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Chapter 3

ELEMENTS OF GROUP 3

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3.1 BORON

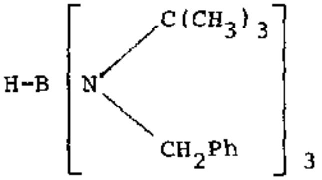
3.1.1 Boranes

A new method has been described for the qualitative construction of m.o's for an approximately spherical cluster of boron atoms. This gave a useful insight into electron-counting rules for such clusters.[1] A descriptor-system and methods for describing uniquely closed and non-closed polyboron hydrides have now been extended to polyboron hydride structures consisting of two or more linked polyhedra or polyhedral fragments.[2] Another mathematical model has been developed to predict structures of boron hydrides and related compounds. Closo-compounds are considered as clusters of boron atoms in which each atom is bonded to all of the others. Nido-, arachno- and hypho-compounds are then obtained by successive additions of electron pairs to the cluster. The complete range of possible structures was calculated, and their classification was significantly different from previously, in better agreement with experiment.[3,4]

Three papers have reported the application of two-dimensional B-B correlation n.m.r. spectroscopy to the elucidation of structures of polyhedral boranes and their derivatives. Only directly bonded boron atoms couple with each other, and not those linked by B-H-B bridges, and so the determination of boron connectivities is greatly helped. The two-dimensional spectroscopic results also assist in the assignment of conventional one-dimensional spectra.[5-7]

Quantum mechanical calculations were used to calculate the energies of rotational transitions for HBO, HBNH and HBF^+.[8]

Boron trichloride reacts with three molar equivalents of $LiN(CH_2Ph)C(CH_3)_3$ to form (1). This gives monoclinic crystals, spce group C2/c, and the mean B-N bond length is 142pm.[9]



(1)

MBH_4, where M = Li, Na or K, react with molecular hydrogen to give 90-95% yields of B_2H_6.[10] An ab initio calculation was performed to determine the force field of methyldiborane. It was possible to calculate values for 35 observed wavenumbers of $B_2H_5CH_3$ and $B_2D_5CH_3$, with an average difference between experiment and calculation of 8.9 cm^{-1}.[11]

Four methods have been devised to prepare $B_4H_8PMe_3$ i.e. removal of one PMe_3 from $B_4H_8.2PMe_3$ by B_2H_6; hydride removal from $B_4H_9.PMe_3{}^-$ by B_2H_6; boron framework expansion of $B_3H_7.THF$ using $B_2H_4.2PMe_3$; and the reaction of $B_3H_6.2PMe_3{}^+B_3H_8{}^-$ with NMe_3. $B_4H_8.P(NMe_2)_3$ was prepared by hydride removal from $B_4H_9.P(NMe_2)_3{}^-$. It is possible to prepare mixed bis(base) adducts from both of these, e.g. $B_4H_8.PMe_3.L$, where L = NMe_3 or $P(NMe_2)_3$.[12]

Mass spectra have established the existence of direct exchange between D_2 and B_4H_{10} in the gas-phase. The results strengthen the view that the equilibrium (1) plays a key role in borane

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

interconversion reactions.[13]

Gas-phase photolysis at 300nm of B_5H_9 and hexafluoroacetone gives good yields of both the basal and apical perfluoropropanol-substituted compounds: $2\text{-}[HO(CF_3)_2C]B_5H_8$ and $1\text{-}[HO(CF_3)_2C]B_5H_8$, as well as a novel B-O bonded perfluoropinacol derivative: $1\text{-}[HO\{C(CF_3)_2\}O]B_5H_8$. Similarly, photolysis of $2,4\text{-}C_2B_5H_7$ and hexafluoroacetone produces $5\text{-}[HO(CF_3)_2]\text{-}2,4\text{-}C_2B_5H_6$ and $5\text{-}[HO\{C(CF_3)_2\}_2O]\text{-}2,4\text{-}C_2B_5H_6$.[14]

$PtBr_2$ has been found to be a general dehydrodimerisation catalyst for boranes and carbaboranes. The products are B-B linked polyhedral cage compounds. A number of new coupled cage boranes and carbaboranes were produced using this technique; including $1{:}1'\text{-}(B_4H_9)_2$, $1{:}2'\text{-}(B_4H_9)(B_5H_8)$, $1{:}2'\text{-}(B_4H_9)(1'\text{-}MeB_5H_7)$, $1{:}2'\text{-}(2\text{-}MeB_5H_7)(3'\text{-}MeB_5H_7)$ and $2{:}2'\text{-}(1,6\text{-}C_2B_4H_5)_2$. Also, improved synthetic routes were established to previously-known compounds, e.g. $1{:}2'\text{-}(B_5H_8)_2$ and $2{:}2'\text{-}(1,5\text{-}C_2B_3H_4)_2$.[15] Halogenation and deprotonation were used to prepare various derivatives of $1{:}2'\text{-}(B_5H_8)_2$ and $2,2'\text{-}(B_5H_8)_2$. Cleavage of the intercage B-B σ-bond was observed in 1,2', but not in $2,2'\text{-}(B_5H_8)_2$, in the presence of X_2 and HX (X = halogen).[16] High-field ^{10}B and ^{11}B n.m.r. spectra were used to observe B-B coupling in 2-centre, 2-electron bonds linking coupled-cage boranes and carbaboranes, such as 1:1'-, 1:2'- and 2:2'-$(B_5H_8)_2$, 3:3'-, 1:3'- and 3:5'-$(2,4\text{-}C_2B_5H_6)_2$ etc.[17]

An analysis was made of solvent effects on the ^1H and ^{11}B n.m.r. spectra of $B_{10}H_{14}$, both on the chemical shifts, and on the resolution of fine-structure.[18]

The first neutral dodecaborane, $B_{12}H_{16}$, has been prepared from $K^+B_6H_9^-$ and $FeCl_2/FeCl_3$ in Me_2O at -78°C (i.e. oxidative borane fusion). The structure involves B_8 and B_6 units joined at a common B-B edge, with B-H-B bridges at the perimeter.[19] Oxidative fusion of dodecahydrononaborane(-1) clusters, using $HgBr_2$, produces n-octadecaborane(22), $B_{18}H_{22}$. Much better yields were achieved than in previous experiments.[20]

3.1.2 Borane Anions and their Metallo-derivatives

$Li[BHEt_3]$ acts as a stereospecific trisalkylating agent towards B_5H_9, to give exclusively 2,3,4-triethylpentaborane(9). $Li[BH^sBu_3]$ gives only a monoalkyl product, 2-(s-butyl)pentaborane-(9).[21] A general method has been reported for the preparation of potassium trialkoxyboranes, $K[(RO)_3BH]$, where R = Me, Et, ^iPr, ^sBu, ^tBu, Ph etc.). The scheme involves reactions (2) and (3).

$$3ROH \;+\; BH_3.SMe_2 \;\xrightarrow{\Delta}\; (RO)_3B \;+\; 3H_2\uparrow \;+\; SMe_2 \qquad ...(2)$$

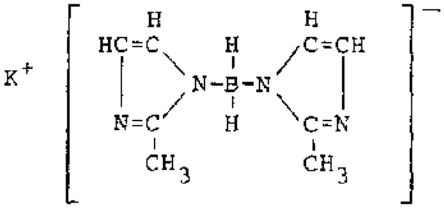
$$(RO)_3B \;+\; KH \;\xrightarrow{THF}\; K[(RO)_3BH] \qquad ...(3)$$

