C_2B_4H_6$ can also be used to prepare such complexes.[116] $(PhCH_2)_2C_2B_4H_6$, on treatment with NaH/THF, followed by $FeCl_2$, produces $[(PhCH_2)_2C_2B_4H_4]_2FeH_2$. Treating this with O_2 gives $(PhCH_2)_4C_4B_8H_8$. This is non-fluxional, unlike other $R_4C_4B_8H_8$ derivatives, due to the severe steric crowding by the $PhCH_2$ groups.[117] The reactions of thermally-generated Fe, Co or Ni atoms with *nido*-2,6-$C_2B_7H_{11}$ and cyclopentadiene, toluene, mesitylene or 2-butyne yield a number of new metallacarbaborane clusters, e.g. with Fe and $C_6H_5CH_3$, 2-$(\eta^6\text{-}C_6H_5CH_3)$Fe-6,9-$C_2B_7H_9$ and 2-$(\eta^6\text{-}C_6H_5CH_3)$Fe-1,6-$C_2B_7H_9$; or with Co and C_5H_6, 2-CpCo-1,4-$C_2B_7H_9$ and 4-CpCo-2,3-$C_2B_7H_9$.[118]

The crystal structures of 3-(η^5-indenyl)-3,1,2-$CoC_2B_9H_{11}$ and 3-Cp-3,1,2-$CoC_2B_9H_{11}$ have been reported. The indenyl complex shows that the η^5-indenyl ligands are 'slipped' so that the junction carbon atoms are 7 pm further from the metal atom.[119] Crystal structures have also been reported for the following cobalt complexes: $Cs[Co(C_2H_8B_9Br_3)_2]$,[120] $Cs[Co(C_2H_{10}B_9I)_2]$,[121] $Cs[Co(C_2H_{11}B_9)(C_2H_{10}B_9I)]$,[122] and $[(C_2B_9H_{10})\text{-}S\{CH_2CO(OMe)\}\text{-}(C_2B_9H_{10})]Co$,[123] as well as the rhodium complex $(Ph_3P)(Ph_2PC_6H_4)\text{-}Rh(C_2B_9H_{11})$.[124] The slipping distortion parameters were determined from the crystal structure of 3-$(\eta^2,\eta^2\text{-}C_8H_{12})$-3,1,2-$PdC_2B_9H_{11}$; there were shown not to correlate fully with the observed B(8) chemical shift.[125] $Pt(PPh_3)_4$ reacts with *closo*-$SeB_{11}H_{11}$ in refluxing ethanol to form $[PtH(PPh_3)_3][SeB_{10}H_{11}]$ and 2,2-$(PPh_3)_2$-1,2-$SePtB_{10}H_{10}.CH_2Cl_2$. The latter has a dodecahedral $SePtB_{10}$ cage, with adjacent Se and Pt atoms.[126]

There have been several reports about new aluminacarbaboranes. Thus, Na[Al(η^2-2,7-$C_2B_6H_8$)$_2$] was prepared and characterised by single-crystal X-ray diffraction. Variable temperature ^{1}H and ^{11}B n.m.r. spectra showed that the anion was fluxional at room temperature in solution - involving interconversion of two enantiomers.[127] 2,3-Dimethyl-1-ethyl-1,2,3-aluminadicarbadodecaborane, from $AlMe_3$ and 7,8-dimethyl-7,8-dicarbadodecaborane, is a useful prcursor for the synthesis of icosahedral main-group carbaboranes.[128] Treating Na[5,6-$C_2B_8H_{11}$] with $Et_2AlCl.OEt_2$ in refluxing toluene forms the novel aluminacarbaborane *nido*-[μ-6,9-AlEt(OEt_2)-6,9-$C_2B_8H_{10}$]. This was characterised by single-crystal X-ray diffraction.[129] A related reaction involving Et_2AlCl gave Na[Al(η^2-6,9-$C_2B_8H_{10}$)$_2$].[130] An unusual aluminacarbaborane sandwich complex, *commo*-3,3'-Al[(*exo*-8,9-(μ-H)$_2$AlEt$_2$-3,1,2-$AlC_2B_9H_9$)-(3',1',2'-$AlC_2B_9H_{11}$)] was also reported. The bonding faces of the two cluster ligands are nearly parallel. This is the first aluminium sandwich complex to be reported.[131]



(6)

Silicarbaboranes [$(Me_3Si)_2C_2B_4H_4$]Si^{II} and [$(Me_3Si)_2C_2B_4H_4$]$_2$-Si^{IV} have been prepared, and the structure of the latter determined by X-ray crystallography.[132] A silicon sandwich complex has also been made: *commo*-3,3'-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$, from $SiCl_4$ and Li$_2$(*nido*-7,8-$C_2B_9H_{11}$).[133] A related germanium sandwich complex, [$(Me_3Si)_2C_2B_4H_4$]$_2$Ge, is prepared from $GeCl_4$ and Li$^+$-[$(Me_3Si)_2C_2B_4H_5$]$^-$.[134]

The complex (6) forms monoclinic crystals, space group $P2_1/n$.

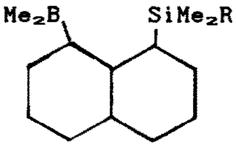
The tin coordinates only to three boron atoms in the 5-atom face of the carbaborane ligand. The Sn-N donor-acceptor bonds confirm the Lewis acidity of the stannocarbaboranes.[135] A number of analogous donor-acceptor complexes have been made.[136,137]

3.1.5 Compounds containing B-C Bonds.

Benzene and BCl_3 react at 800°C to form a graphite-like solid, BC_3.[138] The crystal structure of $[Li(12\text{-crown-}4)_2]^+[BMes_3]^{\cdot-}$, where Mes = 2,4,6-$Me_3C_6H_2$, shows that the addition of one electron to $BMes_3$ has only a small effect on the ground state structure. [139] Di-*i*sopropyl- and di-*tert*butyl-boranes, R_2BX, where X = F, Cl, Br, I, OR', SMe, NH_2, NHR' or NR'_2, can be prepared from the readily accessible (dimethylamino)diorganylboranes $R_2B\text{-}NR'_2$, where R = $CHMe_2$, CMe_3; R' = Me or Et.[140]

The gas-phase pyrolysis of bis(9-borabicyclo[3.3.1]nonane) gives the 1-bora- and 8-bora- forms of borabicyclo[4.3.0]nonane. Heating the 8-bora-isomer further produces a stable 1,2:1,2-diborane(6) unit.[141] (7), where R = Me, OEt or F, and their adducts with F^- have been prepared. There is crystallographic evidence for coordination of both B and Si to F^- in the adducts.[142]

A series of new boron-containing bis-ylides, (8) has been reported, where R^1, R^3 = H or Me, R^2 = C_6H_{11}. They are potentially useful ligands.[143] N-Substituted 2-carboxamidophenylboronic acid anhydrides were prepared by the lithiation of 2-phenyl-2-oxazolines, with subsequent reaction with $B(OMe)_3$ and hydrolysis.[144] Ligand exchange reactions between aryltrimethylsilanes ($ArSiMe_3$) and halogenoboranes (BX_3 or $Ar'BX_2$) gave the species $ArBX_2$, ArAr'BX and Ar_2BX.[145] The first crystal structure of a boron-stabilised carbanion has been reported, $[Li(12\text{-crown-}4)_2][CH_2\text{-}C_6H_2(3,5\text{-}Me_2)(4\text{-}B\{2,4,6\text{-}Me_3C_6H_2\}_2)].Et_2O$. Stabilisation is achieved by extensive delocalisation, with the B-C bond length indicative of substantial "boron ylide" character.[146]



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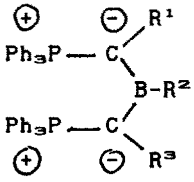
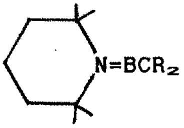


(8)

Some evidence was found for the existence of (9) as an intermediate in the thermal decomposition of fluoro(tetramethylpiperidino)[(trimethylsilyl)organyl]boranes in solution.[147] Metastable amino(9-fluorenylidene)boranes have been prepared, e.g. (10). Other methylene boranes can be prepared, with sufficently bulky amines.[148]



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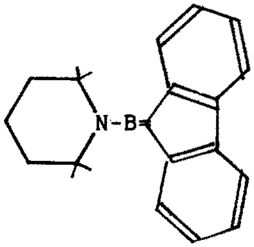

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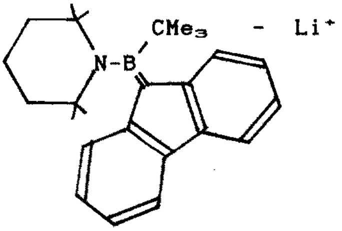

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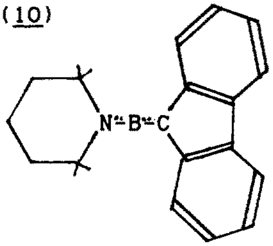


(12)

The formation of (tmp)B(CMe_3)$C_{13}H_8Li$, where tmp = 2,2,6,6-tetramethylpiperidino, i.e. (11), by the dehydrofluorination of (tmp)B(F)$C_{13}H_9$ using Na($HBEt_3$), is thought to proceed *via* the methyleneborane intermediate (12).[149] The structure and dynamics of 25 (C_5Me_5)BXY compounds were followed using ^1H DNMR spectra. The results were consistent with a 1,5-sigmatropic rearrangement (1,2-shift) in many cases.[150]

$H_3(CO)_9Os_3BCO$ and BH_3/THF react to give the triosmium borylidene carbonyl, $H_3(CO)_9Os_3BCH_2$, an electronic and structural analogue of the vinylidene cluster $H_3(CO)_9Os_3CCH_2$.[151] U.v. photoelectron spectra were reported and assigned for $(\mu\text{-}H)_3Os_3(CO)_9BL$, where L = CO or PMe_3. These results, together with M.O. calculations, suggest that the boron is acting as a pseudo-metal cluster atom relative to the metal centres as well as to attached ligands.[152]

$(R_2B)_2O$, where R = Et or Ph, react with excess pyrazole (Hpz) to give $R_2B(\mu\text{-pz})_2BR_2$. $(Me_2NBPh)_2O$ and Hpz form the triply-bridged pyrazabole, $PhB(\mu\text{-pz})_2(\mu\text{-OBPhO})BPh$, and smaller amounts of

$[(pz)PhB(\mu\text{-}pz)_2BPh]_2O$, in which the B-O-B bridge links the two pyrazabole moieties. Triphenylboroxin, $(PhBO)_3$ and Hpz give the adduct $(PhBO)_3.Hpz$ at room temperature, in which two boron atoms of the ring are coordinated to pyrazole nitrogen atoms.[153] The triply-bridged pyrazaboles $RB(\mu\text{-}pz)_2(\mu\text{-}OBRO)BR$, where R = Et or Ph, are thermally quite stable. Halogenation of them yields $RClB(\mu\text{-}pz)_2BRCl$, a useful source for further pyrazaboles.[154]

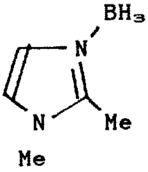
3.1.6 Compounds containing B-N, B-P or B-As Bonds

Potential energy surfaces of the mono- and dications of aminoborane, NH_2BH_2, and ammoniaborene, NH_3BH, have been calculated using high-level *ab initio* methods. These suggest that NH_3BH^{2+} is 60.6 kcal mol^{-1} more stable than $NH_2BH_2^{2+}$.[155] The HeI photoelectron spectra of the unstable species H_2NBX_2, where X = H, F, Cl or Br, have been assigned by analogy with related species, semi-empirical and *ab initio* m.o. calculations. It seems that B-halogenation weakens the B-N π-bond.[156,157]

Preparations and vibrational spectra were reported for $Me_2NCl.BX_3$, where X = F, Cl or Br. The crystal structure was determined for X = Cl (B-Cl 183 pm., B-N 167 pm.).[158] Natural abundance ^{15}N n.m.r. spectra of amino-borane adducts, such as $H_3N.BH_3$, $Et_3N.BH_3$, $Me_3N.BX_3$ (X = F, Cl, Br, I), gave values for the $^1J(^{15}N^{11}B)$ coupling constants, which could be correlated with the $^1J(^{31}P^{11}B)$ coupling constants in the corresponding phosphine boranes.[159] It is possible to obtain both B-N and B-P bonded BH_3 adducts of Me_2PNMe_2 - characterised by ^{11}B and ^{31}P n.m.r. spectra.[160] Natural abundance ^{15}N n.m.r. spectra were recorded for a range of azole-borane adducts, such as (13).[161]

N-Metallation of R_2BNH_2 or R_2BNMeH gives lithium amides $R_2BNR'Li$, with sterically demanding R groups (^tBu, ^iPr). These compounds are useful precursors to symmetrical and unsymmetrical substituted diborylamines and B-functional diborylamines.[162]

^1H and ^{11}B n.m.r. data on mono- and bis-borane adducts of aryl-, benzyl-, phenethyl- and phenylenediamines showed no simple relationship with the nature of the N-B bond.[163] 2-Chloro-1,3,2-diazaborolidines react with $Me_3SiN{=}C{=}NSiMe_3$ to form borylated carbodi-imides, e.g.(14).[164] $Ph_2B\text{-}N(H)Me$ was studied by ^{11}B, ^{13}C, ^{14}N and ^{15}N n.m.r. The ^{13}C data were consistent with hindered rotation about the B-N bond.[165]



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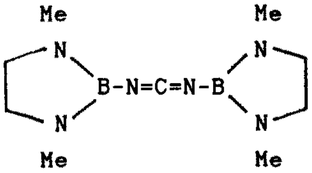
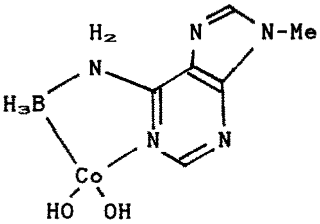


(14)

It has been possible to prepare boron analogues of choline, i.e. $MeC(O)OCH_2CH_2N(Me_2)BH_3$, and several substituted derivatives. [166,167] Several complexes have been prepared which contain trimethylamine-carboxylatoborane ligands, $[M_3O\{(CH_3)_3N.-BH_2CO_2\}_6R_3]^+X^-$, where M = Cr(III) or Fe(III), R = H_2O or MeOH, X = NO_3 or Cl. The carboxylatoborane ligand acts just like the carbon carboxylato analogues.[168] The cobalt(III) complex *cis*-$[Coen_2-$



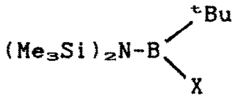
(15)

$(Me_3NBH_2CO_2)_2]^+$ contains unidentate trimethylamine-borane carboxylato ligands. Co(II), Zn(II) and Cu(II) (= M) form bidentate complexes of this ligand, $[M(Me_3N.BH_2CO_2)]^+$.[169]

The key intermediate in the capture of borane by aromatic 2-amino-N-heterocycles in water is a chelate complex containing borane, an amine and a metal ion, possibly (15).[170] The new amine-(α-cyano-organo)boranes, $Me_3N.BH_2CRR'CN$, where R = H, R' = Ph; R = R' = Me, have been prepared and characterised. It is suggested that $BH_3CRR'CN^-$ is more reactive to $Me_3N.HCl$ than is BH_3CN^-.[171]

One amino-group can be introduced to BX_3, where X = Cl or Br, by the reaction of benzyl-*tert*-butylamine, RR'NH, with the BX_3, forming $RR'N-BX_2$. $(RR'N)_2BX$, however, can only be prepared *via* the metal amide LiNRR'. The compound $(RR'N)_2BX$ reacts with BBr_3 or $AlCl_3$ to form bis(amino)boron salts, such as $[(RR'N)_2B]^+AlCl_4^-$. The cation has an allene-type structure, with a linear NBN skeleton and short B-N bonds (133.2pm).[172] $({}^{i}Pr_2N)_2BBr$ reacts with MBr_3 (M = Al or Ga) to give stable salts $[({}^{i}Pr_2N)_2B]^+MBr_4^-$.[173] N.m.r. data ($^1H$, ^{11}B, ^{13}C and ^{14}N) for di-*iso*-propyl- and di-*tert*-butylboranes show that for the former the steric effects are small, but that for the latter the C_2BNC_2 conformation deviates from planar. The effect is greater the more bulky is NR'_2. HeI photo-electron spectra lead to the same conclusion.[174]

$({}^{t}BuP)_2BN({}^{i}Pr)_2$ reacts with potassium or potassium naphthenide with P-P bond cleavage in the 3-membered ring and formation of $K[{}^{t}BuP\text{-}BN({}^{i}Pr)_2\text{-}P{}^{t}Bu]K$. This is only stable below -78°C, however, as above that temperature it rearranges to the unsymmetrical compound $K[{}^{t}BuP\text{-}P({}^{t}Bu)\text{-}BHN({}^{i}Pr)_2]$.[175]



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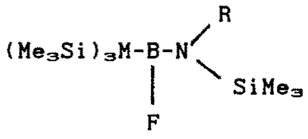


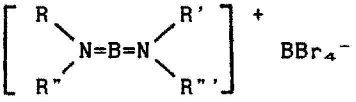
(<u>17</u>)

(<u>16</u>), where X = Cl, reacts readily with $LiAlH_4$, $LiOCH_2CF_3$, MeMgBr or excess NH_3, to give derivatives with X = H, OCH_2CF_3, Me or NH_2 respectively. A wide range of further compounds can be made from these, and especially the amino compound.[176] The aminoborane $Ph_2BN(CMe_3)SiMe_3$ has a long B-N bond (143.3pm) and a non-planar C_2BNCSi skeleton. The structures of 5 diborylamines were also determined. $(Mes_2B)_2NH$ and $(Mes_2BNH)_3B$ have coplanar conformations for the C_2BNHBC_2 (or C_2BNHBN_2) units, while $(Ph_2B)_2NH$ and $(Ph_2B)_2NMe$ have twist conformations. For ${}^{t}Bu_2BNMe$-9-borafluorene an orthogonal conformation was detected, with the ${}^{t}Bu_2B$ fragment almost perpendicular to the BNC-9-borafluorene plane.[177]

$(Me_3Si)_3MLi$, where M = C or Si, and the aminohalogenoboranes $F_2B\text{-}N(R)SiMe_3$, where R = Me, Et, ${}^{i}Pr$, $SiMe_3$ or CMe_3, react to form (<u>17</u>).[178] The diborylamines $R_3SnN(BR'R'')_2$ are readily obtained from $N(SnR_3)_3$ and R'R"BX, where R = Me or Et; R' = R" = Et, ${}^{i}Pr$, Bu or Ph; R' = Cl, Br, R" = NMe_2, Cl or Br; X = Cl or Br.[179] The preparation has been reported for chain-type polynuclear pyrazolyl bridged spiro-species containing boron and metal centres. Thus, $[B(pz)_4]^-$ and LPdX, where L = non-reactive ligand(s), X = halogen, give $(pz)_2B(\mu\text{-}pz)_2PdL$ (1:1 reagent ratio) or $[LPd(\mu\text{-}pz)_2B(\mu\text{-}pz)_2\text{-}$

Pdl]$^+$ (1:2 reagent ratio). Several related species were also described.[180]

Fluoro[(trimethylsilyl)amino]boranes and excess BBr_3 produce (18), where R-R"' = CMe_3, CH_2Ph or $SiMe_3$, for which the thermal stability decreases with increasing numbers of $SiMe_3$ groups.[181] The reaction of (*tert*-butylimino)(2,2,6,6-tetramethylpiperidino)-borane with $M(CO)_6$ gives (19). For M = Cr, X-ray diffraction shows that the two "B=N" bonds are non-equivalent, with a long Cr-N bond.[182]



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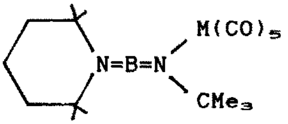

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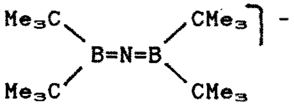

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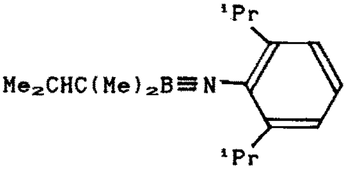


(21)

The reaction between $^tBu_2B$-NH-B^tBu_2 and ^tBuLi.TMEDA produces the diborylamide (20) as the Li(TMEDA)$^+$ salt. The i.r. spectrum of this confirms the presence of a linear, allene-like B=N=B unit. [183] The addition of Br_2 to the BN triple bond of RB≡N^{t}Bu, where R = Me, Et, Pr, Bu etc, leads to the N-bromoaminoboranes, Br-(R)B=N(^{t}Bu)-Br.[184] (21) is prepared from dibromothexylborane and 2,6-di-isopropylaniline. The BN triple bond stretching mode is at 2030 (^{10}B), 1995 (^{11}B) cm^{-1}.[185]

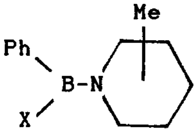
L_2BF, where L = mesityl, and $LiPPh_2$ react to form (dipenylphosphino)dimesityl borane, L_2BPPh_2. This was shown to be monomeric, with a B-P distance of 185.9(3)pm, consistent with a largely double BP bond.[186] BP double bond character was also found for $[Li(12\text{- crown-}4)_2][MesPBMes_2]$ and $Li(Et_2O)_2P(Mes)BMes_2$, where Mes = 2,4,6-$Me_3C_6H_2$.[187]

The reactions of BH_3.THF with Me_2AsNR_2, where R = Me, Et, ^{n}Pr or ^{i}Pr, show that with R = Me, an N-B adduct is formed at low temperature (this decomposed to several B-N compounds and Me_4As_2).

For R = Et, equimolar amounts of As-B and N-B adducts were formed at low temperatures, but mainly N-B adducts at higher temperatures. For R = ^{n}Pr, there was more As-B than N-B bond formation at low temperature, but the former rearranged to the latter on warming. The species with R = ^{i}Pr gave only an As-B adduct. The results show that the coordination preference of the boron is mainly sterically controlled.[188] ^{1}H and ^{11}B n.m.r. chemical shifts were measured for $Me_nAsH_{3-n}.BX_3$, where n = 1, 2 or 3, X = Cl, Br or I, and also ^{11}B data for $Me_nAsH_{3-n}.BX_2Y$ and $Me_nAsH_{3-n}.BXYZ$, where X, Y and Z = different halogens.[189]

3.1.7 Compounds containing B-O or B-S Bonds

The microwave spectrum of the BO radical was analysed to give molecular parameters for the ^{10}B and ^{11}B forms.[190] The detailed electronic structure of $H_2O.BF_3$ was investigated by a combination of electron energy loss spectroscopy (EELS) and u.v. photoelectron spectroscopy, together with m.o. calculations.[191] Phase transformations in triethylcyclotriboroxane, $(BEt\text{-}O)_3$ were shown to be due to co-operative effects involving intermolecular B...O and repulsive intermolecular H...H interactions.[192] A variable temperature ^{13}C n.m.r. study of alkoxy and alkylthio derivatives of 2- and 3-methylpiperidinophenylboranes, (<u>22</u>), with X = MeO or EtS, show that pπ-pπ bonding between B and O is about 3 kcal mol^{-1} stronger than between B and S.[193]



(<u>22</u>)

The structure determination of the newly-prepared complex $[Cp(OC)Fe(Me_3CCO)_2]BF_2$ shows that the ferra-chelate ring is in the boat conformation, with the Cp ligand in the axial position.[194] The related complex $Cp(OC)Fe(MeCO\{[H_2C{=}C(Me)]CO\}BF_2$ forms monoclinic crystals, with the chelate ring again in the boat conformation, but with the CO ligand axial. There was no evidence for extensive π-delocalisation in the ring.[195]

The ionic character of the $M\text{-}BO_2$ bond (where M = Li, Na or K) has been estimated. The total dissociation energies of $LiBO_2$ and $NaBO_2$ were estimated by the extended Huckel M.O. method, showing that the increase in the energy of the $Li-BO_2$ bond is due to the sp-hybrid state of the lithium.[196]

Phase relationships were established in the following systems: $LiIO_3-LiBO_2-H_2O$, $LiIO_3-Li_2B_4O_7-H_2O$;[197] $LiBO_2-ZnO$;[198] $H_3BO_3-CH_3CH_2CH_2COOH-H_2O$;[199] and $HIO_3-H_3BO_3-H_2O$.[200] The i.r. spectra of borates formed in boric acid-amine-water systems show that primary amines give a triborate ring anion, secondary and tertiary amine give pentaborate ring anions, and primary diamines form tetraborate ring anions.[201] I.r. data were used to identify compounds formed in the $H_3BO_3-HCONH_2$ and $H_3BO_3-HCONH_2-H_2O$ systems.[202]

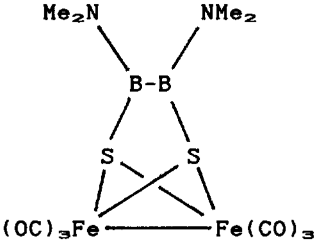
The previously unknown $NaLi_2(BO_3)$ has been reported.[203] $CsLi_5(BO_3)_2$ is prepared from $CsO_{0.48}$, Li_2O and B_2O_3, in the ratio 1.1:2.2:1.[204] $Na_4Li_5(BO_3)_3$ has been prepared for the first time, from the appropriate oxide mixture.[205] The photoredox chemistry of $[BW_{12}O_{40}]^{5-}$ in the presence of MeOH has been reported - involving the formation of $[BW_{12}O_{40}]^{6-}$, H_2 and formaldehyde.[206] ^{11}B n.m.r. data were used to follow the temperature dependence of boron coordination in sodium borate glasses, especially at 36 mol% Na_2O, 64 mol% B_2O_3.[207]

Studies on systems comprising boric acid or a borate and amines or amides were reviewed.[208] Examples of specific systems of this type are: boric acid-3-aminopropanol-H_2O,[209] and boric acid-trimethylamine- H_2O.[210] Phase diagram determinations were reported for $Tb_2O_3-Fe_2O_3-B_2O_3$;[211] $PbO-2PbO.B_2O_3-2PbO.P_2O_5$; [212] and $Bi_2O_3-B_2O_3-ZnO$ systems.[213]

Interactions were studied between H_2O and several magnesium borate minerals, e.g. $Mg_2(OH)[B_2O_4(OH)]$ etc.[214] The formation of alkali and alkaline earth peroxoborates, including $B(OOH)_4^-$ and $[B_2(O_2)_2(OH)_{4-n}(OH)_n]^{2-}$, as a function of cation composition and pH of the solutions was studied by high-resolution ^{11}B n.m.r.[215]

A solid 1:1 molar ratio mixture of $K_2B_4O_7.4H_2O$ and $KB_5O_8.4H_2O$ reacts under conditions of high humidity to produce a new potassium borate, $KB_3O_5.3H_2O$. This was shown to be $KB_3O_3(OH)_4.-H_2O$, containing isolated $B_3O_3(OH)_4^-$ anions, built up from one tetrahedral and two trigonal boron atoms. The ring is almost planar, with B_{trig}-O(ave.) = 136.6pm, B_{tet}-O(ave.) 147.0pm.[216] Magic-angle spinning (MAS) ^{11}B n.m.r. spectra of solid borates, e.g. $MgB_3O_3(OH)_5.H_2O$, $Na_2B_4O_6(OH)_2.3H_2O$ etc., can be used to give quantitatively reliable BO_3/BO_4 ratios.[217] I.r. and Raman spectra have been obtained for the new β-barium metaborate. There was evidence for dynamic coupling between the external and internal motions of the $B_3O_6^{3-}$ ring and the Ba^{2+} ion.[218]

Electrochemical studies show the Cl^- reacts with molten $Na_2B_4O_7$ to produce oxochloro complexes or BCl_3. Addition of reducing agents (B_4C, SiC) to molten $Na_2B_4O_7$ gave boron, which then dissolved in the melt.[219] Solubility measurements were carried out on the systems $M_2B_4O_7$-$MHCOO$-H_2O (M = Na or K);[220] $M_2B_4O_7$ (M = Li, Na, K or NH_4)-$H_2NCONHCOCH_3$-H_2O;[221] and $Na_2B_4O_7$-$HCONH_2$-H_2O.[222]



(23)

The crystal structure of the urotropinium salt of $[B_5O_6(OH)_4]^-$ shows that it belongs to the space group $P2_1/c$.[223] Solubilities were measured in the systems MB_5O_8-$H_2NCONHCOCH_3$-H_2O;[224] and MB_5O_8-$C_6H_5NR_2$-H_2O (M = Li, Na or K; R = H, Me or Et).[225] Solubilties and refractive indices were measured at 25°C for saturated solutions in alakali metal pentaborate-glycine-water systems.[226]

$M_2S_2Fe_2(CO)_6$, where M = Li or Na, could be used to prepare a wide range of compounds, $XBS_2Fe_2(CO)_6$, where X = NR_2, R or halogen, as well as (23).[227]

3.1.8 Boron Halides

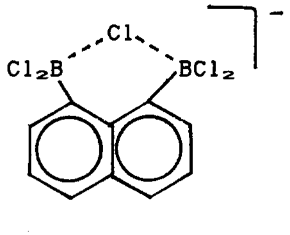
$^{11}BF^+$ and $^{10}BF^+$ radical cations were generated and trapped in neon matrices at 4K. E.s.r. measurements yielded magnetic parameters for $^{11}BF^+$. C.I. m.o. calculations gave excellent agreement with the experimental results.[228] I.r., u.v. and luminescence spectra have been described for $F_2B(L)$, where L = acetylacetonate, benzoylacetonate or dibenzoylmethanate. The luminescence spectra of the crystals are markedly different from those of the solutions.[229]

The nucleophilic substitution of one halogen in (tetramethylpiperidino)boron dihalides, $(tmp)BX_2$, where X = F, Cl or Br, is determined chiefly by steric factors. One fluorine can be replaced by $SiMe_3$ or $CHMe_2$, but Cl and Br cannot. $LiCHPh_2$ gives $(tmp)B(X)-CHPh_2$ for all X, but $LiC(SiMe_3)Ph_2$ leads to substitution of one F only, and not Cl or Br.[230] Rotational transitions were observed in the 3(E') state of $^{10}BF_3$;[231] and the pure rotational spectrum of $^{11}BF_3$ was analysed in great detail.[232] The structure of the weakly bound complex $HCl.BF_3$ was determined by molecular beam electric resonance spectroscopy. The molecule is a near-prolate symmetric top, with the Cl atom 317pm above the boron atom, on or very near the three-fold axis.[233]

The cubic unit cell of the new clathrate hydrate $HBF_4.5.75H_2O$ has a = 1174.4(5)pm at -165°C.[234] $BF_3.OEt_2$ reacts with three molar equivalents of $^nBuLi.HMPA$ to form $LiBF_4.4HMPA$, where HMPA = $O{=}P(NMe_2)_3$. The solutions were shown to contain Li and BF_4 components held tightly together by Li...F interactions.[235] MBF_4 molecules, where M = Li-Cs, not only decompose on heating, to MF + BF_3, they also, for M = K, Rb or Cs, form $M_2(BF_4)_2$ molecules.[236] The coordination of the BF_4^- ligand in $Cp(OC)_2(R_3P)MoFBF_3$, where R = Me or Et, was confirmed by a ^{19}F n.m.r. study at -80°C.[237]

Selective vibrational excitation of $^{10}BCl_3$ and $^{11}BCl_3$ was achieved using CO_2 laser radiation.[238] (<u>24</u>) contains a B-Cl-B bridge, the first such to be reported. The species is formed by the reaction of 1,8-naphthalenediylbis(dichloroborane) with chloride ion donors.[239]

An r.f. discharge converts BCl_3 in the presence of Hg to B_2Cl_4. Disproportionation of B_2Cl_4 produces 2n framework electron clusters B_nCl_n, where n = 8-12, and $(B_9Cl_8)_2$. The proportions of the products were very temperature dependent, and the relative



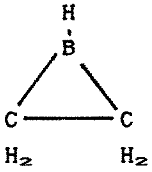
(<u>24</u>)

thermal stabilities were found to be $B_9Cl_9 > B_{10}Cl_{10} > B_{11}Cl_{11} > B_{12}Cl_{12} > B_8Cl_8$, i.e. they do not correspond with the sequence for 2n+2 framework electron clusters.[240] The He(I) photoelectron spectra for B_nCl_n, where n = 4, 8 or 9, were assigned from m.o. calculations. The results fit into the following sequence for B-B overlap populations: $B_9Cl_9^{2-} > B_9Cl_9 > B_8Cl_8^{2-} > B_4Cl_4(T_d) > B_4Cl_4(D_{4h}) > B_2Cl_4(D_{2d}) > B_2Cl_4(D_{2h})$.[241]

The i.r. and Raman spectra of $[C_7H_7]^+[BX_4]^-$ gave complete sets of vibrational wavenumbers for BX_4^- anions, including BI_4^-: $\nu_1(a_1)$ 169; $\nu_2(e)$ 83; $\nu_3(t_2)$ 515 (^{11}B), 543 (^{10}B); $\nu_4(t_2)$ 117cm^{-1}.[242]

3.1.9 Boron-containing Heterocycles

The optimum geometries and relative energies of the 5 most probable isomers of the formula C_2H_5B were calculated using SCF and fourth-order perturbation theory. It appears that the closed ring form (25) is the most stable, and a true minimum on the C_2H_5B potential surface.[243] Possible pathways for dimerisation of borirene to (26) and (27) were studied by semi-empirical and *ab initio* m.o. calculations.[244]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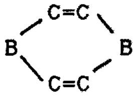
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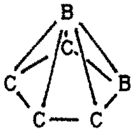
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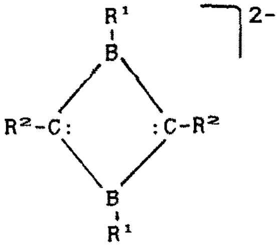
The dianion (28) is a precursor to two 1,3-diboretanes with very different geometries, the puckered (29) and the nearly-planar (30), where $R^1 = N^iPr_2$ and $R^2 = SiMe_3$.[245] The simplest boron-containing heterocycle analogous to cyclobutadiene has been prepared, whose n.m.r. spectrum suggests that the resonance structures (31) and (32) both play a significant role, where R = CMe_3, R' = $SiMe_3$.[246]