The products were characterised by ^{11}B n.m.r.[22]

Single-crystal structure determinations have been carried out on the new compounds $B(Me_2pz)(Me_2pzH)$ and $[HB(Me_2pz)_3BH]^+MCl_6^-$ (M = Nb or Ta), where Me_2pzH is 3,5-dimethylpyrazole. The former contains a BN_4 group distorted from regular tetrahedral geometry, but n.m.r. shows that the N-H proton is scrambled among four equivalent Me_2pz groups at room temperature in solution.[23] Me_3SnCl and $K[HB(pz)_3]$, where pz = 1-pyrazolyl, $C_3H_3N_2$, react to give $[HB(pz)_3]SnMe_3$. X-ray diffraction shows this to contain tin, bound to three methyl and three pyrazolyl groups.[24]

KBH_4 and 3 equivalents of 1-H-3(5)-methylpyrazole react at 195-200°C to form a hydrotris(methylpyrazolyl)borate anion. This forms a complex, $[Mo(CO)_3\{HB(Mepz)_3\}]^-$, with the $Mo(CO)_3$ unit, and the crystal structure of the NEt_4^+ salt of this was determined.[25] Gas-phase u.v. photoelectron spectra were reported for $M[HB(pz)_3]_2$, where M = Zn, Fe, Cu, Ni or Co. The series from Fe to Cu showed smooth increases in the ionisation energies of the M 3d subshells. For M = Ni and Cu this gave good energy-matching with the combinations of nitrogen lone-pairs, and hence predominantly covalent M-L bonding.[26] $Re^{V}OCl_2[HB(pz)_3]$ has been prepared, and characterised spectroscopically.[27] $HB(pz)_3^-$ and $ClSn[Co(CO)_4]_3$ react to form $\{Co[HB(pz)_3]_2\}^+[Sn_2Co_5Cl_2(CO)_{19}]^-$. The cation contains octahedral cobalt, with 2 tridentate tris(pyrazolyl)borate ligands.[28] The species $Cu[HB(pz)_3](C_6H_{10}).CuCl$, where C_6H_{10} = cyclohexene, forms triclinic crystals, space group $P\bar{1}$.[29] I.r. and u.v./visible spectra have been reported and discussed for $M(NCS)_2[HB(pz)_3].xL$, where x = 1, M = Th, L = THF; M = U, L = THF, $MeCONHMe_2$, PMe_2PhO etc; x = 2, M = Th, L = $MeCONMe_2$, PMe_3O, PMe_2PhO etc; M = U, L = PMe_3O; x = 1.5, M = Th, L = $P(NMe_2)_3O$, and some analogues containing 3,5-Me_2pz.[30]

The new ligand (2) has been prepared, together with a number of its complexes with first-row transition metals, in which it acts as a bidentate ligand, through the pyridyl nitrogen atoms.[31]



(2)

New preparations have been reported for the Na^+ and $N^nBu_4^+$ salts of $BH_2(CN)_2^-$, e.g. (4). The properties of these showed that

$$PhNH_2.BH_2CN + NaCN \rightarrow NaBH_2(CN)_2 + PhNH_2 \quad ...(4)$$

$BH_2(CN)_2^-$ is a much weaker reducing agent than BH_3CN^-.[32] The first metal complexes of $BH_2(CN)_2^-$ have also been reported, i.e. $(Ph_2MeP)_3Cu(NC)_2BH_2$ and $P^3Cu(NC)_2BH_2$, where P^3 = 1,1,1-tris-((diphenylphosphino)methyl)ethane. The coordination via a Cu-N-C-B bridge was confirmed by i.r. and ^{11}B n.m.r. spectroscopy, with one "terminal" C-N group remaining.[33]

The preparations have been reported for $(\mu\text{-H})(\mu\text{-CO})Fe_3(CO)_9BH_2$, $(\mu\text{-CO})Fe_3(CO)_9BH_2^-$ and $Fe_3(CO)_9BH_4^-$. ^{11}B n.m.r. shows that the 'capping' boron in the first complex is very similar to the capping carbon in the isoelectronic $HFe_3(CO)_{10}CH$ cluster.[34] Molecules of $(THF)_3Li(\mu\text{-H})_3BC(SiMe_2Ph)_3$ - made by reaction of {tris(dimethylphenylsilyl)methyl}boron with $LiAlH_4$ - have been shown to have approximately C_3 symmetry, with tridentate hydrogen bridges between Li and B.[35]

Crystal and molecular structures have been determined for $(MeBH_3)_4U(Me_2PCH_2CH_2PMe_2)$ and $(MeBH_3)_3U(Me_2PCH_2CH_2PMe_2)_2$. Both complexes involve coordination of the BH_3 via tridentate hydrogen bridges.[36] $CoH(BH_3CN)(PPh_3)_3$, a rare Co(II) hydride, is prepared from $Co(ClO_4)_2.6H_2O$, PPh_3 and $NaBH_3CN$. The BH_3CN^- ligand is coordinated via the nitrogen atom.[37] Ni(II), with $NaBH_3CN$ and $Ph_2P(CH_2)_2PPh_2$, gives products with coordinated BH_3CN^- in Ni(II)-diphos complexes.[38]

The heat capacity of $LiBH_4$ has been measured from 10 to 450K. A phase transition is seen at 383K.[39] Redox processes involving BH_4^- have been classified. BH_4^- or its hydrolysis products can be the effective reducing agents.[40] $Ca(BH_4)_2(MeOCH_2CH_2OMe)_2$ can be prepared from $Ca(BH_4)_2.2THF$ by ligand displacement. I.r. and n.m.r. data are consistent with the presence of non-ionic BH_4, but specific binding to Ca^{2+} could not be deduced unambiguously. The crystal structure shows that the lattice is built up from molecules in which BH_4 is linked by three B-H-Ca bonds.[41]

$Cp_2Zr(BH_4)_2$ is prepared in high yield from Cp_2ZrH_2 and diborane or catecholborane in THF.[42] Single hydrogen-bridge attachment of BH_4 to Fe is found in $FeH(dmpe)_2(BH_4)$, where dmpe = 1,2-bis(dimethylphosphino)ethane - the first example of such binding to iron. N.m.r. spectra reveal rapid terminal$\rightleftharpoons$bridging exchange of BH_4 hydrogens.[43] Dynamic n.m.r. studies show that the barrier to exchange of bridging and terminal hydrides in $Co(terpy)(H_2BH_2)$, where terpy = 2,2':6',2"-terpyridyl, is 11.1(±0.1) kcal.mol.$^{-1}$. This is the highest value yet recorded for a bidentate $H_2BH_2^-$ complex.[44]

$Os(BH_4)H_3[P(\underline{c}\text{-}C_5H_9)_3]_2$, prepared from $OsH_6[P(\underline{c}\text{-}C_5H_9)_3]_2$ and $BH_3.THF$, contains a BH_4 unit which is bound to the metal in bidentate fashion. At 90°C the bridging hydrogen atoms only exchange rapidly with hydride ligands on the osmium.[45] Multiple-luminescence has been observed for $Cu(PPh_3)_2BH_4$. The results were explicable in terms of both intra- and inter-(solute-solvent) molecular effects.[46] The crystal structure of $[\{Cu(PPh_3)_2\}_2BH_4]^+ ClO_4^-$ shows the presence of a μ-BH_4 group bridging two tetrahedral Cu(I) atoms through bidentate hydrogen-bridges.[47]

$Cp_2Sc(BH_4)$ contains a triply-bridged ScH_3BH unit. Multinuclear (^1H, ^{11}B, ^{45}Sc) n.m.r. data were reported for $Cp_2Sc(BH_4)$ and $Sc(BH_4)_3$. There was no evidence for the exchange of Cp and BH_4 protons in $Cp_2Sc(BH_4)$, as has been claimed for $Cp_2Zr(BH_4)_2$.[48] $NaBH_4$ and MCl_3 (where M = Sc or Y; $[NaBH_4]:[MCl_3] \approx 4$), in 1,2-dimethoxyethane (DME), form colourless complexes $NaM(BH_4)_4.4DME$. Heating these at 100Pa produces volatile $M(BH_4)_3.DME$. The crystal structure of $Y(BH_4)_3.DME$ shows that it contains polymeric chains, with $Y(BH_4)_2.DME$ units bridged by BH_4 groups.[49] ^1H and ^{11}B n.m.r. data show that $U(BH_4)_3$ and $U(BH_4)_4$

$$3U(BH_4)_3 \rightarrow U(BH_4)_5^{2-} + 2U(BH_4)_2^+ \qquad ...(5)$$

$$3U(BH_4)_4 \rightarrow U(BH_4)_6^{2-} + 2U(BH_4)_3^+ \qquad ...(6)$$

undergo dissociation in THF solution, equations (5) and (6).[50]

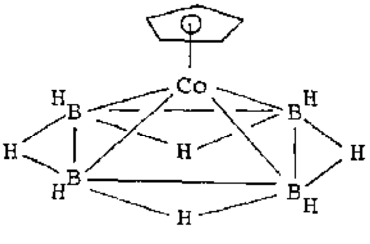
Ab initio m.o. calculations have been reported for the $B_2H_7^-$ ion. Use of a 6-31G** basis set predicts a bent B-H-B central linkage, in agreement with experiment.[51]

Several disubstituted derivatives of $B_3H_8^-$ have been reported, e.g. $B_3H_6Cl_2^-$, $B_3H_6Cl(NCS)^-$ etc. N.m.r. results show such ions to be fluxional in solution. Their molecular structures show that the two substituents are trans, with the basic $B_3H_8^-$ structure preserved.[52] Ylide derivatives of triborane (7), $PPh_3CHRB_3H_7$, where R = H, Me or Ph, have been prepared from B_3H_7.-THF by ligand displacement. Their structures were established by ^{11}B, ^1H and ^{31}P n.m.r.[53]

The crystal structures of $[(Ph_3P)_2N]^+[B_3H_7(NCX)]^-$, where X = S or Se, have been determined at ambient and low temperatures. The room-temperature data suggest the presence of both edge- and face-bridging hydrogens, but low-temperature data show only one type of hydrogen (edge-bridging).[54] The species $Mg(B_3H_8)_2.2DG$; $Ca(BH_4)(B_3H_8).2DG$ and $Sr(B_3H_8)_2.3DG$, where DG = diglyme, are formed from the corresponding tetrahydroborates with B_2H_6 in diglyme at 55-70°C. They decompose thermally to pentaborane(9) and the tetrahydroborates and closo-dodecahydrododecaborates of the metals.[55]

A discussion has been published on the possible two- and three-centre bond schemes for $B_nH_n^{c-}$, where n = 4-12, c = 0, 2 or 4, and isoelectronic analogues, with closo-deltahedral shapes. Localised bond structures can be devised for all the species that would be predicted (by m.o. calculations) to have closed-shell electronic configurations, i.e. $B_nH_n^{2-}$, for n = 5-12, and $B_nH_n^{c-}$, c = 0 or 4, n = 4, 8, 9, 11. There was also generally good agreement with m.o. calculations on those systems not expected to be stable, e.g. $B_4H_4^{2-}$, $B_nH_n^{c-}$ (c = 0 or 4, n = 5, 7 or 10).[56]

Structural studies (X-ray; n.m.r., i.r. and u.v. spectra) on $1\text{-}[(\eta^5\text{-}C_5R_5)Co[B_4H_8$, where R = H or Me, confirm that the structure is (3). The short Co-B distance (197.7pm) suggests that there is a strong $Co\text{-}B_4H_8^{2-}$ bond. The terminal hydrogen atoms are only bent slightly out of the B_4 plane.[57] KB_4H_9 reacts with trans-$IrCl(Co)[P(CH_3)_2Ph]_2$, $RhCl(PPh_3)_3$, $NiBr_2[Ph_2P(CH_2)_2PPh_2]$ (in the presence of additional KH) and $CuBr(PPh_3)_2.\frac{1}{2}C_6H_6$ to form (respectively) $Ir(\eta^4\text{-}B_4H_9)(CO)[P(CH_3)_2\text{-}Ph]_2$, $Rh(\eta^3\text{-}B_4H_8)H(PPh_3)_2$, $Ni(\eta^3\text{-}B_4H_8)[Ph_2P(CH_2)_2PPh_2]$ and $Cu(\eta^3\text{-}B_4H_9)(PPh_3)_2$. These were characterised by ^{11}B and $^1H\{^{11}B\}$ n.m.r. Crystals of the iridium complex were obtained, and its structure confirmed by X-ray diffraction, i.e. an open five-atom cluster with the Ir at an apical vertex, and bound to the four boron atoms of the $\eta^4\text{-}B_4H_9$ ligand. It is formally an analogue of arachno-B_5H_{11}.[58]



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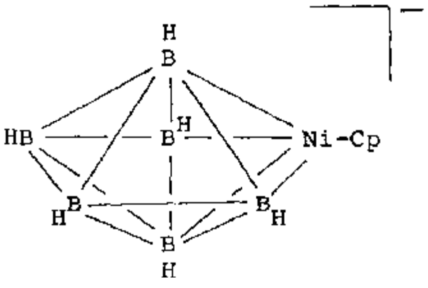


(4)

An effective method has been devised for separating $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$, based on the different solubilities of the $N^nBu_4^+$ salts in diglyme at room-temperature.[59] $(Bu_4N)_2B_6H_6$ and nickelocene react in MeCN solution to give an ionic complex $(Bu_4N)[(\eta^5-C_5H_5)NiB_6H_6]$. ^1H, ^{11}B n.m.r, i.r. and mass spectra support a structure (4) i.e. a pentagonal bipyramid with equatorial Ni, obeying the skeletal-electron counting rules. It is the first metallaborane with 6 boron atoms in the core to be characterised.[60]