(33) reacts with $:SnR^3_2$ to give the stable stanna-ethene, (34), where $R^1 = SiMe_3$, $R^2 = CMe_3$ and $R^3 = CH(SiMe_3)_2$.[247] [2+2]-Cycloaddition of (35) to $Cp_2Ti{=}CH_2$ yields (36).[248] C-unsubstituted 3-borolenes, (37), are obtained by treating RBX_2, i.e. $MeBBr_2$, $C_6H_{11}BCl_2$, $PhBCl_2$, o-tolBCl_2, mesBCl_2, Me_2NBCl_2, Et_2NBCl_2 or



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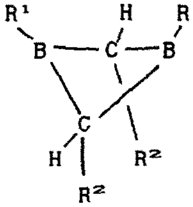

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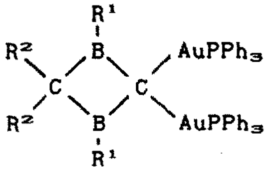

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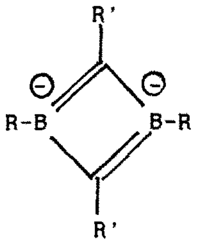

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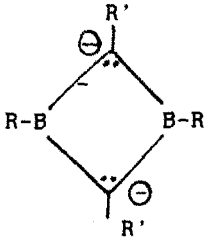

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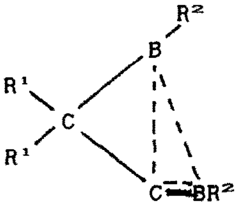

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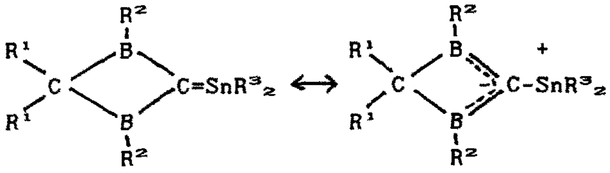

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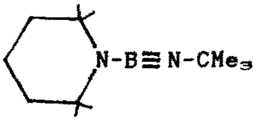

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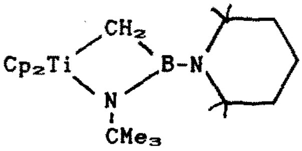
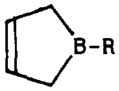


(36)

$^iPr_2NBCl_2$, with $Mg(C_4H_6).2THF$ in ether. For R = Ph, NMe_3, NEt_2 or N^iPr_2, the 3-borolenes undergo catalytic isomerisation, *via* $[RhCl(C_2H_4)_2]_2$, to 2-borolenes, (38).[249]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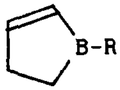
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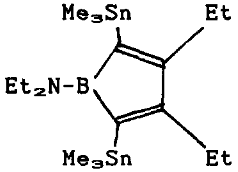
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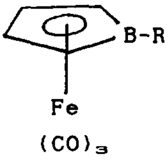
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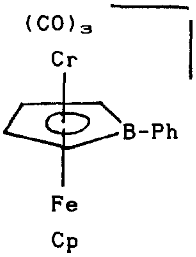
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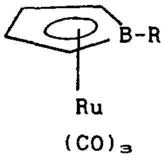
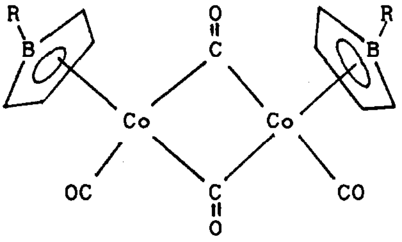

(42)

New borol compounds have been prepared by organoboration the alkynylborane $Et_2NB(C\equiv C-SnMe_3)_2$, i.e. (39).[250] 2- and 3-borolenes, C_4H_6BR, where R = Ph, Me, C_6H_{11} or OMe, react with carbonyls of Mn, Fe or Co, to form simple metal (5-borole)metal complexes such as (40).[251] The first 30-electron triple-decker anion, (41), has been prepared from $[CpFe(C_4H_6BPh)]^-$ and $Cr(CO)_3-(NH_3)_3$.[252] Dehydrogenating complexation of borolenes with $M_3(CO)_{12}$, where M = Ru or Os, or $RhCl(PPh_3)_3$ etc., produces (η^5-borole)metal complexes of Ru, Os or Rh, e.g. (42), where R = Ph, OMe or Me.[253] A large variety of (η^5-borole)cobalt complexes has been prepared, starting from $\mu-(CO)_2[Co(CO)(\eta^5-C_4H_4BR)]_2$, where R = Me or Ph, e.g. (43).[254]

Products of the reduction of 2,3-dihydro-1,3-diborole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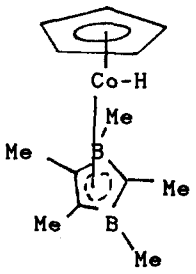
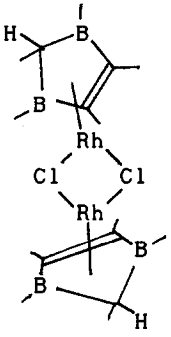
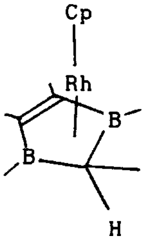

(44)

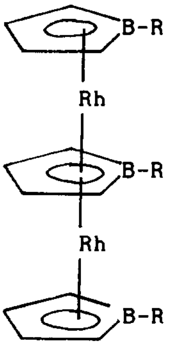
derivatives with potassium include complexes with CpCo such as (<u>44</u>).[255] $[(C_2H_4)_2RhCl]_2$ and 2,3-dihydro-1,3-diboroles form (<u>45</u>). The chloro-bridges can be cleaved to give e.g. (<u>46</u>).[256]



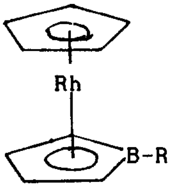
(<u>45</u>)



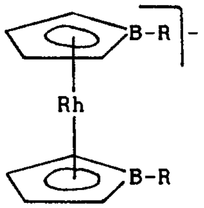
(<u>46</u>)



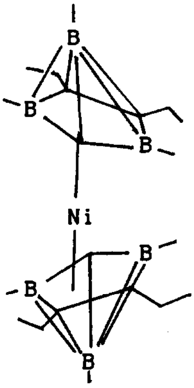
(<u>47</u>)



(<u>48</u>)



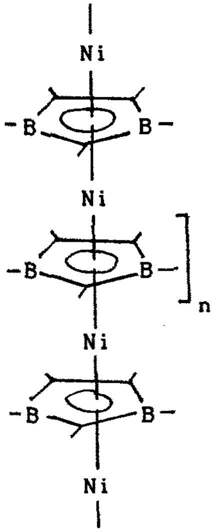
(<u>49</u>)



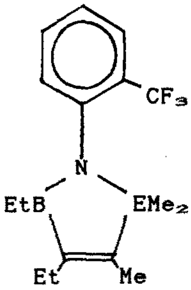
(<u>50</u>)

The borolenes C_4H_6BR, where R = Me or Ph, react with $[Rh(\eta^2-C_2H_4)_2Cl]_2$ to give (<u>47</u>). Treatment of these with NaCp gave (<u>48</u>) and (<u>49</u>).[257] (<u>50</u>), from $Ni(C_2H_4)_3$ and 2,3-dihydro-1,3-diborole,is analogous to nickelocene, for example in its e.s.r. spectrum and its electrochemical behaviour.[258] A 'polydecker' sandwich compound has ben prepared for the first time, by thermal condensation of a parent dinickel species, (<u>51</u>). It is thermally very stable, but oxygen sensitive.[259]

Multinuclear n.m.r. (^1H, ^{11}B, ^{13}C, ^{29}Si and ^{119}Sn) spectra gave evidence for hindered rotation about the N-acyl bond in (<u>52</u>),



(51)



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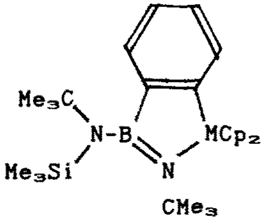
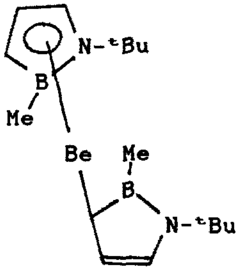
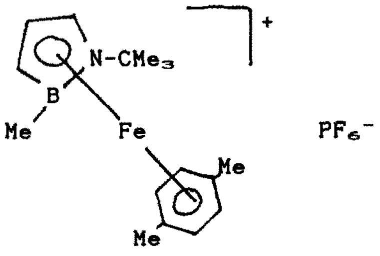


(53)

where E = Si or Sn.[260] The aminoiminoborane $^tBu(Me_3Si)N$-B≡N-^tBu reacts with thermally generated aryne species $Cp_2M(C_6H_4)$ to give (53). For M = Ti, X-ray diffraction showed that the BC_2TiN ring is planar.[261] (1-t-Butyldihydro-2-methyl-1*H*-azaborolyl)lithium (AbLi) reacts with $BeCl_2$ to form Ab_2Be, a beryllocene analogue. The crystal structure shows that this contains one η^5- and one η^1-ligand, (54).[262] The p-xylene ligand in (55) can be readily

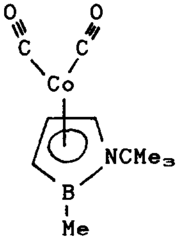




(54)

(55)

substituted by 3 phosphine or phosphite ligands.[263] 1-*Tert*-butyl-2,5-dihydro-2-methyl-1*H*-1,2-azaborole and $Co_2(CO)_8$ react in petroleum ether solvent at 60-80°C to produce a 40% yield of (56). This undergoes photolysis in the presence of 1,5-cyclo-octa-diene to (57).[264]



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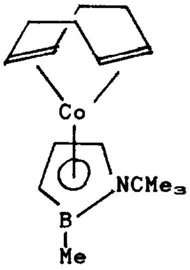

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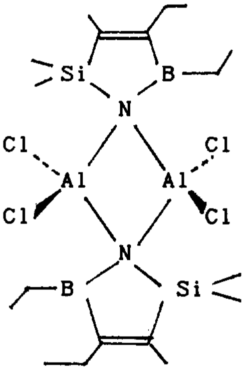

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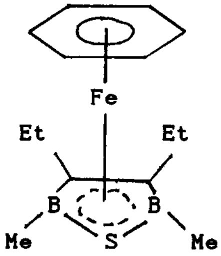

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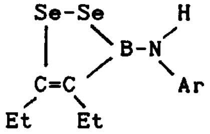
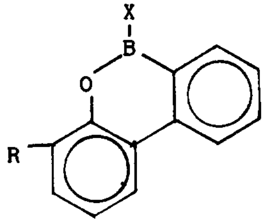


(60)

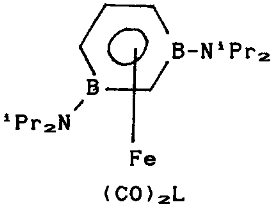
Preparations have been reported for a large number of BNSi-containing compounds, including (58).[265] Bis(arene)iron, where Arene = p-xylene, benzene or 1,4-difluorobenzene, react (in the range -100 to -60°C) with 3,4-diethyl-2,5-dihydro-2,5-dimethyl-1,2,5-thiadiborole, to give, for example, (59). Reactions, spectroscopic data and crystal structure were reported for the benzene compound.[266]

(<u>60</u>), where Ar = 2,6-$Me_2C_6H_3$, forms monoclinic crystals, space group C2/c. ^{1}H, ^{11}B, ^{13}C, ^{14}N and ^{77}Se n.m.r. data were also reported.[267] 2'-Hydroxy-*m*-terphenyl or 2-hydroxybiphenyl react with ^{n}BuLi or Na, followed by BX_3, to give (<u>61</u>), where R = Ph or H, X = Cl or Br. Preparations were also given for a number of related systems.[268]

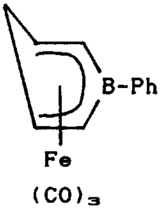
The first complexes with a 1,3-diborabenzene skeleton have been described, (<u>62</u>), where L = CO or PMe_3.[269] A number of transition metal π-complexes have been prepared from phenylbora-2,5-cyclohexanone, e.g. (<u>63</u>). In (<u>64</u>) there is evidence for strong metal-boron interactions.[270]



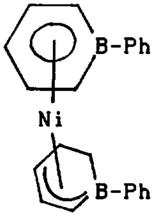
(<u>61</u>)



(<u>62</u>)



(<u>63</u>)



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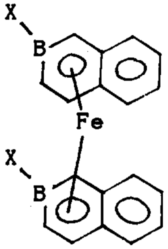

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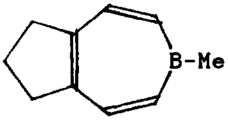
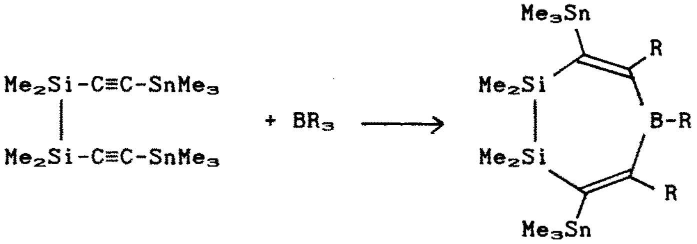


(<u>66</u>)

Lithium-2-boratanaphthalenes, Li(XBC_9H_7), where X = Ph or $N^{i}Pr_2$, and $FeBr_2$ form crystalline metal derivatives, (<u>65</u>). In this and related systems, the metal is η^6-bonded to the boron-containing moiety of the naphthalene-type skeleton.[271] The neutral boron analogue of tropylium, (66), has been prepared. N.m.r. data were consistent with a substantial ring current, and/or electron donation from C to B. The u.v. spectrum shows that the boron atom is extensively conjugated to the hexatriene moiety.[272]

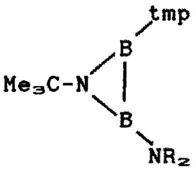
The new 1,1,2,2-tetramethyl-3,7-bis(trimethylstannyl)-4,5,6-trialkyl-1,2-dihydro-1,2,5-disilaborepins, were prepared by (4),



.....(4)

where R = Me, Et or ^{i}Pr.[273]

Dehalogenation of diborylamines $Me_3CN(BXNR_2)_2$, where X = Cl or Br, gives the three-membered B_2N compounds (67), where NR_2 = $N(CHMe_2)_2$ or tmp; tmp = tetramethylpiperidino. N.m.r. data suggest that there is no restricted rotation about the exocyclic B-N bond. The cyclic B-N bond distances were found to be 146.3(2) and 141.1(2)pm, and the B-B distance 161.0(3)pm, i.e. very short for a diborane derivative.[274] The lithium salt of N,N'-bis(t-butyldimethylsilylhydrazine) reacts with $Me_3SiNRBF_2$, where R = CMe_3 or $SiMe_3$, to form *N,N'*-bis(silyl)-*N*-fluoroboryl-hydrazines. These then react with ^{t}BuLi, giving three-membered diazaboracyclopropanes, (68), where R = CMe_3 or $SiMe_3$.[275] Diazadiboretidines, (69), where R = Me, Et, $CHMe_2$, Ph or Cl, are obtained from the reaction of RBX_2, where X = Cl or Br and diazadistannetidine, $[Me_2Sn-N^tBu]_2$. The product with R = Me dimerises, but those with R = Et, $CHMe_2$ or Ph do not. The compound with R = Cl is metastable



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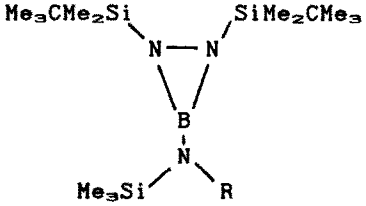

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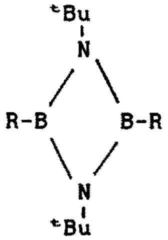
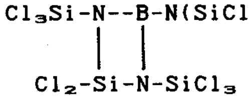


(69)

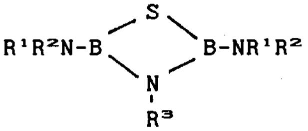
at -20°C, but it dimerises irreversibly at 20°C.[276]

Several new compounds have been prepared which contain BNSi units, including the four-membered ring compound (70).[277] 3,5-Bis(diamino)1,2,4,3,5-dithiazadiborolidines react with sodium with ring contraction and the formation of the 1,3,2,4-thiazadiboretidines (71), where $R^1 = R^2 = {}^iPr$, R^3 = Me or Ph; $R^1 = R^2 = SiMe_3$, R^3 =Me; $R^1 = R^2$ = Et, R^3 = Ph.[278] Borazines and pyrazole (Hpz) give R(pz)B(μ-pz)(μ-NHR')BR(pz), containing a central B_2N_3 ring system, (72), where R = Et or Ph, R' = H or Me. There was evidence for the existence of conformational isomers of these, but they could not be isolated.[279]



$$\begin{array}{l} Cl_3Si-N--B-N(SiCl_3)_2 \\ \qquad\ \ | \quad\ \ | \\ \ \ Cl_2-Si-N-SiCl_3 \end{array}$$

(70)