Arachno-4-iridanonaboranes are deprotonated by KH. Subsequent reaction with *cis*-$PtCl_2(PMe_3)_2$ gives *arachno*-6,9-dimetalladecaboranes, such as $(PMe_3)_2PtB_8H_{10}IrH(PMe_3)_2(CO)$, characterised by multinuclear n.m.r. Mild thermolysis or u.v. photolysis of *arachno*-4-iridanonaboranes produces *nido*-2-iridanonaboranes. X-ray structural analysis of $(OC)(PMe_3)_2IrB_8H_{11}$ confirms that it is the first *nido*-, 9-vertex metallaborane to be fully characterised. The IrB_8 cluster is based on a bicapped Archimedean square anti-prism, with an equatorial five-connected vertex missing, and the Ir atom on the open face.[61] $AuBr_2(S_2CNEt_2)$ reacts with *arachno*-$B_9H_{14}^-$ to give an *arachno*-, 9-vertex compound, 4-(S_2CNEt_2)-4-AuB_8H_{12}, and an *arachno*-, 10-vertex compound, 6,9-$(S_2CNEt_2)_2$-6,9-$Au_2B_8H_{10}$. The metal-to-borane bonding is similar to that in related Ir and Pt complexes.[62]

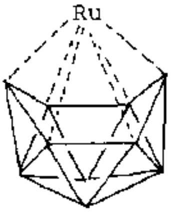
The structural and fluxional characters of B_9H_{14}-derivatives containing neutral or anionic ligands have been investigated by high-field ^{11}B and ^1H n.m.r. spectroscopy. $B_9H_{13}(NCS)^-$ and $B_9H_{13}(NC)BH_3^-$ showed significant differences from the parent anion or from neutral species such as $B_9H_{13}(SMe_2)$.[63]

Metal-atom synthesis was used to prepare the first $(\eta^6$-arene)metallaborane and $(\eta^6$-arene)metallaoxaborane clusters. Thus, decaborane(14) and mesitylene react with thermally-generated iron atoms to give 5-$[\eta^6-C_6(CH_3)_3H_3]FeB_9H_{13}$, 1-$[\eta^6-C_6(CH_3)_3H_3]FeB_9H_9$, 1-$[\eta^6-C_6(CH_3)_3H_3]FeB_{10}H_{10}$ and a small amount of 2-$[\eta^6-C_6(CH_3)_3H_3]$Fe-6-O-B_8H_{19}. The FeB_9H_{13} species is derived from $B_{10}H_{14}$, with the Fe atom occupying the cage 5-position, on the open face.[64]

Nido-$B_9H_{12}^-$ and an equimolar amount of *trans*-$Ir(CO)Cl(PMe_3)_2$ react to give new 9-vertex *arachno*-iridanonaboranes *asym*-4,4,4,4-(CO)-*endo*-H-*cis*-$(PMe_3)_2$-*arachno*-4-IrB_8H_{12}, 1-Cl-*sym*-4,4,4,4-(CO)-*endo*-H-*cis*-$(PMe_3)_2$-*arachno*-4-IrB_8H_{11}, as well as the known 10-vertex *nido*-[6,6,6-$H(PMe_3)_2$-6-IrB_9H_{13}]. There were also very small amounts of a third new species: *sym*-4,4,4,4-*endo*-H-*mer*-

$(PMe_3)_3$-4-IrB_8H_{12}. The 9-vertex species all have the gross *arachno*-nonaborane structure of *iso*-B_9H_{15}.[65]

$B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ and $(SCN)_2$ in CH_2Cl_2 solution form mixed thiocyanato-species from which it is possible to isolate pure 1- and 2-$(SCN)B_{10}H_9^{2-}$, 1,10-$(SCN)_2B_{10}H_8^{2-}$ and 1-$(SCN)B_{12}H_{11}^{2-}$. The structures were determined by ^{11}B and $^{11}B\{^1H\}$ n.m.r. I.r. and Raman spectra contained a band due to νCN at 2120-2140cm^{-1}, showing *S*-coordination of the SCN^-.[66] Pure isomers of $X_nB_{10}H_{10-n}^{2-}$, where X = Cl, Br or I, n = 1 or 2, can be isolated by ion-exchange chromatography. The structures were determined by ^{11}B and $^{11}B\{^1H\}$ n.m.r. spectroscopy. Successive electrophilic substitution preferably occurs on equatorial, and not apical, boron atoms. I.r. and Raman spectra of 2-$XB_{10}H_9^{2-}$ species are very similar in the νBH and B_{10} cage regions. Two low-wavenumber bands dependent on X are assigned to νB_{10}-X and δB_{10}-X modes (X = Cl, 355, 213 cm^{-1}; Br, 249, 188 cm^{-1}; I, 215, 164 cm^{-1}).[67]



(5)

The new ruthenaundecaborane, $(PPh_3)_2RuB_{10}H_8(OEt)_2$ is an 11-vertex member of a previously unrecognised series of metalloboranes which are formally derived by the single-capping of an *arachno*-type, rather than a *nido*-type, cluster geometry. The metal centre can be thought of as contributing four orbitals to the cluster bonding schemes, (5).[68]

Arachno-6,9-$(SMe_2)_2B_{10}H_{12}$ or *arachno*-6,9-$(MeCN)_2B_{10}H_{12}$ react with *cis*-$PtCl_2(PMe_2Ph)_2$ to produce the *nido*-platinaundecaborane, 8-Cl-7,7-$(PMe_2Ph)_2$-7-$PtB_{10}H_{11}$. Analogous reactions with the dimers $[PtCl_2(PR_3)_2]_2$, where $R_3 = Me_{3-n}Ph_n$, n = =, 1 or 2, however, produce the *nido*-platinaundecaboranes, 7-Cl-7-(PR_3)-8-(SMe_2)-7-$PtB_{10}H_{11}$. The *arachno*, 9-vertex species 4-(L)-B_9H_{13}, where L = MeCN or SMe_2, were also detected.[69]

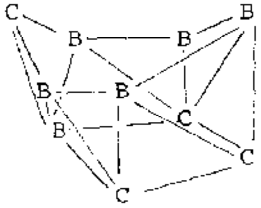
The pure isomers $X_nB_{12}H_{12-n}^{2-}$, where X = Cl (n = 1-3), Br (n =

1 or 2) or I (n = 1), were isolated by ion-exchange chromatography. The structures were determined by ^{11}B and ^{11}B{^{1}H} n.m.r. spectroscopy. The i.r. and Raman spectra of $1\text{-}XB_{12}H_{11}^{2-}$ show 2 characteristic bands due to $\nu B_{12}\text{-}X$ and $\delta B_{12}\text{-}X$ at 331, 207 cm^{-1} (X = Cl); 242, 180 cm^{-1} (Br); 196, 156 cm^{-1} (I).[70]

3.1.3 Carba- and other Non-metal Heteroboranes

The model compound HB_4H_4CH was used to examine the preferred CH ligand orientation when the borane, "butterfly" fragment $HB_4H_4^{+}$ is attached to CH^{-} to give a closo- or an arachno-HB_4H_4CH cluster. BH and $Fe(CO)_3$ are formally isolobal, and analogies were found between HB_4H_4CH and $HFe_4(CO)_{12}CH$.[71]

Several types of previously unobserved long- and short-range spin-couplings were observed in the n.m.r. spectra of closo-2,4-$C_2B_5H_7$ and some of its derivatives.[72]



(6)

The first C_4B_6 carbaborane has been prepared, $Et_4C_4B_6Et_6$, by a series of reduction and oxidation reactions from $Et_2C_2B_3Et_3$.[73] The structure is believed to be based on the skeleton (6).