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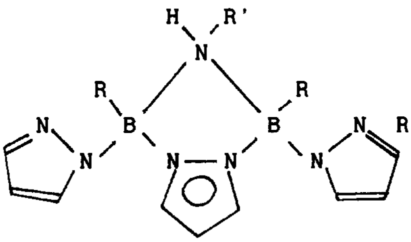

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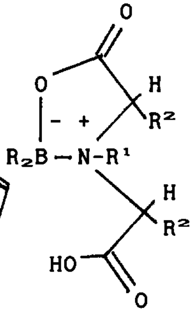

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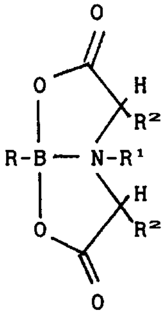
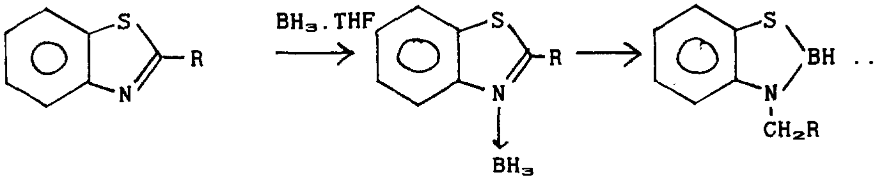


(74)

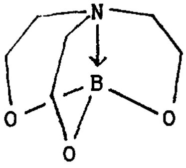
BR_3, where R = Et or Ph, react with α-aminodiacids, $R^1N(CHR^2COOH)_2$, where R^1 = H, Me or $PhCH_2$; R^2 = H, Me, to form both mono- and bicyclic compounds, (73) and (74).[280] (73), where R = Et, R^2 = H, react with H_2O, MeOH or $^iPrNH_2$ to produce aminodiacids and tricoordinated boron compounds.[281]

The He(I) photoelectron spectra of a series of boratrans based on (75) were measured and assigned using the results of *ab initio* m.o. calculations (with minimum basis sets).[282] BH_3.THF reacts with a variety of heterocyclic reagents with ring opening and the formation of new borolidine heterocycles, *via* borane adducts, i.e. reaction (5), where R = H, Me or Ph. The products were



...(5)

characterised by ^{11}B n.m.r. spectra.[283] The considerable stability of (76) was ascribed to coordinative interaction between S and B.[284]



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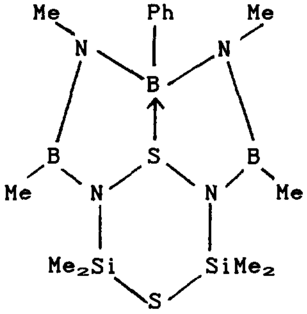

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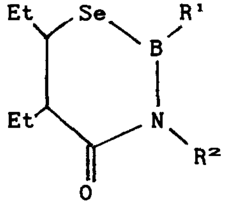

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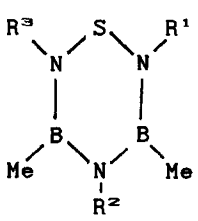

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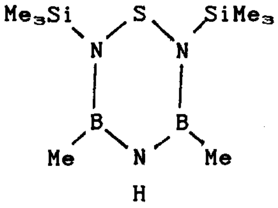

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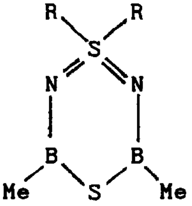
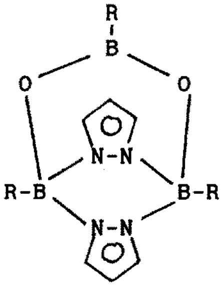


(80)

3-Alkyl-1,2,3-diselenaboroles and *n*- or *i*-alkyl isocyanates react to form 2,3-dihydro-4*H*-1,3,2-selenaza-borin-4-ones, (77), where R^1 = Me, R^2 = Me, Et, ^{n}Pr, ^{i}Pr or ^{n}Bu; R^1 = ^{n}Bu, R^2 = Me. These react with elemental sulphur to give the sulphur analogues.[285] 3,5-Dimethyl-1,2,4,3,5-dithiazadiborolidines and sulphur di-imides form (78), where R^1 = ^{t}Bu, R^2 = Ph, R^3 = $SiMe_3$; R^1 = R^3 = $SiMe_3$, R^2 = Ph or ^{n}Bu. A variety of other new boron-containing heterocycles were also described.[286] Ammonolysis of

3,5-dimethyl-2,6-bistrimethylsilyl-1,4-dithia-2,6-diaza-3,5-diborinane yields (79). This in turn reacts with $W(CO)_5(THF)$ to form an $S-W(CO)_5$ complex.[287] *S*,*S*-Dialkyl-*N*,*N*'-bis(trimethylsilyl)sulphodi-imides and 1,2,4,3,5-trithiadiborolanes react with splitting of the Si-N bond and formation of $1\lambda^6$,4,2,6,3,5-dithiadiazadiborines, (80), where R = Me, Et or ^{i}Pr. A number of related BNS cyclic systems were produced from these.[288]

Tri-B-organylboroxins, $(-BR-O-)_3$ and pyrazole (Hpz) produce pyrazaboles in which the two boron atoms are also bridged by an -O-BR-O- link, (81), where R = Et or Ph. These metal species are structurally related to diboracations of the type $[RB(\mu\text{-pz})_3BR]^+$.[289] BH_3.THF and methylamine give mixtures of eee and eea isomers of 1,3,5-trimethylcycloborazane, $[MeN(H)BH_2]_3$. The isomers were separated by fractional crystallisation, and their crystal structures determined.[290] Preparations were reported for (82), where X = Cl, OMe, $OCMe_3$ or CMe_3, from $MeON(SiMe_3)_2$ and Cl_2BX, where X = Cl or OMe. These with $NaOCMe_3$ or $LiCMe_3$ gave the remaining derivatives. $PhBCl_2$ and $MeON(SiMe_3)_2$ gave (83).[291]



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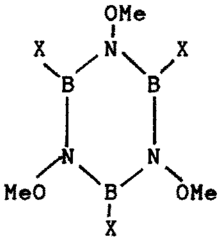

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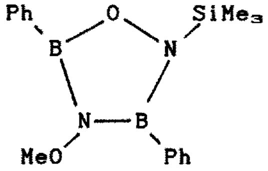
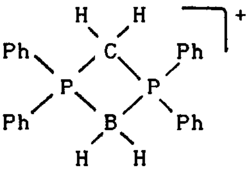


(83)

The nature of the electronic excitation and π-electron interaction in $B_3N_3H_6$ were studied by comparing its spectra with those of benzene and cyclohexane. The data were consistent with a planar D_{3h} structure, with electron π-delocalisation very similar to that in benzene.[292] Polycyclic borazines were readily obtained *via* interaction of a tris(dialkylamino)borane with a diamine or amine alcohol.[293] The 8-membered ring molecule $Ph_2P\text{-}NPh\text{-}BH_2\text{-}NPh\text{-}PPh_2\text{-}NPh\text{-}BH_2\text{-}NPh$ was synthesised by reacting $PhNHPPh_2{=}NPh$ and $Me_2S.BH_3$. A side product was $PhNH\text{-}PPh_2\text{-}BH_3$. Both were characterised by ^1H, ^{31}P and ^{11}B n.m.r. and i.r. spectra.

[294]

BH_3 and BH_2I adducts of $Ph_2PCH_2PPh_2$ were prepared, i.e. $Ph_2PCH_2PPh_2.BH_3$ and $[(Ph_2P)_2CH_2BH_2]^+I^-$. It was suggested that the latter cation is (84).[295] Dehydrohalogenation of chloro[(1,1-diethylpropyl)phosphino](2,2,6,6-tetramethylpiperidino)borane gave the diphosphadiboretane dimer, (85). The B-P bond lengths are 191.6 and 193.3pm, suggesting a weak B-P interaction.[296] $(Tmp)BCl_2$ and $ArP(SiMe_3)Li$, where tmp = 2,2,6,6-tetramethylpiperidino, Ar = $2,4,6\text{-}{}^tBu_3C_6H_2$, give $[(tmp)BPAr]_2$, containing a strained B_2P_2 4-membered ring. Thermolysis of this dimer gave the boraphosphene (tmp)B=PAr in the vapour phase (characterised by its mass spectrum).[297] The species (86), where E = P or As, R = mesityl, R' = 2,2,6,6- tetramethylpiperidino, have been prepared. The crystal structure was determined for E = P.[298]



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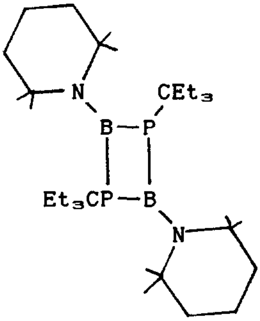

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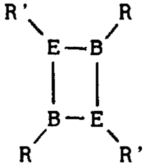
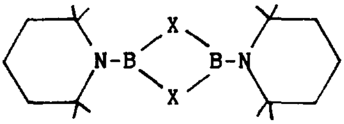


(86)

X-ray crystal structures of (87), where X = O, S or Se, show that all three contain planar 4-membered rings. The Group 6 atom has no marked influence on the BN bond length.[299] New β-keto-amine complexes of boron have been prepared and characterised, (88), where R, R' and R" = a variety of alkyl groups.[300]



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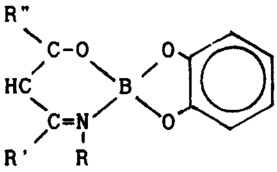
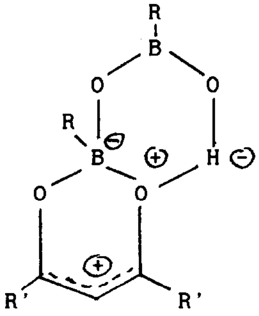
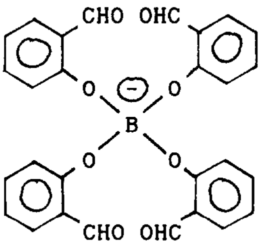


(88)

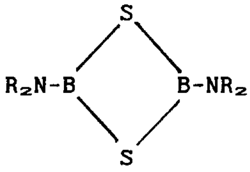
The trialkylboroxines $(RBO)_3$, where R = Me or Et, react with the enolisable 1,3-diketones $(R'CO)_2CH_2$, where R' = Me or Ph, to form (<u>89</u>). The bicyclic structures in the solid phase are in equilibrium in solution with partially ring-opened compounds.[301] Syntheses have been reported for a number of new spiroborate species with 5-, 6- and 7-membered rings, e.g. (<u>90</u>) [302]



(<u>89</u>)



(<u>90</u>)



(<u>91</u>)

Thermal decomposition of µ-(aminoborondithiolato)bis(tricarbonyliron) compounds gave (<u>91</u>), where NR_2 = NMe_2, N^iPr_2 or tetramethylpiperidino. $(Me_2NBS)_2$ reacts in solution to form the trimer $(Me_2NBS)_3$.[303] The 6-membered ring systems of 2,3-dihydro-1,4,2,3-dithiadiborine, 1,4,2,3-dithiaborinane and 2,3-dihydro-1,4,2,3- benzodithiaborinane derivatives undergo ready isomerisation, in which the $\overline{\text{S-C-C-S-B-B}}$ skeleton rearranges to a 5-membered ring unit $\overline{\text{S-C-C-S-B}}\text{-B}$.[304]

3.1.10 <u>Metal Borides</u>

Laser-sputtering from solid boron produced B_2 molecules, which were trapped in neon or argon matrices. The ground state was shown to be $^{3}\Sigma^{-}_{g}$. E.s.r parameters were in good agreement with *ab initio* C.I. calculations.[305]

Electronic structures were calculated for borides MB_2, with the AlB_2 structure. The interaction of transition metal orbitals with those of a planar, graphite-like net of boron atoms, and those of other metals were both important in influencing the properties of such species. In ReB_2 and RuB_2, puckering of the boron-atom networks is due to metal-metal repulsions. In AlB_2 itself, the strongest interactions are between the boron atoms, which thereby attain a graphite-like electron count and associated stability.[306] Chemical vapour transport of TiB_2, using halides as transport agents, in silica tubes was shown to involve significant interaction of TiB_2 with the silica.[307] Mg_2IrB_{2-x} has a homogeneity range $0.2 \leqslant x \leqslant 0.35$. It forms monoclinic crystals, space group C2/m. The boron atoms are partially disordered.[308]

The borides $Ca_2Os_3B_5$ and $Eu_2Os_3B_5$ are isotypic, and they crystallise in the monoclinic space group C2. Both were prepared by the reaction of the elements in sealed tantalum tubes.[309] The body-centred tetragonal (space group $I4_1/acd$) crystals of $ErRh_4B_4$ contain B_4 tetrahedra.[310] $Sc(Sc_6I_{12}B)$ is prepared by heating Sc, ScI_3 and B at 850°C for 2 weeks - it was characterised by X-ray powder diffraction.[311] A critical review of data on the homogeneity range of LaB_6 shows that <2000K there is less than 2% variation in the B/La ratio. Above 2000K, however, the homogeneity range is much wider.[312]

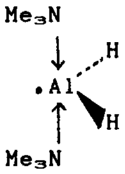
3.2 ALUMINIUM

3.2.1 Aluminium Hydrides

Spectral analysis of the light emitted after impact of Al^+ (^1S, ^3P) on H_2 molecules showed that an AlH^+ species was present in both $\underline{A}^2\Pi$ and $\underline{B}^2\Sigma^+$ states.[313] E.s.r. spectra previously assigned to AlH^+ have now been shown to be due to the radical AlH(OH). AlH^+ and AlD^+, however, have been generated and characterised by e.s.r.[314]

The e.s.r. spectrum of the radical $(Me_3N)_2AlH_2^{\cdot}$ is consistent with a quasi-trigonal bipyramidal structure. (**92**).[315] *Ab initio* m.o. calculations on the formyl complexes H_2MCHO, where M = B or

Al, have been carried out. The aluminium complex is calculated to favour η^2 (i.e. bridged) coordination. with largely ionic metal-formyl interactions.[316] The ^{27}Al n.m.r spectra of $AlH_{4-n}(OR)_n^-$, where R = Me, Et, ^iPr, ^tBu, n-C_5H_{11}, n-C_9H_{19}, *cyclo*-C_6H_{11}, Ph or $MeOCH_2CH_2$, as their $^tBu_4N^+$ salts in benzene, show distinct hydrogen-splitting, consistent with the presence of n = 0-4. The aluminium chemical shifts and Al-H coupling constants were measured for each case.[317]



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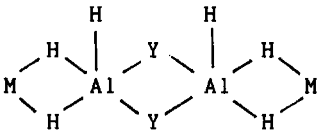


(93)

Several tungsten and rhenium aluminopolyhydrides have been reported, containing (93), with M = W or Re; Y = H or ^nBu cores. The crystal structure was determined for $(Me_3P)_3H_3W(\mu\text{-}H)_2Al(H)(\mu\text{-}O^nBu)_2Al(H)(\mu\text{-}H)_2WH_3(PMe_3)_3$, confirming this.[318] The Ru(II) and Os(II) complexes $L_3HM(\mu\text{-}H)_2AlH(\mu\text{-}H)_2AlH(\mu\text{-}H)_2MHL_3$, where M = Ru or Os, L = various phosphines, have been characterised by ^{1}H, ^{31}P and ^{27}Al n.m.r. spectra.[319] The aluminohydride complexes $[(dmpe)_2HCr(\mu\text{-}H)_2Al(H)(\mu\text{-}H)]_2$, where dmpe = $Ph_2PCH_2CH_2PPh_2$, $[(Me_3P)_4HM(\mu\text{-}H)_2Al(H)(\mu\text{-}H)]_2$, where M = Mo or W, and $[(Me_3P)_4ClW(\mu\text{-}H)_2Al(H)(\mu\text{-}H)]_2$ were all shown to be non-rigid molecules.[320] Cp^*_2TiCl and $LiAlH_4$ react to give $\{[Cp^*(C_5Me_4\overline{CH_2)TiH_2Al}]_2O\}_2.2C_6H_6$. The Ti-Al linkage is accomplished *via* a double hydrogen bridge and the $\eta^5C_5Me_4CH_2$ methylene group of the ring.[321]

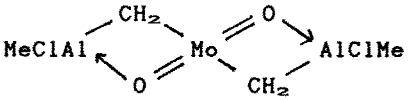
The reaction between GeH_4 and $LiAlH_4$ in ethereal solvents produces $LiGeH_3AlH_3$ and H_2. The $GeH_3AlH_3^-$ decomposes rapidly on removing the solvent, but it was characterised by i.r. and ^{1}H n.m.r. spectra.[322] Reactions in the LiOH-$LiAlH_4$ system were followed by DTA.[323]

$Zr(BH_4)_4$ and AlH_3 in diethyl ether form $Zr(AlH_4)_3BH_4$ and $Zr(BH_4)_4.AlH_3$, solvated by Et_2O.[324] Cp_3UAlH_4 is believed to have a polymeric structure, with trigonal planar Cp_3U units linked by bridging bidentate AlH_4 groups.[325]