7,9-$C_2B_9H_{12}^{-}$ and $NaNO_2$ or Na_2SO_3 in dilute hydrochloric acid give 6,8-$C_2B_7H_{13}$ and the new thiacarbaborane 4,6,8-$SC_2B_6H_{10}$ (the structure is based on ^{1}H and ^{11}B n.m.r.).[74] Nido-$(Me_3Si)_2$-$C_2B_4H_6$ can be converted by thermal elimination of trimethylsilane to nido-$(Me_3Si)_2C_4B_8H_{10}$.[75] The reversible cage rearrangement of the tetra-C-alkyltetracarbadodecaboranes, $R_4C_4B_8H_8$, where R = Me, Et or ^{n}Pr, was studied by multinuclear n.m.r. Each exists in solution as two isomers - in one of which there is a distorted icosahedron with 2 four-sided open faces. In the other there is an open framework built up of two pyramidal C_2B_4 units joined at their basal B-B edges.[76]

Oxidation of 7,8-dimercapto-7,8-dicarbaundecaborate(10) by I_3^{-}

in H_2O forms 7,7':8,8'-bis(dithio)bis(7,8-dicarbaundecaborate(10), $[\overline{SCB_9H_{10}CS-SCB_9H_{10}CS}]^{2-}$. The crystal structure shows this to consist of two 7,8-dicarbaundecaborate(10) units bonded by S-S bridges so that the two cages are *anti*- to each other.[77]

Successive reaction of equimolar amounts of ^nBuLi and pentamethyldiethylene triamine with 1-methyl-1,2-dicarba-*closo*-dodecaborane, $C_2B_{10}H_{11}Me$, gave $Li[C_2B_{10}H_{10}Me][MeN(CH_2CH_2NMe_2)_2]$. An unusual feature of the structure is that the Li forms a formally single Li-C bond to the six-coordinate carbon of the carbaborane.[78] E_2Cl_2, where E = S or Se, react with *o*- and *m*-carbaboranes in the presence of $AlCl_3$ to form 9,12-*o*- or 9-10-*m*-$C_2B_{10}H_{10}(EH)_2$.[79] Alkali-metal salts of $B_{11}H_{11}CH^-$ were synthesised and studied by i.r. and u.v. spectroscopy.[80] 1-Dimethylamine-1-carba-*closo*-dodecaborane(11), 1-Me_2NH-1-$CB_{11}H_{11}$, can be smoothly demethylated with I_2 in weakly alkaline solution to form 1-methylamine-1-carba-*closo*-dodecaborane(11), 1-$MeNH_2$-1-$CB_{11}H_{11}$.[81] 7-Me_3N-7-$C_2B_{10}H_{12}$ and $Me_3NB_3H_7$ at 180-200°C react with loss of a methyl group and B-insertion, forming 1-Me_2NH-1-$CB_{11}H_{11}$. This can be methylated to 1-Me_3N-1-$CB_{11}H_{11}$, and in turn reduced by Na in liquid NH_3 to the parent anion 1-$CB_{11}H_{12}^-$.[82]

3.1.4 Metallo-heteroboranes

The *closo*-osmacarbaborane, 1-$Os(CO)_3$-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$, is prepared by the reaction of $Os_3(CO)_{12}$ with either *closo*-$Sn(Me_3Si)_2C_2B_4H_4$ or *nido*-$(Me_3Si)_2C_2B_4H_6$. The former gave a much better yield.[83]

$Na^+[\underline{C}-SiMe_3-\underline{C}'-R-C_2B_4H_5]^-$, where R = H, Me or $SiMe_3$, react with $SnCl_2$ in THF to produce gram quantities of the sublimable white solids $Sn(Me_3Si)(R)C_2B_4H_4$. Mossbauer data show the presence of Sn(II). Other spectroscopic data are consistent with a pentagonal-bipyramidal structure, in which the tin occupies an apical position, and directing its unshared electron pair outwards.[84] A second report appeared of the preparation of this C_2B_4 complex. In addition $SnMe_2(C_2B_9H_9)$ and $(C_{10}H_8N_2)Sn(Me)_2$-$C_2B_9H_9$ were prepared - the former by the reaction of $SnCl_2$ with $Na_2(Me_2C_2B_9H_9)$, the latter by treating the former with 2,2'-bipyridine. The second involves bonding of Sn to three boron atoms, and can hence be regarded as an η^3-borallyl complex.[85]

$C_8H_8^{2-}$ and $Et_2C_2B_4H_5^-$ react in THF with $TiCl_3$ or VCl_3, giving as major products $(\eta^8-C_8H_8)M(Et_2C_2B_4H_4)$, where M = Ti or V. With $CrCl_3$, however, no C_8H_8 complex is isolated - only a low yield of $(\eta^7-C_7H_7)Cr(Et_2C_2B_4H_4)$. Structures were determined by X-ray diffraction. All contain a seven-vertex pentagonal-bipyramidal MC_2B_4 cage, with planar C_8H_8 or C_7H_7 also coordinated to M. All are air-stable in the solid state.[86]

Thermally-generated iron atoms react with B_5H_9, toluene and 2-butyne forming, as a major product, a (π-arene)ferracarbaborane sandwich complex: $1-(\eta^6-C_6Me_6)Fe-2,3-Me_2C_2B_4H_4$, along with smaller amounts of four-carbon metallacarbaborane species: $1-(\eta^6-C_6Me_6)Fe-4,5,7,8-Me_4C_4B_3H_3$, $1-(\eta^6-C_6H_5Me)Fe-4,5,7,8-Me_4C_4B_3H_3$ and $2-(\eta^6-C_6H_5Me)Fe-6,7,9,10-Me_4C_4B_5H_5$. The FeC_4B_3 unit was shown to comprise an *arachno*-type cage geometry derived from a bicapped-square antiprism missing 2 vertices, with the Fe atom occupying the five-coordinate 1-position, and the four carbons occupying positions on the open face of the cage. The CC distance involving non-metal-bonded carbon atoms was very short - consistent with a localised C=C bond.[87]

$NiCp_2$ and $4-CB_8H_{13}^-Na^+$ in diglyme at 130-140°C produce unstable $6-\eta^5-CpNi-\eta^5-1-CB_8H_9$. This rearranges to $10-\eta^5-CpNi-\eta^4-1-CB_8H_9$. Different reaction conditions yield bimetallic $6,7-(\eta^5-CpNi)_2-\eta^5-1-CB_7H_8$. Treatment of $4-CB_8H_{14}$ with C_5H_6 and $CoCl_2.6EtOH$ in EtOH/KOH gave $[2-\eta^5-CpCo-\eta^5-1-CB_8H_9]^-$.[88]

$[(C_5Me_5)Rh]_2(SB_9H_8Cl)$ forms monoclinic crystals, space group $P2_1/c$. The structure comprises a distorted icosahedron of 2Rh, 1 S and 9 B vertices. The presence of a terminal B-Cl bond was unexpected. The rhodium atoms occupy adjacent vertices.[89]

Zone-fusion can be used to separate mixtures of Co(III) complexes of the general type $CS_n[(B_9C_2H_{11})_2Co_n(B_5C_2H_{10})_{n-1}]$, where n = 1-4.[90] $8,8'-\mu-I-3-Co(1,2-C_2B_9H_{10})_2$, with an iodonium bridge between cage groups, was prepared by treating $8-I-C_2B_9H_{10}CoC_2B_9H_{11}^-$ with $AlCl_3/C_6H_6$. The product behaves as a Lewis acid.[91] $6,9-C_2B_8H_{10}^{2-}$ and *cis*-PtL_2Cl_2, where L = PPh_3 or SEt_2 etc., give square-planar $\mu-6,9-PtL_2-6,9-C_2B_8H_{10}$. These are *nido*-metalladicarbaboranes in which an unusual metallic bridge links both skeletal carbon atoms of the carbaborane ligand.[92]

$[N(PPh_3)_2][W(\equiv CR)(CO)_2(\eta^5-1,2-C_2B_9H_9Me_2)]$, where R = $4-MeC_6H_4$, and $RhCl(PPh_3)_3$, $[Rh(PPh_3)_2(diene)]BF_4$, (diene = COD or norbornadiene) or $AuCl(PPh_3)$ react to give species with W-Rh or

W-Au bonds.[93]

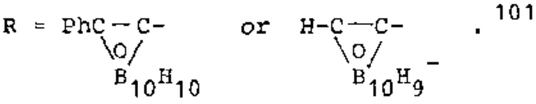
It has been shown that *closo*-3,3,3-$(CO)_3$-3,1,2-$RuC_2B_9H_{11}$ is highly reactive towards nucleophiles. This is an important example of CO activation.[94] Reactions of *closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ and *closo*-2,2-$(PPh_3)_2$-2-H-2,1,12-$RhC_2B_9H_{11}$ with 1-butyl acetate were studied, in order to elucidate the role of *closo*-rhodacarbaboranes as catalysts for acrylate ester hydrogenation.[95] The crystal structure of 9,9-bis(triphenylphosphine)-7,8-dicarba-9-rhoda-*nido*-undecaborane shows that the rhodium possesses pseudo-square planar coordination, with $C_2B_8H_{11}$ as a bidentate ligand.[96] *Closo*-3,3-$(PPh_3)_2$-3-H-1-(R)-3,1,2-$IrC_2B_9H_{10}$, where R = Me or Ph, on refluxing in toluene undergo rearrangement to *closo*-2,2-$(PPh_3)_2$-2-H-8-(R)-2,1,8-$IrC_2B_9H_{10}$, with no detectable amounts of any other possible isomers. The crystal structure of the 2,1,8-species with R = Ph was reported.[97]

The hydridoalkyliridium(III) complex, Ir(H)[σ-$CHCH_2C(O)OC(O)$]-[7-Ph-1,7-$C_2B_{10}H_{10}$](CO)(PhCN)(PPh_3) undergoes a reductive-elimination reaction with succinic anhydride under mild conditions.[98]

9-*o*- and 9-*m*-carbaboranyl carboxylic acids were used to synthesise σ-(*o*- and σ-(*m*-carbaboran-9-yl)-π-cyclopentadienyldicarbonyl iron. The carboxylic acids were produced by the oxidation of 9-alkyl-*o*- and -*m*-carbaboranes with CrO_3 in CH_3COOH.[99] Compounds containing B-Hg-Ge or Ge-Hg-B-B-Hg-Ge chains (where the boron atoms are in carbaborane cages) are prepared by treatment of $(C_6F_5)_3GeGeEt_3$ with *m*-$C_2H_2B_{10}H_9HgX$, where X = Cl or $OCOCF_3$, or *m*-$C_2H_2B_{10}H_8(HgOCOCF_3)_2$. The products undergo oxidative addition with $Pt(PPh_3)_n$, (n = 3,4), to give, for example, B-Hg-Pt-Ge chains.[100]

$Sn(acac)_2$ inserts into Hg(II) derivatives of carbaboranes to produce polymetallic, chain-like compounds, equation (7), where

$$R_2Hg \ + \ Sb(acac)_2 \rightarrow RSn(acac)_2HgR \qquad \ldots(7)$$



$$R = \underset{B_{10}H_{10}}{\underset{\backslash O /}{PhC - C-}} \quad or \quad \underset{B_{10}H_9^-}{\underset{\backslash O /}{H-C - C-}} \ .$$[101]

3.1.5 Compounds containing B-C or B-Si Bonds

Boronic esters react readily with $LiAlH_4$ in Et_2O/pentane at 0°C to form the corresponding lithium mono-organylborohydrides, with precipitation of dialkoxyalanes, equation (8), where R = Me, Et or

$$LiAlH_4 \quad + \quad (RO)_2BR' \rightarrow LiBH_3R' \quad + \quad (RO)_2AlH\downarrow \qquad \ldots(8)$$

${}^{i}Pr$; R' = Ph, ${}^{t}Bu$, C_5H_{11} etc. This is a general and quantitative synthesis for lithium mono-organylborohydrides.[102]

It has been reported that there is a serious danger of explosions when handling $(BH_2CN)_n$.[103]

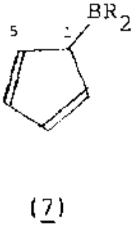
Vinylboronic acids, $RHC{=}C(H)B(OH)_2$, where R = $Me(CH_2)_7$, $Cl(CH_2)_3$, $I(CH_2)_3$ or $H_3COOC(CH_2)_8$, react with vinylmercuric acetates, giving high yields of symmetric divinylmercurials.[104] Detailed vibrational assignments were given from i.r. and Raman spectra of $(CH_2{=}CH)_2BF$. In the liquid- and gas-phases at least two conformers are present, but only one (of C_s symmetry) in the solid.[105] Crystals of $(\underline{Z}\text{-}MeCH{=}CSiMe_3)_3B$ are triclinic, space group $P\bar{1}$. The coordination at the boron is trigonal planar, with bond angles exactly 120°.[106]

Addition of 1 mole of borinic ester to $LiAlH_3(OEt)$ in Et_2O at 0°C gives rapid precipitation of dialkoxyalane, leaving a quantitative yield of lithium dialkylborohydride, equation (9),

$$R_2B(OMe) \quad + \quad LiAlH_3(OEt) \rightarrow LiBH_2R_2 \quad + \quad AlH(OMe)(OEt)\downarrow \qquad \ldots(9)$$

R = ${}^{n}Bu$, n-hexyl, cyclohexyl etc.[107]

M.o. calculations on the 1,5-sigmatropic reaction of cyclopentadienylborane compounds show that the σ-structure, (7, R = H, F, OH, NH_2, Cl or SH) is the ground state, with the η^2-structure, (8), as the transition state.[108]



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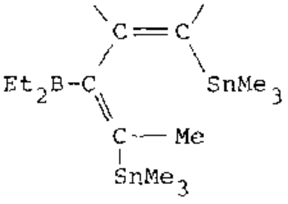
(8)

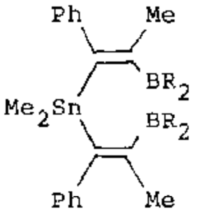


(9)

An attempted synthesis of 1,4-bis(trimethylstannyl)-3-bora-1,4-pentadiene gave instead a 2,5-distannyl-3-borolene, (9).[109]

The crystal structure of $(Me_3Si)_3CBPh_2$ showed that coordination at the boron is strictly planar, but the $(Me_3Si)_3C$-B-C(Ph) angles (122.5°,127.1°) are greater than (Ph)C-B-C(Ph) (110.4°). However, the three B-C distances are the same, within experimental error (158.3pm).[110]