3.2.2 Compounds containing Al-C or Al-Si Bonds

Aluminium atoms and CO in adamantane at 77K form $Al(CO)_2$, with $\nu_s(CO)$ at 1985, $\nu_{as}(CO)$ at 1904 cm^{-1}. There was also i.r. evidence for Al_2CO and $Al_2(CO)_4$ in this system.[326] Methyl iodide and aluminium powder, when subjected to ultrasound, form $Me_3Al_2I_3$. This gives a good yield of reasonably pure trimethylaluminium on treating with triethylaluminium.[327] $AlMe_2^+$ can be stabilised by [18]crown-6 or [15]crown-5 in $[AlMe_2.crown][AlMe_2Cl_2]$.[328] The i.r. spectra of monomeric Me_2AlCl and $MeAlCl_2$ were observed in argon matrices. The Al-Cl bond strengthens with increasing alkyl content. Several chlorine-bridged dimers, $Me_{6-n}Al_2Cl_n$, where n = 2-6, were also identified.[329]

$(PhCH_2)_3Al.OEt_2$ forms monoclinic crystals, space group $P2_1$. The average Al-C distances are 198.6pm, with an Al-O distance of 190.1(4)pm, i.e. the latter is shorter than usual.[330] The reaction between MoO_2Cl_2 and $AlMe_3$/THF gives (<u>94</u>) - this bis(methylene) complex is thermally labile, giving oligomeric species.[331]

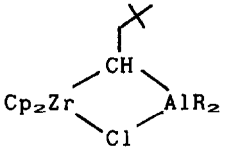


(<u>94</u>)

Ultrasound treatment of ethyl bromide in the presence of aluminium and magnesium powders forms $Et_3Al_2Br_3$. Subsequent addition of diethyl ether gives a good yield of $Et_2O.AlEt_3$, as a one-pot synthesis.[332] Al_2Et_6 reacts with a variety of tetradentate Schiff-base ligands, forming ethane and the corresponding AlEt(L), where L = Schiff-base ligand. The latter are stable in the absence of water and HCl. The susceptibility to attack by water depends strongly on the flexibility of the ligand.[333] Triethylaluminium and water, in a 2:1 molar ratio, form a mixture of ethyl-oligoaluminoxanes, tetraethyldialuminoxane trimer, $[(Et_2Al)_2O]_3$, and triethylaluminium. The trimer was isolated using gel permeation chromatography.[334]

The reaction of aluminium atoms and ethene to produce aluminocyclopentane is believed to involve a concerted process, with two ethene molecules reacting simultaneously with the aluminium atom.[335] The ^{27}Al n.m.r. chemical shifts of $[Et_2AlOCH_2CR_2X]_2$, where R = H; X = OMe or NEt_2; or CR_2X = $2-H_4C_5N$, show no temperature dependence in the range 223 - 310K. There is thus no evidence for equilibrium between 4- and 5-coordinate aluminium.[336] Variable-temperature ^{13}C n.m.r. studies and ^1H and ^{27}Al n.m.r spectra for $Na[Al_2Et_6F]$ + Al_2Et_6 mixtures gave evidence for facile exchange of $AlEt_3$ between the two. ΔH for the exchange process is very similar to that for Al-F bond dissociation in the anion $Et_3Al-F-AlEt_3^-$.[337]

(95), where R = Me or ^{i}Bu, have been characterised. The crystal structure for the species with R = ^{i}Bu confirms the cyclic structure.[338] The reactions of $C_5H_{11}CH(Al^iBu_2)_2$ with Et_2NH, N-methylaniline, methanol etc. lead to selective cleavage of both Al-^{i}butyl and/or Al-C-Al bridge bonds.[339] Organo-aluminium compounds derived from $RC{\equiv}CCH_2Br$ react with acetals to give only α-allenic ethers.[340]



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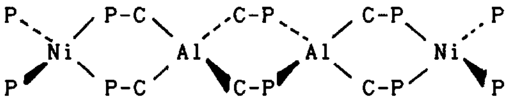


(96)

$[(Me_3P)_2Ni(Me_2PCH_2)_2Al(CH_2PMe_2)]_2$ is a trispirocyclic compound containing the skeleton (96).[341] Aluminium and dimesitylmercury react to form trimesitylaluminium. The molecule is monomeric, with the expected Al-C distances. The ^1H, ^{13}C and ^{27}Al n.m.r. data were reported.[342]

The $Al_2Si_2^{2-}$ two-dimensional networks in the $CaAl_2Si_2$ structure can be derived from the wurtzite lattice. There are two four-coordinate sites, one regular tetrahedral, the other highly distorted.[343]

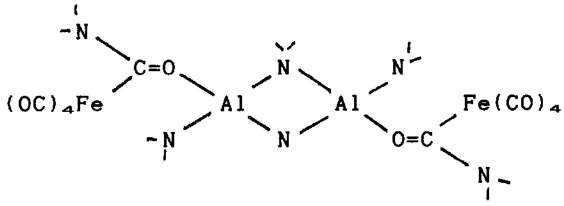
3.2.3 Compounds containing Al-N or Al-P Bonds

Raman and i.r. spectra of molten $AlCl_3.NH_3$, $AlCl_3.ND_3$ and $AlBr_3.NH_3$ have been obtained. There was some evidence for dissociation, e.g. (6), with K approximately 3 X 10-3 (mole

$$2AlCl_3.NH_3 \rightarrow AlCl_4^- \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

fraction basis). The molecule $Al_2Cl_6.NH_3$ appears to be present in binary $AlCl_3$-$AlCl_3.NH_3$ melts.[344] Vapour-phase i.r. spectra were obtained for $AlBr_3.NH_3$ and $GaBr_3$. All i.r.-active modes of the former were assigned except for the symmetric NH_3 stretch and the $AlBr_3$ rock. For $GaBr_3$, all monomer and dimer i.r.-active fundamentals were assigned except for the dimer ring puckering. The monomer data were consistent with D_{3h} planar geometry.[345]

$[Al(NMe_3)_2]_2$ and $Fe(CO)_5$ or $Mn_2(CO)_{10}$ give bimetallic compounds, $Fe_2(CO)_8[C(NMe_2)OAl(NMe_2)_2]_2$, (<u>97</u>), or $Mn_2(CO)_8[C(NMe_2)OAl_2(NMe_2)_5]$.[346]

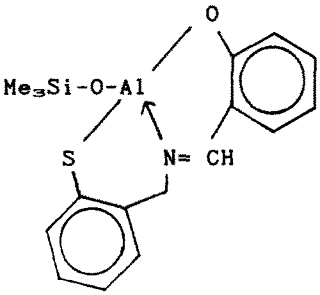


(<u>97</u>)

Trimethylaluminium and 1,4,8,11-tetrazacyclotetradecane form $(Me_3Al)_2[C_{10}H_{20}N_4](AlMe_3)_2$. The central cavity of the macrocycle is occupied by an $\overline{\text{Al-N-Al-N}}$ four-membered ring. The Al...Al distance shows that there is no significant interaction between the Al atoms.[347] Triorganoaluminium compounds react with stoichiometric quantities of α-iminoketones to form, for example, $(AlMe_3)_2\{\sigma,\sigma\text{-N,O-}(R^1N{=}C(R^2)C(R^3){=}O\}$. The crystal structure was determined for R^1 = Me, R^2 = R^3 = Ph. In many cases, however, this adduct underwent rapid conversion to stable ketone-alkylated products, such as $Me_2\overline{Al(R^1)N\text{-}C(R^2)C(R^3,Me)O}AlMe_3$.[348]

A number of azomethine derivatives of aluminium, containing Al-$OSiMe_3$ groups, have been made - they are resistant to hydrolysis, e.g. (<u>98</u>).[349] Mixtures of aluminium and gallium oxinates were analysed using synchronous derivative fluorimetry.[350] ^{27}Al n.m.r data for $M(oxine)_3$, where M = Al, Ga, In or Tl, oxine = 8-hydroxyquinolinate, were reported and discussed.[351] Raman spectra were obtained for films (200 nm thick) of (Pc)MCl, where M = Al, Ga or In; Pc = phthalocyaninato.[352]

$MeCuPCy_3$ reacts with $AlMe_3$ etc., resulting in ligand exchange between Cu and Al, and the formation of the adduct $Me_3Al.PCy_3$,



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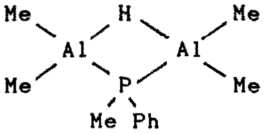


(99)

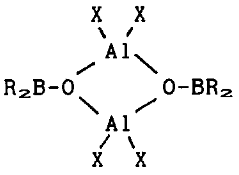
before final decomposition.[353] Me_2AlH and PMePhH interact with the formation of "$Me_2AlPMePh$". In benzene solution this is a trimer, as a mixture of possible isomers. The removal of benzene gave a polymeric material. There was also evidence for (99).[354] Electron diffraction was used to determine the molecular structure of $(Me_2AlPMe_2)_3$. A chair model, of C_{3v} symmetry, fitted the data, and gave a reasonable set of geometrical parameters.[355]

3.2.4 Compounds containing Al-O or Al-S Bonds

Ion-beam studies on the process $Al^+ + O_2 \rightarrow AlO^+ + O$ suggest that $IP(AlO) \leqslant 9.75 \pm 0.13eV$; $D_o{}^o(AlO) \geqslant 1.50 \pm 0.12eV$.[356] *Ab initio* calculations on Al_2O, with allowance for electron correlation, suggest a singlet ground state, with an excited triplet state, about 50 kcal. mol^{-1} higher in energy. The deformational potential surface close to the minimum is very flat.[357] The thermal dissociation of AlOCl has been studied in the range 293-1173K by TGA, X-ray diffraction, chemical analysis and mass spectrometry.[358]

Ab initio calculations on the stability, equilibrium geometry, force constants, vibrational wavenumbers etc. have been reported for Al_2O_3. The molecule has a linear $(D\ _h)$ structure, O=Al-O-Al=O. The bipyramidal structure (D_{3h}) is unstable to unimolecular decomposition, to $Al_2O + O_2$.[359] M.o. calculations on the dioxygen ligand in $[Al_2Me_6(\mu-O_2)]^-$ suggest that the ligand has properties close to those of a gaseous $O_2{}^-$ species. The electronic mechanism for the bonding of O_2 to Al is markedly different from that for O_2-transition metal species.[360]

Tetra-organodiboroxanes, R_2BOBR_2, where R = Et, R_2 = 1,5-cyclo-octanediyl, and AlX_3, where X = Cl or Br, react with elimination of R_2BX to give (100). The structures were based on ^1H, ^{11}B, ^{13}C,



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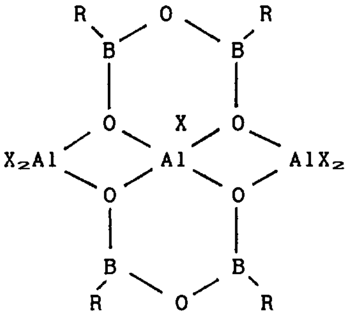


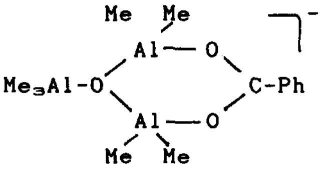
(101)

and ^{27}Al n.m.r. data.[361] Four moles of $(RBO)_3$, where R = Me, Et, Bu or Ph, and 6 moles of AlX_3, where X = Cl or Br, react to give high yields of (101). The structure was confirmed by X-ray diffraction studies for R = Ph, X = Cl.[362]

Equilibria were studied in the system $Al^{3+}-CO_2(g)-OH^-$, using e.m.f. measurements. There was evidence for $AlOH^{2+}$, $Al_3(OH)_4^{5+}$ and $Al_{13}O_4(OH)_{24}^{7+}$, as well as $Al_2(OH)_2CO_3^{2+}$ and $Al_3(OH)_4HCO_3^{4+}$.[363] Potentiometric measurements were used to study equilibria in the Al(III)-OH^--lactic acid system.[364] Aluminium hydroxide equilibria under physiological conditions (37°C, 0.15 molar aqueous NaCl) show that the following are present: $AlOH^{2+}$, $Al(OH)_3$, $[Al(OH)_4]^-$, $[Al_3(OH)_{11}]^{2-}$, $[Al_6(OH)_{15}]^{3+}$ and $[Al_8(OH)_{22}]^{2+}$.[365] ^{27}Al chemical shifts have been determined from n.m.r. spectra of $Al(OH_2)_6^{3+}$, $Al_2(OH_2)_5^{2+}$ and $AlO_4Al_{12}(OH)_{24}(OH_2)_{12}^{7+}$.[366]

Polarised i.r. reflection spectra have been obtained from single crystals of $AlCl_3.6H_2O$. The results were discussed in terms of hydrogen bonds, Al-H_2O interaction and the orientation of the H_2O molecules in the lattice.[367] ^{27}Al, H, D and ^{17}O nuclear magnetic relaxation studies were used to characterise aqueous $AlCl_3$ solutions. It was found that increasing concentration leads to destruction of order within the $Al(H_2O)_6^{3+}$ complex.[368] There is evidence from Raman spectra for Al^{3+}-DMSO interactions in Al^{3+}-DMSO-H_2O systems, even at high water concentrations.[369] ^1H n.m.r. spectra for hydrolysed Al(III) perchlorate solutions in $(CD_3)_2C{=}O$ were used to distinguish bound H_2O and OH entities. It was also possible to determine the number of protons around a given aluminium atom, and so potentially provide structural data on the polymeric species present.[370]

CO_2 is trapped by (TPP)Al(OAc) in the presence of a secondary amine, forming an aluminium carbamate on the opposite side to the acetate group (with respect to the porphyrin plane).[371] Several $[Al(OR)_2(\beta\text{-diketonate})]_n$, where OR = alkoxide or siloxide, and $[Al(OR)(\beta\text{-diketonate})_2]_2$ complexes have been prepared and characterised. The dimers contain octahedral aluminium centres bridged by alkoxides.[372] $[PhCOO(AlMe_3)_2OAlMe_3]^-$ has the cyclic structure (102).[373] $AlCl_3$ and tetramethylurea form the adduct (103), whose structure was confirmed by X-ray diffraction. The solution in tetramethylurea contained $\{Cl_2Al[OC(NMe_2)_2]_2\}^+$ $AlCl_4^-$.[374]



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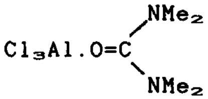
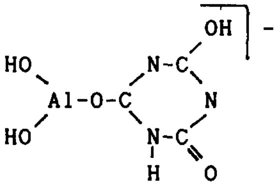


$Cl_3Al.O{=}C(NMe_2)_2$

(103)



(104)

Several aluminium(III) complex cyanurate salts have been prepared, e.g. $[Al(OH)_2(HC_3N_3O_3)]^-$, characterised by i.r. spectra and thermal analysis as (104).[375] Kinetic studies on ligand isotopic (^{14}C) exchange for $Al(acac)_3$ in Hacac are consistent with an interchange mechanism involving an intermediate containing both a unidentate $acac^-$ and an Hacac molecule or a water molecule.[376] N.m.r. and vapour-phase osmometry show that bis(acetylacetonato)-(2-hydroxyphenolato)aluminium in solution exists as 3 geometrical isomers of the dimer in equilibrium. At high concentrations, there was evidence for monomer, trimers and/or polymers.[377] The kinetics of complex formation of Al(III), Ga(III) or In(III) with 4-isopropyltropolone (Hipt) in Me_2SO solution is consistent with

$$M^{3+} + \text{Hipt} \overset{K_{as}}{\rightleftharpoons} M^{3+}\ldots\text{Hipt} \overset{k^*}{\rightleftharpoons} M(\text{ipt})^{2+} + H^+ \quad \ldots..(7)$$

the sequence (7).[378]

Phase transitions in different forms of Al_2O_3, formed during the thermal decomposition of $Al(NO_3)_3$, were studied in the temperature range 100 - 1000°C. The appearance of the polymorphic forms γ- and α-Al_2O_3 was demonstrated for the first time, by X-ray optical analysis and X-ray diffraction.[379] Solid-state ^{27}Al n.m.r. spectra of polycrystalline aluminates and aluminate hydrates containing various types of condensed AlO_4 tetrahedra, show that these tetrahedra give very similar ^{27}Al chemical shifts. They vary, however, in the electric field gradient tensor at the aluminium.[380] There was ^{27}Al n.m.r. evidence for the formation of $Al_{13}O_{40}$ cations on dilution of concentrated, highly-basic aluminium chloride solutions.[381] ^{27}Al n.m.r. spectra have been obtained for polycrystalline calcium aluminates with various CaO/ Al_2O_3 ratios. Structural effects were shown more clearly in quadrupole coupling than in chemical shift data.[382]

$K_2O.Al_2O_3.nH_2O$, where n = 3, 2 or 1, were found in the system K_2O-Al_2O_3-H_2O. The trihydrates contain dimeric anions, with tetrahedrally-coordinated Al^{3+}. The others have more complicated anions, derived from AlO_4 units.[383] Double basic salts of aluminium and lithium were synthesised by reaction of crystalline $Al(OH)_3$ and solutions of LiX, where X = Cl, Br or I, or Li_2SO_4.[384]