$Me_2Sn(C\equiv CPh)_2$ and BR_3 give (10), for R = Et, (11), for R = Et or ^iPr, together with related species. The products were characterised by ^{13}C and ^{119}Sn n.m.r.[111]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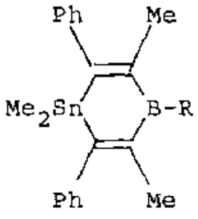

(11)

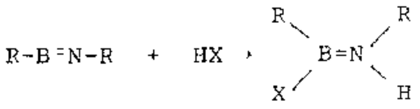
Solubility measurements were made for Cs^+ and Tl^+ salts of $BPh_3(CN)^-$, and Cs^+ and Hg^{2+} salts of BPh_4^- in H_2O and ROH/H_2O, where R = Me, Et or ^tBu.[112] The new organoborates $Li[ArBR_3].OEt_2$, where R = Me or Et, have been prepared. They exist in solution as undissociated molecules, with B and Li atoms bonded through alkyl and/or aryl groups.[113]

(η^5-Cyclopentadienyl)(η^6-tetraphenylborato)iron, $CpFe(C_6H_5BPh_3)$, forms monoclinic crystals, space group $P2_1/c$, isostructural with the Ru analogue.[114]

The reactions of $(RO)_3SiBr$ with $ClB(NR^1R^2)_2$ and potassium in hexane give $(RO)_3SiB(NR^1R^2)_2$, where R = ^iPr or ^tBu; R^1,R^2 = CH_3 or $-CH_2-$. $(RO)_2SiBr_2$ produces mixtures including compounds with the bond sequences $>B-\overset{|}{\underset{|}{Si}}-B<$ and $>B-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{Si}}-B<$.[115]

3.1.6 Compounds containing B-N or B-P Bonds

Iminoboranes, RB≡NR, where R = Pr, ^iPr, Bu, ^iBu, ^sBu, $n-C_5H_{11}$, are formed by thermal decomposition of azidoboranes, R_2NBN_3, in the gas-phase or in solution. The monomers can be trapped at low temperatures from the gas-phase for R = ^iPr, ^iBu or ^sBu. All give dimers, trimers or polymers on standing.[116] Protic reagents, HX, where X = Cl, OR or NR_2, add to the triple bond of iminoboranes, ^{i}PrB N^{i}Pr or ^{t}BuB N^{t}Bu, in a rapid and uncatalysed



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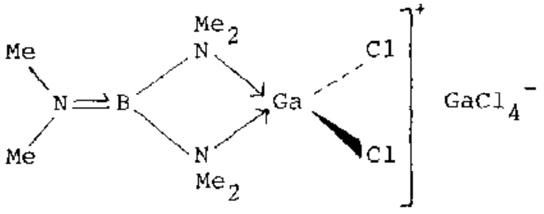
reaction, (10).[117]

^{t}BuNBPh$_2$ forms orthorhombic crystals, space group Pbca. The allene-like molecule has a dihedral angle of 94.4° between the C_2BN and NCC_2 planes. The B-N and N-C bond lengths (136.6, 124.4pm) and B-N-C angle (178.2°) indicate very substantial π-contributions to both bonds.[118]

The sterically demanding 2,4,6-tri-t-butylanilido ligand, NHAr, confers unexpected thermal stability on the compounds B(NHAr)X_2, where X = F, Cl or NH_2. For X = F, the B-N bond has definite double-bond character. For X = NH_2, one B-NH_2 bond is longer than the other, and both are longer than B-NHAr.[119]



(12)

Me_2BNMe_2 and RB$(NMe_2)_2$, where R = Me or Ph, form 1:1 adducts with $AlCl_3$, $AlBr_3$ and $GaCl_3$. B$(NMe_2)_3$ forms a 1:2 adduct with $GaCl_3$. The 1:1 adducts contain a simple Al-N or Ga-N coordinate bond, but the 1:2 species is (12).[120] Several esters derived from the boron analogues of amino-acids have been prepared, with general formula: amine.BH_2COOR, where amine = Me_3N, Me_2NH, $MeNH_2$ or NH_3; R = Me, Et, CH_2CH_2Cl. The method involves condensing the corresponding acids and alcohols with dicyclohexylcarbodi-imide in CH_2Cl_2 at room temperature.[121]

The adduct py.BF_3 forms monoclinic crystals, space group $P2_1/c$. The B-N distance is 160pm, with B-F in the range 133-136pm.[122] The ^{14}N nuclear quadrupole double resonances of several amine-trifluoroboranes and amine-boranes have been examined. The nitrogen coupling constants increase with increasing substitution of N-H by organic groups. This is consistent with a higher electronegativity for C than for H.[123] 1:1 crystalline complexes are formed between 18-crown-6 and $BF_3.NH_3$ or $BH_3.NH_3$. Crystal structures reveal an all-gauche conformation for the 18-crown-6 molecule. Bonding occurs via N-H---O interactions.[124]

The effect of the structure of the amine-fragment on the reactivities of borane-amine adducts towards hydrolysis, hydroboration and reduction has been studied. BH_3-N-phenylamine was found to be especially reactive towards hydroboration and reduction. Some suggestions were made about mechanisms, based on these data.[125] Kinetic studies have been made on the hypochlorite B-chlorination of tertiary alkylamine-boranes. Direct chlorination occurs, whereas for secondary amine-boranes oxidation occurs first, followed by chlorination of the free amine.[126] Rotational spectra have been reported for $BF_3.L$, where L = NCCN, CO_2 or NO_2. The NCCN adduct is a symmetric rotor, with a B-N bond length of 264 pm.[127]

Crystals of $(Me_2NBBr_2)_2$ have been prepared, and their entropy of sublimation determined. The i.r. spectrum of the dimer has νB-N at 940 cm^{-1}, with νB-Br as a doublet (790, 770 cm^{-1}).[128] Several new species, $(Me_3Si)_2NB(R)X$, where X = Cl, R = ^tBu, ^iPr or CH_2SiMe_3; X = ^tBu, R = CH_2SiMe_3; X = NMe_2, R = Me, ^iPr, ^tBu or CH_2SiMe_3, were prepared from $(Me_3Si)_2NBCl_2$ by chloride displacement with organometallic reagents and Me_3SiNMe_2. Rotational barriers about the B-NMe_2 bond were determined by dynamic ^1H n.m.r. spectroscopy, and discussed in terms of steric interactions between bulky groups on the boron.[129]

Several boron analogues of amino-acids, i.e. (ethylcarbamoyl)-borane adducts, have been prepared by the reaction sequence (11),

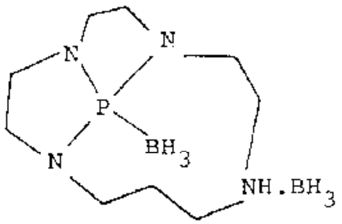
$$Me_3N.HCl \;+\; NaBH_3CN \xrightarrow{THF} Me_3N.BH_2CN \xrightarrow{Et_3O^+BF_4^-}$$

$$Me_3N.BH_2CNEt^+BF_4^- \xrightarrow{M.NaOH} Me_3NBH_2C(O)NHEt \xrightarrow{RR'NH}$$

$$RR'NH.BH_2C(O)NHEt \qquad \ldots(11)$$

where R,R' = H or Me. All were characterised by elemental analyses, i.r., ^1H, ^{11}B and ^{13}C n.m.r.[130]