MAS-^{27}Al n.m.r. spectra were used to establish the modes of aluminium coordination in aluminoborate glasses in the system Li_2O -Al_2O_3-B_2O_3.[385] Phase relationships were established in the systems $BaAl_2O_4$-$BaGa_2O_4$;[386] and $Sr_3Al_2O_6$-$Sr_3Ga_2O_6$.[387]

The numbers of framework and non-framework aluminiums were determined by X-ray photo-electron spectroscopy for HY dealuminated zeolites.[388] High-temperature X-ray phase analysis shows that zeolite Li-A decomposes at 220°C, at atmospheric pressure, to $Li_2O.Al_2O_3.2SiO_2.0.18H_2O$. At 470°C this in turn forms $Li_2O.Al_2O_3.2SiO_2$, a phase similar to low-temperature eucryptite.[389] The zeolite Li-A(BW), i.e. $LiAlSiO_4.H_2O$, has been prepared hydrothermally. Its crystals belong to the space group $Pna2_1$.[390]

MAS-^{27}Al n.m.r. data were recorded for a range of aluminosilicate glasses - the influence of changes in the cation was found to be quite small.[391] The high-resolution (MAS) ^{27}Al n.m.r. spectra of aluminosilicates show that the ^{27}Al chemical shifts are closely parallel to those for ^{29}Si.[392] There have been two separate reports on the ^{27}Al n.m.r. chemical shifts of penta-coordinated aluminium.[393,394]

$Na_8[AlSiO_4]_6(OH)_2$ forms cubic crystals, space group P43n. The aluminosilicate framework is completely ordered, as for the sodalite phases.[395] Mesolite, $Na_2Ce_2Al_6Si_9O_{30}.8H_2O$, has orthorhombic crystals, space group Fdd2, also with complete ordering of AlO_4/SiO_4 sites.[396] Phase relationships have been elucidated in the following systems: SiO_2-Al_2O_3-CaO-CaF_2;[397] SiO_2-Al_2O_3-CaO-ZnO and SiO_2-Al_2O_3-TiO_2-V_2O_5;[398] MgO-CaO-Al_2O_3-SiO_2;[399] and Na,K,Li || $AlSiO_4$,OH.[400]

A review has been published on aluminium orthophosphates, their formation and structures.[401] An aluminophosphate gel, from H_3PO_4 and hydrated Al_2O_3, forms, with piperidine, "$AlPO_4$-17", a microporous framework structure.[402] The aluminium phosphate hydrate $AlPO_4.1.5H_2O$ forms orthorhombic crystals, space group Pbca, and contains both AlO_4 tetrahedra and $AlO_4(OH)_2$ octahedra.[403] The ^{17}O n.m.r spectra of ^{17}O-enriched aluminophosphates ($AlPO_4$-5, -11 and -17) and gallosilicates (gallium analogues of zeolite Na-X and sodalite) have been obtained. Quadrupole coupling constants and other data were given.[404] Aluminium phosphate-isopropylamine hydrate, $7AlPO_4.2^iPrNH_2.2H_2O$, forms monoclinic crystals, space group C2/c. Two octahedral aluminium atoms are connected by 3 tetrahedral species ($2PO_4$ + AlO_4), to form a five-atom cluster, consisting of three four-membered rings. The chemical formula is best written as $Al_7P_7O_{28}(OH)_2.2^iPrNH_3$.[405]

Two sparingly soluble potassium aluminium diphosphates have been prepared, i.e. $K_2Al(OH)P_2O_7.4H_2O$ and $KAlP_2O_7.4H_2O$.[406] Several methods have been proposed for the preparation of $Na_3AlP_3O_9N$, which was then characterised by X-ray powder diffraction and ^{27}Al n.m.r. spectroscopy.[407]

Density, viscosity, pH and electrical conductivity have been measured for concentrated aqueous solutions of $Al_2(SO_4)_3$ at 25°C and 50°C. Raman and i.r. spectra were also recorded for such solutions, showing their similarity to the crystalline hydrate, $Al_2(SO_4)_3.18H_2O$.[408] The i.r. and Raman spectra of $MAl_3(SO_4)_2(OH)_6$, where M = K, Na, H_3O or NH_4. They were assigned under the centrosymetric D_{3d}^5 space group.[409] The influence of pH on the stability of $Ca_6Al_2(OH)_{12}(SO_4)_3.26H_2O$ has been studied. It was shown to be stable in the pH range 13.0 to 9.7.[410] Phase diagrams were reported for the systems: H_2SO_4-Na_2SO_4-$Al_2(SO_4)_3$;[411] $NaAl(SO4)_2$-$MAl(SO4)_2$-H_2O (M = K or Rb);[412] $Al(IO_3)_3$-$Al_2(SO_4)_3$- H_2O;[413] and M_2O_3-SeO_2-H_2O (M = Al, Ga or In).[414]

Single crystals of $Al(IO_3)_3.8H_2O$ were prepared, and its unit cell parameters determined.[415] The i.r. spectrum has been reported for $Al(IO_3)_3.8H_2O$ and its thermal dehydration products. $AlO(IO_3)$ and two crystalline forms of $Al(IO_3)_3$ (α- and β-) were obtained for the first time. The Al-OIO_2 bonds are largely ionic, but there is a greater covalent contribution in $AlO(IO_3)$, with a polymeric structure.[416]

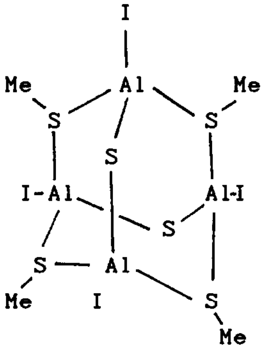
The vibrational spectrum of $LiAlTiO_4$ was assigned using $^6Li/^7Li$ and $^{46}Ti/^{50}Ti$ substitutions, in terms of the factor group D_{2h}^{16}.[417] Phase studies were given for K_2O-V_2O_5-Al_2O_3;[418] and $M(NO_3)_3$-Na_3VO_4-H_2O (M = Al, Ga or In).[419] Thermal analyses were carried out on $2M_2O_3.3V_2O_5.mH_2O$, where M = Al, Ga or In, m = 20, 16 or 14.[420] Crystalline aluminium decavanadates dissolve incongruently in water at (22 ± 1)°C, to give sparingly soluble hydroxoaluminium decavanadates.[421] The crystalline decavanadates $Al_2V_{10}O_{28}.24H_2O$, $Na_3AlV_{10}O_{28}.21H_2O$ and $K_3AlV_{10}O_{28}.13H_2O$ were isolated from aqueous-acetone solutions.[422]

I.r. spectral and thermal analysis data were reported for $Al(MO_4)_3.7H_2O$, where M = Tc or Re.[423] The phase equilibrium diagram of the system CaO-FeO-Al_2O_3-SiO_2 was determined.[424] ^{59}Co n.m.r. spectra of $LaCo_{1-x}Al_xO_3$, where $0 < x < 0.15$, solid solutions show that the presence of the Al^{3+} leads to formation of units Co^{2+}-O-Co^{4+}.[425]

Phase diagrams were determined in the systems $MHCOO$-$Al(HCOO)_3$-H_2O, where M = Na,[426] or K.[427] Al, Ga and In can be extracted from oxalate solutions by tri-*n*-octylamine (TOA), as $(TOAH)_3[M(C_2O_4)_3]$. The extraction efficiency decreases in the order Ga > In > Al.[428] A ^{27}Al n.m.r. study has been made of interactions between Al(III) and hydroxycarboxylic acids, i.e. oxalic, citric, D-tartaric, malonic, DL-malic and DL-mandelic acids.[429]

$Cl_2Al(acac)$ and dimethoxyethane (DME) react to give $[(acac)_2Al(DME)]^+(AlCl_4^-)$. ^1H and ^{27}Al n.m.r data were consistent with the presence of the complex in the *cis* form only. Dimethylformamide (DMF), on the other hand, gives $[(acac)_2Al(DMF)_2]^+(AlCl_4)^-$.[430] Aluminium tris(trifluoroacetylacetonato) was identified by X-ray diffraction. The crystals belong to the space group Pcab.[431] Syntheses have been reported for $ZrAl_2(O^iPr)_{10-x}L_x$, where L = acetylacetone, benzoylacetone, methylacetoacetate or ethylacetoacetate, x = 1, 2, 4, 6.[432] $AlZr(O^iPr)_7$ and some β-diketones or β-diketoesters form $ZrAl(O^iPr)_{7-x}L_x$, where L = acetylacetonate etc., x = 1 or 2.[433]

An excess of trimethylaluminium reacts with 1,4,8,11-tetrathiacyclotetradecane, [14]aneS_4, to form crystalline $[AlMe_3]_4$-([14]aneS_4), with 4 Al-S bonds, average length 252.2pm.[434] Me_2S_2 and $GaAlI_4$ react to give $Al_4I_4(SMe)_4S_2$. The crystal structure of this shows that it is (<u>105</u>). Aluminium compounds with such adamantane-like skeletal structures are very rare.[435]



(<u>105</u>)

3.2.5 <u>Aluminium Halides</u>

AlF^+ can be generated by photo-ionisation of gaseous AlF, produced by laser-sputtering and high-temperature vaporisation. The ground state of AlF^+ was established as $^2\Sigma$.M.o. calculations were performed on the system, and e.s.r. measurements made at high temperatures.[436] Evidence was found for mixed complexes $Al(OH)F^+$ and $Al(OH)F_2$ in weakly acidic media. In weakly basic media, $Al(OH)_4^-$ and $Al(OH)_3F^-$ are formed.[437]

The hitherto-unknown compound $Na_5AlF_2(PO_4)_2$ has been reported. PO_4 tetrahedra and AlO_4F_2 "octahedra" are linked *via* common vertices to form two-dimensionally extended heteropolyanions.[438]

The AlF_3-KCl system was found to contain the compound $AlF_3.KCl$, while $3AlF_3.2K_2SiF_6$ is formed in the system AlF_3-K_2SiF_6.[439] I.r. spectra were reported and partly assigned for a variety of fluoroaluminates, $KAlF_4$, $K_2AlF_5.H_2O$, K_3AlF_6 etc.[440] Liquidus curves were established for dissolving LiF or Li_3AlF_6 in molten Na_3AlF_6. Mole fractions were calculated for LiF, NaF, Na_3AlF_6, Na_2AlF_5 and $NaAlF_4$ in these systems.[441] $NaAlF_4$ decomposes on heating to $Na_5Al_3F_{14}$ and AlF_3 - the process is rapid in the temperature range 700 - 900K.[442] Calculations suggest that AlF_5^{2-} should be present in molten cryolite. Thermodynamic properties were calculated for Na_2AlF_5.[443]

A new complex fluoroaluminate $Na_3AlF_6.Al_2O_3.2SiO_2.6H_2O$ has been reported.[444,445] Thermolysis of K_2HAlF_6 (20-600°C) was studied by X-ray diffraction and i.r. spectroscopy. Above 50°C, loss of HF forms $KAlF_4.0.5H_2O$, which then dehydrates in two steps.[446] The fusion diagram of the 3Li,3Na,3K || AlF_6 system has been studied for the first time. Two components are potentially useful as fluxes for welding aluminium alloys.[447] Fluoride ion can be precipitated from aqueous solutions containing polymeric aluminium hydroxide as $Al_{13}(OH)_{29}F_{10}$, when r_F is near 0.7, in the pH range 4 - 7.[448]

The i.r. and Raman spectra of CsCl-$AlCl_3$ melts containing oxides showed that some complex oxyaluminium chloride species are present. It was not possible to identify these unambiguously, however.[449] Crystalline $[AlCl_2(THF)_4][AlCl_4]$ can be obtained from solutions of $AlCl_3$ in THF. The cation is octahedral, with a *trans* $AlCl_2$ unit. The average Al-Cl distance is 223.4(9)pm, i.e. longer than in *cis*-$AlCl_2(donor)_4^+$ species. The average Al-O distance is 194(1)pm.[450]

The Raman spectra of vapour mixtures MCl_4-$AlCl_3$, where M = Zr or Hf, show that the predominant species is a 1:1 complex, $MAlCl_7$,

$$ZrCl_4(g) + \tfrac{1}{2}Al_2Cl_6(g) \rightarrow ZrAlCl_7(g) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

and suggest that the enthalpy of reaction for (8) is -34.9 ± 2.5 kcal mol^{-1}.[451] Potentiometric results on CsCl/$AlCl_3$ melts in neutral and weakly acidic systems (up to $x(AlCl_3) = 0.53$) can be

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

explained by the equilibrium (9), with an equilibrium constant of $10^{-7.63}$ at 400°C.[452] Phase equilibrium studies were reported for the following systems: $AlCl_3$-pyridinium chloride;[453] $AlCl_3$-$ZnCl_2$-H_2O;[454] and $AlCl_3$-$Na_3C_3N_3O_3$-H_2O.[455] Structural implications of the presence of hydrogen-bonding in the room temperature ionic liquids based upon (MeEtim)X-AlX_3 have been discussed, where MeEtim = 1-methyl-3-ethylimidazolium, X = Cl or Br.[456]

Electrical conductivity measurements were made on the basic aluminium chlorides $AlCl_3.4Al(OH)_3.nH_2O$, where n = 3.6, 5.9, 7.5 or 11.1.[457] A study of the $AlCl_3$-$MgCl_2$ phase diagram shows the presence of two intermediate compounds, one of which is $MgAl_2Cl_8$. The FT i.r. spectra of melts, containing 0 - 30% $MgCl_2$, show the presence of Al_2Cl_6, strongly-perturbed $Al_2Cl_7^-$ and $AlCl_4^-$. The $AlCl_4^-$ can act as a bi- and a tridentate ligand towards Mg^{2+}.[458] The active species in the chlorinating system S_2Cl_2-$AlCl_3$-SO_2Cl_2 has been shown to be $SCl_3^+AlCl_4^-$.[459]

The sequence distribution has been established for the inorganic copolymer β-$(TiCl_3)(AlCl_3)_{0.33}$ - using e.s.r. and magnetic susceptibility measurements. A regular Ti-Ti-Ti-Al-Ti-Ti-Ti-Al- sequence is the only one to fit the observed data.[460] X-ray diffraction of the molten $AlCl_3$-NaCl system suggests that $AlCl_4^-$ ions are the fundamental structural units, at 50-70 mol% $AlCl_3$.[461]

Single crystals of $Cd(AlCl_4)_2$ were grown from a $CdCl_2$-$AlCl_3$ melt; they are monoclinic. The reduction of $Cd(AlCl_4)_2$ by excess Cd forms $Cd_2(AlCl_4)_2$, containing the ethane-like units Cd_2Cl_6.[462] The complex $[U_3(\mu^3\text{-}Cl)_2(\mu^2\text{-}Cl)_3(\mu^1\text{-}\eta^2\text{-}AlCl_4)_3(\eta^6\text{-}C_6Me_6)]^+AlCl_4^-$ is prepared by a modified Friedel-Crafts reaction from UCl_4, $AlCl_3$, C_6Me_6 and aluminium metal.[463] The crystal structure of $Ti(AlBr_4)_2$ has been reported.[464]

3.2.6 Other Aluminium-containing Species

Collision-induced dissociation of aluminium clusters, Al_n^+, where n = 3 - 26, by argon shows that the main product is Al^+ for smaller clusters, Al_{n-1}^+ for larger.[465]

M.o. and band structure calculations for the $BaAl_4$, $CaAl_2Zn_2$ and f.c.c. aluminium structures have been reported. The first two may be thought of as two-dimensional layers cleaved out of the f.c.c.

lattice. One way of considering the bonding involves five-centre, 6-electron fragments, closely related to the bonding in B_5H_9.[466]

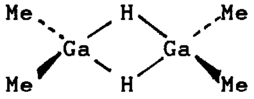
Al_7Te_{10} is prepared from a melt of the elements. The structure is a distorted defect variant of the 4H-polytype. The central unit, a double-barrelane, $[Te_4Al_4-Al_4Te_4]$, contains an Al-Al bond (260 pm) which is somewhat longer than expected for a single bond. The compound can be regarded as a Zintl-phase, $\frac{1}{2}\{[Al^{2+}-Al^{2+}]-[Al^{3+}]_{12}[Te^{2-}]_{20}\}$.[467]

Al_3Ti can be prepared from the elements; it forms tetragonal crystals, space group I4/mmm, and involves Al-Al distances of 272.5 and 288.4pm.[468] The perovskite-type ternary carbides Mn_3MC, where M = Al, Ga or In, are hydrolysed by liquid or vapour H_2O and dilute acids, most rapidly for M = Al.[469] Crystals of $Re_{14}Al_{57-x}$ are triclinic, space group P1. It has a periodic domain structure which is a variant of the monoclinic WAl_4 type.[470]

3.3 GALLIUM

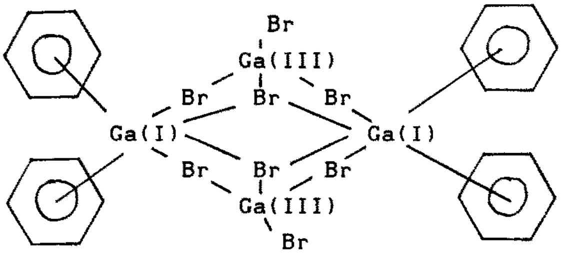
3.3.1 Compounds containing Ga-C or Ga-Si Bonds

Dimethylgallane, from $GaMe_3$ and $NaGaH_4$, has been shown to be a dimer, (106), in the vapour phase at low temperatures.[471] The chemistry of methylgallium(III) compounds in protic solvents has been examined. Aqueous perchloric acid solutions are surprisingly resistant to hydrolytic cleavage of the Ga-C bonds. In the presence of $Ga(ClO_4)_3$, however, $MeGa^{2+}(aq)$ is produced, which is more susceptible to hydrolysis.[472] The structure of glycinatodimethylgallium, $(C_2H_4NO_2)GaMe_2$, comprises discrete monomers linked by N-H...O bonds.[473]



(106)

The crystal structures of (2-dimethylaminomethyl-3-pyridolato)-dimethylgallium, $Me_2GaO(C_5H_3N)CH_2NMe_2$, and bis[8-(quinolinolato)dimethylgallium, $[Me_2GaO(C_9H_6N)]_2$, have been determined. The former contains discrete monomers, with tetrahedrally coordinated gallium. The latter comprises centrosymmetric dimers, containing an almost planar system of 7 fused rings, with 5 coordinate gallium atoms.[474] Trimesitylgallium(III) has been prepared by a Grignard reaction from MesMgBr and $GaCl_3$. The crystal structure shows that the GaC_3 unit is planar, with an average Ga-C distance of 196.8(4)pm.[475] The previously unknown $(C_5Me_5)_3Ga$ has been prepared and characterised. Possible preparations are from $GaCl_3$ and excess NaC_5Me_5 in THF solution, or from $Ga(C_5Me_5)_nCl_{3-n}$ and sodium naphthalenide in THF solution.[476]

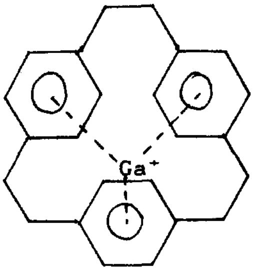


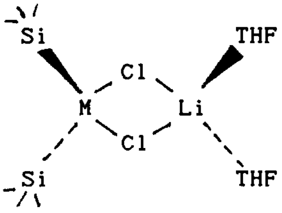
(<u>107</u>)

Solutions of $Ga[GaBr_4]$ in benzene give ^{71}Ga n.m.r. signals for the Ga(I) and Ga(III) centres. Crystals from the benzene solution have the stoichiometry $[(C_6H_6)_2Ga.GaBr_4]_2.3C_6H_6$. The centrosymmetric dimers comprise bis(benzene)gallium(I) and tetrabromogallate(III) units bridged by 6 bromine atoms, (<u>107</u>). Only two bromine atoms are not involved in coordinate bonding.[477] $Ga[GaBr_4]$ and [2](1,4)-naphthalino[2]paracyclophane (= L) form $[Ga^IL](GaBr_4]$. The structure comprises dimeric units, cross-linked into sheets via Ga(I)-arene coordination. Both the benzene ring and the substituted ring of the naphthalene system are η^6-bonded from the outer side of the cyclophane cage. The Ga-benzene ring distance is less than the Ga-naphthalene ring distance, implying stronger coordination to the unperturbed π-system of the former.[478] Similar results are also reported for the chloro-analogue.[479]

(<u>108</u>) is the first tris(arene) complex with neutral arene ligands. All 18 ring carbon atoms are bonded about equally to Ga^+.[480]

$((Me_3Si)_3Si)_2M(\mu-Cl)_2Li(THF)_2$, where M = Ga or In, have been prepared, and their structures determined by X-ray crystallography, (<u>109</u>), with Ga-Si 243.9(5)pm, In-Si 259.1(7)pm, in both cases slightly larger than the sum of the covalent radii.[481]



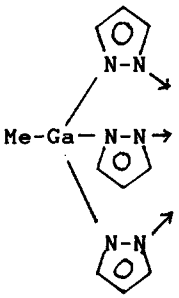


(109)

(108)

3.3.2 Compounds Containing Bonds Between Gallium and Group 5 Elements

Ga(P)X, where P = octamethyl-, octaethyl- or tetraphenyl porphyrinato, X = F, Cl or I, have been prepared. For Ga(TPP)Cl the crystals were shown to be isomorphous with Fe(TPP)Cl.[482,483] The crystal structure of $(MeGapz_3)Mo(CO)_3SnPh_3$, where $MeGapz_3$ = (110), shows that the Ga-N distances are in the range 192.0(3)-193.1(3)pm.[484] The reactions of $LMo(CO)_3^-$, where L = $MeGapz_3$ or related species, with $[Cu(PPh_3)Cl]_4$ or $Rh(PPh_3)_3Cl$, give complexes containing Mo-Cu or Mo-Rh bonds.[485]



(110)

1,4,7-Triazacyclononane and its N,N',N"-trimethyl derivative give the monomeric species $LGaCl_3$ from non-aqueous solutions of $GaCl_3$ and the amine. Alkaline aqueous solutions of $Ga(NO_3)_3$ and the amine produce binuclear complexes, e.g. $[L_2Ga_2(OH)_2(\mu-OH)_2]-(ClO_4)_2.5H_2O$.[486]

Crystal and molecular structures have been determined for $Me_3GaPPh_2CH_2CH_2Ph_2PGaMe_3$. The Ga-P distance, 256.3(3)pm, is much greater than in $Me_3P.GaCl_3$.[487] The amphoteric ligands $(Me_3SiCH_2)_2MPPh_2$, where M = Ga or In, or $(Me_3CCH_2)_2InPPh_2$ have been prepared and characterised.[488] $GaCl_3$ and three equivalents of $^tBu_2ELi$, where E = P or As, or ArP(H)Li, where Ar = 2,4,6-$^tBu_3C_6H_2$, produce $Ga(E^tBu_2)_3$, where E = P or As, or $Ga[P(H)Ar]_3$. $GaCl_3$ and one equivalent of $^tBu_2ELi$ and two of RLi form $[Ga(\mu\text{-}E^tBu_2)R_2]_2$, where R = Me or ^nBu. These contain four-membered Ga_2E_2 rings.[489]

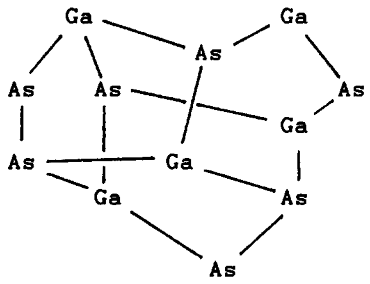
Detailed calculations have been made of the electronic states of GaAs and $GaAs^+$; they showed that the ground state of GaAs was $^3\Sigma^-$, with the $^3\Pi$ state only $1569cm^{-1}$ higher. The ground state of $GaAs^+$ was found to be $^4\Sigma^-$.[490]

Ga_2I_4 and Me_2AsH react to form Me_2AsGaI_2, whose vibrational spectrum is consistent with the presence of arsenic-bridged dimers.[491] Monomeric tris(dimesitylarsino)gallane has been prepared,(10), where R = mesityl. The structure of this was

$3R_2AsLi \;+\; GaCl_3 \;\rightarrow\; (R_2As)_3Ga \;+\; 3LiCl$ ....(10)

determined by X-ray diffraction. The Ga-As bond lengths were all shorter than the mean Ga-As bond length in dimeric compounds.[492] A new arsinogallane was prepared by (11), where R = Me_3SiCH_2. For

$2R_2AsSiMe_3 \;+\; GaCl_3 \;\rightarrow\; \tfrac{1}{2}[(R_2As)_2GaCl]_2 \;+\; 2Me_3SiCl$ ...(11)



(111)

this, cryoscopy shows that the dimer is predominant in benzene solution. There was n.m.r. evidence for fluxionality.[493]

$PhAsH_2$ and $(Me_3SiCH_2)_3Ga$ form $(PhAsH)(R_2Ga)(PhAs)_6(RGa)_4$, where R = Me_3SiCH_2. X-ray studies show that this is a cluster compound containing an As_7Ga_5 core, (<u>111</u>).[494] $(Me_3SiCH_2)_2AsH$ and Ph_3Ga give the dimer $[(Me_3SiCH_2)_2AsGaPh_2]_2$. This contains a highly-strained, planar, four-membered ring, Ga_2As_2.[495]

Phase relationships were established for the $CdAs_2$-GaAs polythermal section of the Cd-Ga-As system.[496] The new compound $Ba_7Ga_4Sb_9$ crystallises in the orthorhombic space group Pmmn. $GaSb_4$ tetrahedra are connected by common corners and edges to form strings, linked by Sb-Sb bonds to give sheets.[497]

3.3.3. Compounds Containing Bonds Between Gallium and Group 6 Elements

SO_2 inserts into the alkyl-gallium bond of gallium(III) porphyrins to form sulphinates, which easily oxidise to the corresponding sulphonato complexes.[498]

$CuGaO_2$ is prepared by the solid state reaction of the binary components. The characteristic structural features of this and the Al, Sc and Y analogues were discussed in terms of Cu^+-Cu^+ interactions.[499] I.r. and Raman spectra have been recorded and assigned for $LnMGaO_4$, where M = ^{64}Zn, ^{70}Zn, ^{24}Mg or ^{26}Mg.[500] $Ga(TcO_4)_3$ and its crystalline hydrates have been prepared. The heptahydrate is formed at room temperature, and is converted into the anhydrous form at about 270°C.[501] $M(tfa)_3$, where M = Ga or In, tfa = trifluoroacetylacetonate, have been studied by X-ray diffraction. Both belong to the space group Pcab.[502]

Solubility has been studied in the system $Ga(IO_3)_3$-HIO_3-H_2O at 25°C.[503] A complete structure determination has been reported for the zeolite of approximate composition $LiGaSiO_4.H_2O$, using neutron powder diffraction and molecular modelling.[504] A new gallosilicate zeolite has been synthesised, $(NMe_4)GaSi_5O_{12}$, with the sodalite structure.[505]

The reduction of the 12-molybdogallate heteropolycomplex, $GaMo_{12}O_{40}^{5-}$, by ascorbic acid, forms heteropoly blues, whose composition was determined spectrophotometrically.[506] Similar studies were made on mixed tungsto-molybdo-complexes.[507] There was evidence from ^{71}Ga n.m.r. spectra for the formation of the cation $GaO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$.[508] Equilibrium compositions of the gas and condensed phases were established in the Ga_2O_3-Cl_2 and Ga_2O_3-Cl_2-SO_2 systems, at temperatures 300 - 1200°C, and gas-phase pressures of 0.01 - 1 atm.[509]

The new compound $Mg_7Ga_2GeO_{12}$ was identified in the system MgO-Ga_2O_3-GeO_2. It is isostructural with Fe_9PO_{12}, and the structure can be regarded as an intergrowth of the rock salt and β-Ga_2O_3 types.[510] The vibrational spectrum of $Ca_2Ga_2GeO_7$ crystals was analysed in terms of the factor group of the $P42_1m$ space group. The data are consistent with local vibrating units $[Ga_2GeO_{10}]O_2^{4-}$.[511] Several new phases were identified in the system SrO-Ga_2O_3-GeO_2.[512] $K_x[Ga_{2+x}Ti_{2-x}O_7]$, where $x \leqslant 0.25$, forms tetragonal crystals, space group I4/m. The structure consists of rutile and β-gallia units parallel to the c axis, mutually joined with octahedral and tetrahedral apices.[513]

Structures have been determined for gallium phosphate clathrates containing isopropylamine, $GaPO_4$-14 and -21.[514,515] Evidence was found for several new compounds in the systems M_2O_3-Ga_2O_3-SiO_2, where M = La or Nd, and La_2O_3-Ga_2O_3-Nb_2O_5.[516] Ga^{3+} can be separated quantitatively from Ga^{3+}/Al^{3+} mixtures *via* a porous membrane impregnated with a long chain alkylated cupferron (N-(alkylphenyl)-N-nitrosohydroxylamide salt) solution.[517]

Crystalline $[Ga(SR)_4]^-$, where R = Me, Et, ^iPr, Ph etc., can be prepared by the reaction of $GaCl_3$ or $GaCl_4^-$ with 5 equivalents of LiSR. The complexes are frequently isomorphous with their Fe(III) analogues. The crystal structure for the compound with R = Et shows almost perfect T_d symmetry for the GaS_4 core.[518] X-ray powder diffraction measurements have been made on the system $NiCr_{2-2x}Ga_{2x}S_4$.[519] Phase diagrams have been established for the following systems: La_2S_3-La_2O_3-Ga_2S_3;[520] Ga_2S_3-Eu_2O_2S;[521] Ga_2S_3-Pr_2O_3;[522] and SmS-Ga_2S_3.[523]

$Ga_9Tl_3O_2S_{13}$ forms hexagonal crystals, space group P6. The gallium atoms are in GaS_4 or GaS_3O tetrahedra.[524] Phase diagrams were deduced for $SmSe$-Ga_2Se_3;[525] GaTe-M, where M = Ni or Co;[526] and $TlGaTe_2$-$TlInSe_2$.[527] Ga_3Te_3I contains a one-dimensional macromolecular structural element built up from $GaTe_3I$ tetrahedra (Ga(III) centres) and Ga_2Te_6 units (Ga(II) centres).[528]

3.3.4 Gallium Halides

The preparations have been reported for $Li(THF)_nMCl_3R$, where R = $C(SiMe_3)_3$, $C(SiMe_2Ph)_3$, n = 2, M = Ga; n = 3, M = In; or R = $C(SiMe_3)_3$, n = 1, M = Tl.[529] The crystal structures of

$LiGaX_4$, where X = Cl or I, show that both are isotypic with $LiAlCl_4$. The mean Ga-X bond lengths are 217.4 pm (Cl), 255.9 pm (I).[530] The crystal structures of $Ga[GaCl_4]$ and α-$Ga[GaBr_4]$ confirm both as $Ga^+GaX_4^-$ species.[531] The geometry and mobility of the $H^+.nH_2O$ ions in $HGaCl_4.2H_2O$ and $HInCl_4.3H_2O$ were determined by ^1H n.m.r. data.[532]

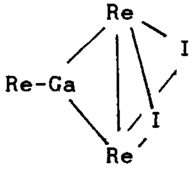
$LiGaBr_4$ and $LiGaBr_3$ are prepared from stoichiometric amounts of LiBr and $GaBr_3$, $GaBr_2$, repectively. The $LiGaBr_4$ crystals are isotypic with those of $LiAlCl_4$. $LiGaBr_3$ is in fact $Li_2Ga_2Br_6$, with a Ga_2Br_6 unit in the eclipsed conformation.[533] Two forms of Ga_2Br_4 have been identified. The α-form is isotypic with Ga_2Cl_4, the β-form with Ga_2I_4. Both are $Ga^+GaBr_4^-$ species.[534]

3.3.5 Other Gallium-containing Species

X-ray diffraction studies of alkali metal tetrahydrogallates show that $NaGaH_4$ is isostructural with anhydrite ($CaSO_4$), while $KGaH_4$, $RbGaH_4$ and $CsGaH_4$ are isostructural with barite ($BaSO_4$). [535]

The species previously thought to be "Ca_2Ga_3" is in fact Ca_3Ga_5. This has a gallium atom framework structure, and Ga-Ga distances of 263.5 - 277.0 pm, compared with a single bond distance of 249 pm.[536] $Ca_{28}Ga_{11}$, prepared from the elements, contains three types of gallium coordination polyhedra, i.e. tricapped trigonal prisms, distorted cubes and distorted cubicosahedra (10-vertex polyhedra).[537]

DTA was used to construct the liquidus surface of the Si-Sn-Ga system.[538]



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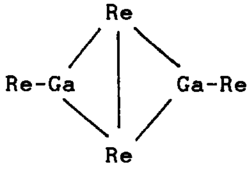


(113)

$Re_2I_2\{Ga[RePPh_3(CO)_4]\}[PPh_3]_2(CO)_4$ contains the fragment (112), with an Re-Re bond. The Ga-Re distances are 249.4(2) - 253.1(3)pm.[539] $Re_2(CO)_8\{Ga[Re(CO)_5]\}_2$ forms tetragonal crystals, space group $I4_1/a$. The central structural unit is (113), with a mean Re-Ga distance of 258.9(5)pm.[540]

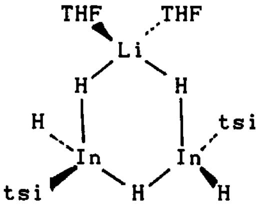
3.4 INDIUM

3.4.1 Compounds containing In-C or In-Si Bonds

$InCl_3$ and InX, where X = Cl, Br or I, react with a mixture $CH_2Cl_2/C_6H_5CH_3$/N,N,N',N'-tetramethylethanediamine (tmen), to give bis(tmen) adducts of $Cl(X)InCH_2InCl_2$. Crystal structures were determined for X = Cl and Br, which show that they are the first examples of di-indium methylene compounds.[541] $InMe_3.OEt_2$ reacts with amines or a phosphine to produce $Me_3In.L$, where L = $NHCy_2$, $N(CH_2CH_2)_3CH$, $N(CH_2CH_2)_3N$, $P(NMe_2)_3$ etc. The complex with $N(CH_2CH_2)_3N$ is a linear polymer of alternating Me_3In and $N(CH_2CH_2)_3N$ units. The former are planar, and the InC_3N_2 skeleton is almost perfectly trigonal bipyramidal, with very long In-N bonds.[542]

The crystal structure has been determined for the methylindium(III) dinuclear cation, $[(H_2O)MeIn(\mu\text{-}mim_2pyCO\text{-}N,N'\text{-}\mu\text{-}O)_2InMe(NO_3)]^+$, in which the alkoxide bridges are formed by bis(N-methylimidazol-2-yl)(pyridin-2-yl)methanolato. Both indium atoms are six-coordinate.[543]

The In-C σ-bond in the indium(III) porphyrins, (P)InL, where L = C_6F_5 or C_6F_4H; P = OEP, TPP etc., has been shown to be stable. Electrochemical studies showed that oxidation/reduction involved the porphyrin ring, and maintained the In-C σ-bond.[544] $In(C_5Me_5)$ forms rhombohedral crystals. There are $[In(C_5Me_5)]_6$ units present in the crystal, but this has only limited stability, as the material is quite volatile, to give monomers in the gas phase.[545]



(<u>114</u>)

(<u>114</u>), where tsi = Me_3Si, has been structurally characterised. This structure, with single Li-H-In and In-H-In bridges, persists in both solid and solution (in toluene or THF).[546]

3.4.2 Compounds Containing Bonds Between Indium and Group 5 Elements

$InCl_3(NMe_3)_2$ forms orthorhombic crystals, space group Pnmb. Discrete trigonal bipyramidal molecules are present, with axial amines.[547] *N*-Methylimidazole (N-MeIm) and pyridine react with (P)InX, where P = OEP, TPP dianions, X = Cl, OAc, SO_3Ph or SO_3Me, with the stepwise formation of 6-coordinate monomeric In-porphyrin species, (P)InX(L) and $[(P)InL_2]^+$, where L = *N*-MeIm or py. This is the first report of monomeric 6-coordinate In(III) porphyrins.[548]

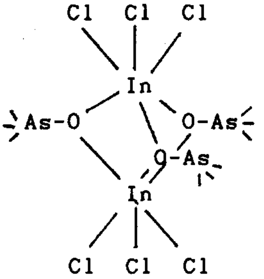
Indium trichloride and the macrocyclic ligands 1,4,7-triaza-cyclononane (L), 1,4,7-trimethyl-1,4,7-triaza-cyclononane (L') and 1,4,7-trithiacyclononane (L") form $LInCl_3$, $L'InCl_3$ and $L''InCl_3$, in $CHCl_3$ solution. $LInBr_3$ is prepared similarly from aqueous $InBr_3$. Treatment of $LInBr_3$ with aqueous hydroxyl ion produces the tetramer $[L_4In_4(\mu\text{-}OH)_6]^{6+}$, the first well-characterised bridging hydroxo complex of In(III).[549]

The electrochemistry of (P)InX has been studied in a variety of solvents, where P = dianion of OEP or TPP, X = SO_3Ph, SO_3Me, Cl or OAc.[550] The complex Rh(OEP)-In(OEP) is synthesised by the reaction of $Na^+Rh(OEP)^-$ and In(OEP)Cl. The presence of a Rh-In bond was confirmed by X-ray diffraction.[551]

The composition of the vapour, as a function of the temperature and composition, above $InP_{1-x}As_x$ solid solutions, has been measured. The results were used to carry out a thermodynamic analysis of the InAs-InP system.[552] Phase equilibria were studied in the system $InBi\text{-}InSb\text{-}Zn_3Sb_2$.[553] $Pb_4In_2Bi_4S_{13}$ forms orthorhombic crystals, space group Pcma, containing both octahedrally and tetrahedrally coordinated indium atoms.[554]

3.4.3 Compounds Containing Bonds Between Indium and Group 6 Elements

X-ray scattering studies on hydrolysed indium(III) nitrate solutions show the presence of polynuclear hydrolysis products, with In-In distances of 389pm, i.e. there are single hydroxo-bridges. The results are consistent with the dominant species being $In_4(OH)_6^{6+}$, with InO_6 units sharing corners, and a tetrahedral arrangement of indium atoms.[555]



(115)

The structure of the adduct $2InCl_3.3Me_3AsO$ is (115). The As-O stretching vibration is at 796 cm^{-1}, consistent with this form of bridging.[556] Interaction in the In-$In_2(SO_4)_3$ system produces the lower indium sulphate, $In^{I}In^{III}(SO_4)_2$.[557] Indium hydroxamates, $In[XC_6H_4$-N(O)-C(O)-R$]_3$, where X = 4-Me, H, 4-Cl, 4-Br, 4-CH=CH_2, 4-MeC(O), 4-MeOC(O), 3-Me, 3-Cl or 3-Br; R = CH=CH_2 or CMe=CH_2, have been prepared and characterised. The In-O stretching vibration is at 522-524 cm^{-1}, almost independent of X and R.[558]

Oxidation of NaIn by Na_2O_2 forms Na_5InO_4.[559] Crystals of $LiInP_2O_7$ are monoclinic, space group $P2_1$. The structure is built up from InO_6 octahedra and pyrophosphate groups. Each InO_6 is linked by In-O-P bonds to 5 pyrophosphate groups.[560] $Cs_2In_2O_6$ and $Rb_2Tl_2O_6$ are prepared by heating appropriate mixtures of Cs and In or Rb and Tl oxides.[561] Several new compounds were isolated from the salt mixtures $In(NO_3)_3/NaVO_3$.[562] $Li_3In_2P_3O_{12}$ forms monoclinic crystals, containing InO_6 and PO_4 units in an infinite, three-dimensional network $[In_2P_3O_{12}]$.[563]

$In_3Mo_{11}O_{17}$ contains linear In_6^{8+} polycations located between clusters of 5 linearly-condensed Mo_6O_{12} units.[564] The species $O\{(Me_3Si)_3CIn\}_4(OH)_6$ was shown by X-ray diffraction to have a structure based on 4-membered In_2O_2 rings, with 5-coordinate indium.[565] The new metastable compound $BaNi_2In_8O_{15}$ has been prepared at high temperatures; its crystals are orthorhombic.[566] The reduction of 12-molybdoindate by ascorbic acid gives 2- and 4-electron reduction products.[567]

$InCl_3$ and two moles of monothiodibenzoylmethane (LH) give $InCl_2L(LH)$. X-ray diffraction shows that this contains 6-coordinate indium, with two *cis* chlorines and two *trans* sulphur atoms.[568] $Ph_4P^+[BrIn(SPh)_3]^-$ forms monoclinic crystals, space group $P2_1/c$. Vibrational spectra were reported for the anion, and the neutral parent compound $In(SPh)_3$.[569] Tris(chelates) of indium(III) with several dichalcogenolene ligands, e.g. 1,3-dithiol-2-thione-4,5-dithiolate, have been prepared.[570]

An X-ray study of the system $ZnIn_2S_4$-$Zn_2In_2Se_4$-In_2Se_3-In_2S_3 was reported. The new compound $ZnIn_2S_2Se_2$ was identified.[571] The equilibrium diagram was constructed for the In_2S_3-Bi section of the system In-Bi-S.[572] $Pb_4In_3Bi_7S_{18}$ contains distorted InS_6 octahedra, linked into chains.[573] $In_{18}Sn_7S_{34}$ forms orthorhombic crystals, space group Pbam. The In^{3+}-S distances were in the range 248 - 293pm.[574] $LiInSe_2$ forms crystals of β-$NaFeO_2$ type, with In-Se 256.8 pm.[575] Equilibrium diagrams were constructed for the systems SnTe-InSe and SnTe-Tl_2Se.[576] There was evidence for In_2Te and Te_2 in the vapour above solid In_2Te_3.[577] $LiInTe_2$ crystals belong to the chalcopyrite structure type, and the In-Te distances (mean value) are 276.8 pm.[578] Evidence was found for $HoInTe_2$ in the system HoTe-InTe.[579]

3.4.4 Indium Halides

Metallic indium, purity >99· can be obtained by electrodeposition from aqueous $InCl_3$ solutions.[580] Equilibrium concentrations of the system (12) in melts of indium halides were determined at

$$In^{3+} + 2In^{(0)}(Hg) \rightleftharpoons 3In^{+} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

various amalgam concentrations. Equilibrium constants and Gibbs free energies of disproportionation were calculated for the indium(I) halides.[581]

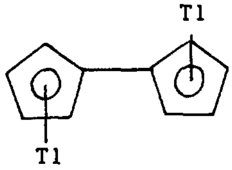
High-resolution He(I) and He(II) photoelectron spectra of gas phase InX_3 were obtained, for X = Cl, Br or I. "InI_3" was shown to be a dimer, with pseudo-tetrahedral geometry at the indium, and not a planar monomer. Xα-SW calculations also support the formulation In_2I_6. There was less conclusive evidence for the other compounds, "$InBr_3$" is probably a dimer, $InCl_3$ mainly monomer.[582]

The crystal structure of $In^{I}In^{III}Br_4$ ('indium dibromide') shows that the structure is like that of $GaCl_2$.[583] $InBr_5(OH_2)^{2-}$ gives i.r. and Raman spectra as expected for C_{4v} symmetry, with νIn-OH_2 at 265, and νIn-Br at 192, 177, 170 and 165 cm^{-1}.[584]

3.5 THALLIUM

3.5.1 Thallium(I) Compounds

There is evidence for considerable covalent character in the Tl-anion bonds of $Tl_2B_{10}H_{10}$. $Tl_2B_{12}H_{12}$, however, has almost totally ionic bonding to Tl^+.[585] $(C_5Me_5)Tl$ forms monoclinic crystals. There is a polymeric zig-zag chain structure, with short Tl-Tl distances, indicative of a high degree of covalent bonding.[586] Dihydrofulvalene and TlOEt in Et_2O/hexane solutions give fulvalenedithallium, (116), as an air-sensitive, but thermally-stable compound.[587] (117) has been shown to be a versatile intermediate for the formation of dinuclear cyclopentadienylmetal carbonyl compounds.[588]



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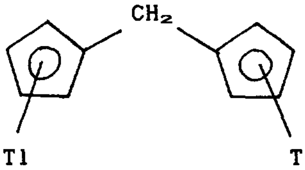


(117)

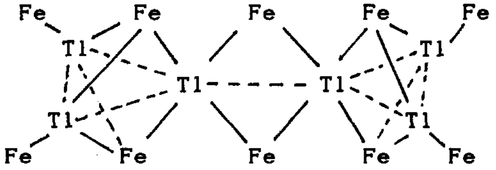
$TlNO_3$ and 1,5-ditolylpenta-azadiene form red $[Tl(TolNNNNNTol)]_2$ as monoclinic crystals. In the dimers, two separate N_5 chains and two thallium atoms are arranged to form trigonal pyramids, TlN_3. The N-N distances within the the N_5 chains are all equal, indicating a largely ionic character for the Tl-N bonds. In $[Tl(PhNNNPh)]_2$ there are planar, four-membered Tl_2N_2 rings.[589] I.r. spectra and thermal decompositions have reported for a wide range of thallium(I) carboxylates, RCOOTl.[590-2]

The phase diagram of the system $TlNO_3$-$NaNO_3$-$Ca(NO_3)_2$ has been established.[593] Crystals of the mixed valence compound $Tl_3\{Tl_{0.5}(H_3O)_{0.5}\}H_{14}(PO_4)_8.4H_2O$ have been shown to be monoclinic, space group C2/c, and not triclinic.[594] TlH_2AsO_4 is isomorphous with TlH_2PO_4.[595] The Tl(I) in Tl_3PO_4 is coordinated to oxygen atoms from three different PO_4 groups. The Tl-O distances are among the shortest known (252.9 - 255.5pm).[596] $TlLn(SO_4)_2.2H_2O$, where Ln = La, Ce, Pr or Nd, and $Tl[Ln(SO_4)_2(H_2O)_3].H_2O$, where Ln = Nd, Sm, Eu, Gd or Tb, have been isolated.[597] Thermodynamic functions for $TlClO_4$ in condensed and gas phases were deduced from a mass-spectrometric study of gaseous $TlClO_4$.[598]

Interactions in the systems Tl^+-HPA, where HPA = $HoW_{10}O_{36}^{9-}$, $Ho(OH)_4W_{10}O_{36}^{13-}$ or $HoW_5O_{18}^{3-}$, were studied by spectrophotometry etc.[599] A polarographic study of complex formation by Tl^+ with cyclohexylthioglycolate (HA) shows the presence of TlA and TlA^{2-}, with logarithmic stability constants of 1.73, 3.18 respectively, at 20°C.[600]

The crystal structures for Tl_4SiX_4, where X = S or Se, show that for X = S, the compound is isostructural with Tl_4GeS_4, while for X = Se the structure is built up from slabs parallel to (001), containing almost planar nets of Tl^+ cations.[601] Phase relationships were established for the following systems: Na_2S-Tl_2S;[602] Cu-Tl-S;[603] and Tl-Cd-S.[604] $Tl_{0.82}V_5S_{4.36}$-$Se_{3.64}$ forms monoclinic crystals, with Tl^+ inserted into quasi-rectangular channels, and Tl-S/Se distances 322.2 - 343.0pm.[605] Phase diagrams were reported for SnSe-TlSe;[606] Tl-Ge-Se;[607] Tl_2Se-Tl_4GeS_4-TlSe, TlSe-$GeSe_2$-Se;[608] Tl-Ga-Se;[609] TlSe-FeSe and TlSe-CoSe.[610] Tl_5Te_3, Ag and Te at 550°C form Tl_3AgTe_2. The structure is of a new type, with ∞ layers $[AgTe_2]$ running along (100), separated by Tl atoms. Layers are built up by pairs of edge-sharing tetrahedra linked by common Te atoms.[611]

A ^{205}Tl n.m.r. study of complexation between Tl(I) and Cl^- in aqueous solution showed that the overall formation constants of TlCl and $TlCl_2^-$ were 1.0 ± 0.2, 0.25 ± 0.05 respectively.[612] The liquidus surface has been determined for the system LiBr-NaBr-TlBr.[613] Solubilty was studied at 25°C in the system CsI-TlI-H_2O.[614] Studies on the vapour above TlI/NdI_3 were consistent with the formation of $TlNdI_4$.[615] Tl^II_3 forms orthorhombic crystals, isotypic with CsI_3.[616]

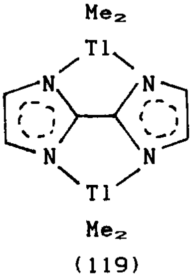


(118)

The structure has been determined for $(Et_4N)_6[Tl_6Fe_{10}(CO)_{36}$. It contains two thallium triangles held together asymmetrically by two μ_3-$Fe(CO)_3$ units (no apparent Fe-Fe bonding). The two triangles are linked by two $Fe(CO)_4$ bridges, giving the metal skeleton (118).[617]

3.5.2 Thallium(III) Compounds

Several crown ether complexes of $R_2Tl(III)$, where R = Me or Et,



(119)

have been prepared, and their Tl-H spin-spin coupling constants measured. The crystal structure of $[LTlMe_2]ClO_4$ was reported, where L = 1,4,7,18,21,24-hexaoxaperhydro[7.7](4a,8a)naphthaleneophane, showing that the CTlC unit is linear.[618] Some heterocyclic derivatives of $Me_2Tl(III)$ have also been prepared, e.g. (119).[619]

The macrocycles 1,4,7-triazacyclononane (L) or N,N',N"-trimethyl-1,4,7-triazacyclononane (L') and $TlCl_3.4H_2O$ form $LTlCl_3$ or $L'TlCl_3$; with $Tl(NO_3)_3$, L gives $[TlL_2](NO_3)_3$, and with $TlNO_3$, L' forms $L'Tl(PF_6)$ (in the presence of $NaPF_6$).[620] Anion-extraction of Tl(III) acetato complexes by trinonyl(octadecyl)ammonium salts was investigated.[621] The crystal structure of the crown ether complex $[Me_2Tl(L)]ClO_4$, where L = tridecalino-18-crown-6, shows that the linear Me_2Tl^+ forms 6 equal Tl-O bonds, with the decalin 'walls' in contact with the methyl groups.[622]

$(pyH)_2TlCl_5$ and cycloheptatriene/NMe_3/CH_2Cl_2 form the adduct $(pyH)TlCl_4.py$, and not cycloheptatrienyl thallium(III) dichloride, as previously claimed.[623] $TlBr_2I(OPPh_3)_2$ has distorted trigonal bipyramidal coordination at the Tl, with equatorial halide ligands.[624] The Tl-O distance (237.7(3)pm) in $TlBr_3$(pyridine-N-oxide) is longer than the sum of covalent radii, due to the donor character of the py-N-oxide ligand.[625] Anhydrous $CsTlI_4$ (by heating CsI/TlI + I_2, or from dehydration of $CsTlI_4.2H_2O$) forms monoclinic crystals, space group $P2_1/c$.[626] $(ET)_2(I_3)(TlI_4)$, where ET = bis(ethylenedithio)tetrathiafulvalene, contains mixed two-dimensional sheets made up of ET donor molecules and I_3^- ions, separated by layers of TlI_4^- ions. The compound is a semiconductor.[627]

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