Crystals of cyclamphosphine-bis(borane) are monoclinic, space group $P2_1/c$. Only one diastereoisomer of (13) is present:

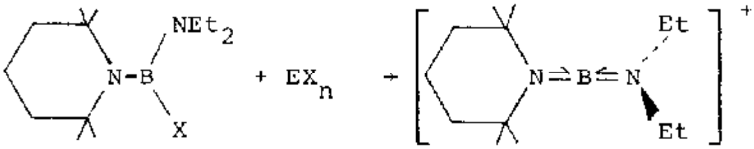


(13)

(R,S;S,R), in which the P-B and N-B bonds are trans to each other, with respect to the mean plane of the molecule.[131]

The salt $Fe(NO)_2[PhP(OCH_2CH_2)_2NH_2{}^+[_2[BPh_4{}^-]_2$ is converted at room temperature to the corresponding bis(phosphane-amine-triphenylborane) adduct: $Fe(NO)_2[PhP(OCH_2CH_2)_2N(H).BPh_3]_2$. Variable-temperature ^{31}P n.m.r. spectra of the latter reveal (in DMF solution) stepwise and reversible dissociation of the two BPh_3 groups.[132]

Bis(amido)boron(1+) cations can be generated from bis(amino)-boron halides and an appropriate halide acceptor, i.e. (12), with



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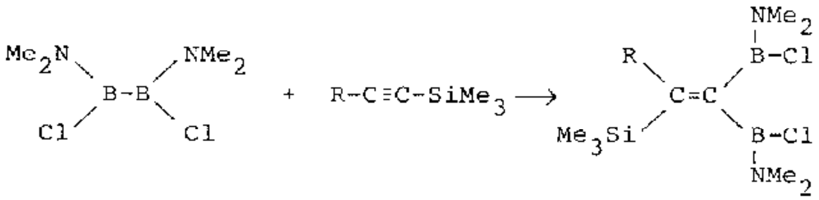
E = Al, Ta or Ga, X = Cl; E = Ga or Ta, X = Br; E = B, Al, X = I. The ease of cation formation increases with decreased strength of the B-X bond.[133]

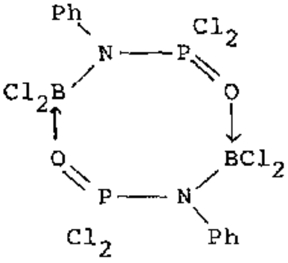
1:1-Diboration of 1-trimethylsilylalkynes has been studied, e.g.



...(13)

(13, where R = Ph or $SiMe_3$) and related systems.[134] Tertiary amines with low steric hindrance readily displace Br^- from bromodifluoroborane adducts of tertiary amines ($D.BF_2Br$; D = donor) to form bis(tertiary amine)difluoroboron cations, $DD'BF_2{}^+$, D=D'= py, quinuclidine, Me_3N, Me_2NEt, $MeNEt_2$; D = quinuclidine; D' = py, Me_3N, Me_2NEt, $MeNEt_2$, Et_3N.[135]

Several routes have been devised for the preparation of (phosphorylamino)boranes, $X_2P(O)-NR'-BR_2$, where X = R = R' = Me; X = NMe_2, R = Me, NMe_2, R' = Me; X = Cl, R' = Me, R = NMe_2, Me, Et, Cl, Br; X = Cl, R' = Ph, R = Cl. Monomers are present in solution for R = X = NMe_2. For X = Cl, NMe_2; R = Me, the isomers $X_2P(NR')-O-BR_2$ are also present. For X = R = Cl, or X = Cl, R = Br, only dimers are present. The crystal structure of $[Cl_2P(O)-NPh-BCl_2]_2$ shows that there is an 8-membered ring present, in a chair-like conformation, (14).[136]



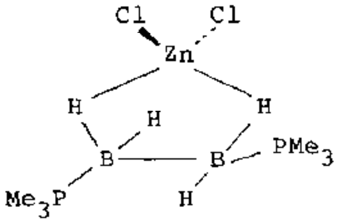
(14)

Rate constants for the reactions (14) are in the sequences:

$$Ph_2BNR_2 + PhNCO \rightarrow Ph_2B-N(Ph)-C(=O)NR_2 \qquad ...(14)$$

NR_2 = $NH^nBu > NMe_2 > NH^tBu$; $NH^nBu > NH^iBu > NH^sBu$.[137]

^{11}B, ^{15}N and ^{31}P n.m.r. data have been reported for $(Me_2N)_3PBH_3$.[138] $B_3H_6.2PMe_3^+$ $B_3H_8^-$ reacts with Lewis bases in a 1:2 molar ratio to form $B_4H_8.PMe_3.L$, $BH_3.PMe_3$ and $BH_3.L$, where L = NMe_3, PMe_3 or $P(NMe_2)_3$.[139]



(15)

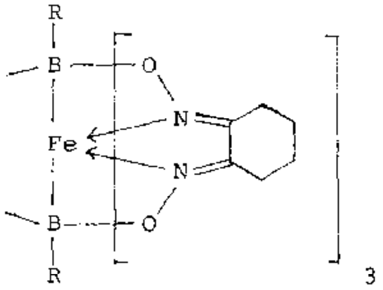
Metal complex formation was reported for the neutral adduct $B_2H_4.2PMe_3$, e.g. $ZnCl_2.B_2H_4.2PMe_3$. N.m.r. data showed the structure to be (15). Characteristic νBH_t and νB-H-M bonds were seen in the spectra of this and related Cu(I) complexes.[140]

3.1.7 Compounds containing B-O or B-S Bonds

A variety of O-diorganoboryl derivatives of (organo)phosphorus acids, e.g. $EtP(=O)OBEt_2$, were prepared from the acids and activated BEt_3, bis-9-borabicyclo[3.3.1]nonane or tetraethyldiboroxane.[141]

Ab initio (Hartree-Fock-Roothaan) m.o. calculations on $LiBO_2$ indicate a linear equilibrium configuration for the atoms. Only fair agreement was achieved between calculated and experimental vibrational wavenumbers.[142] However, matrix i.r. spectra of MBO_2, where M = Li, Na, K, Rb or Cs, show that they have C_s symmetry. Although O-B-O is linear, the M-O-B is definitely non-linear. νM-O modes were identified for the first time: 470/496 cm^{-1} (M = Li), 363 cm^{-1} (Na), 265 cm^{-1} (K), 226 cm^{-1} (Rb) or 207 cm^{-1} (Cs).[143] Solubility and refractive indices were measured in the systems NaX-$PhNH_2$-H_2O, where X = BO_2, B_4O_7 or B_5O_8.[144]

The compounds $Fe(Niox)_3(BR)_2$, where H_2Niox = cyclohexanedione oxime, R = F, OH, OMe, OEt, OBu, OPh, have been prepared and shown to have a macrobicyclic structure, (16).[145]



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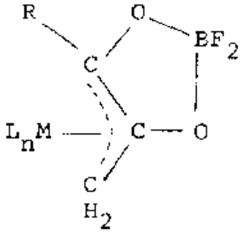


(17)

When ferra-, mangana- or rhena-β-diketonate complexes, $L_nM(CH_3C\overline{O)(RC\underline{O)}}BF_2$ are treated with KH, proton loss occurs from the acetyl ligand to form anionic, η^3-allyl complexes,

$\{L_nM[\eta^3\text{-}CH_2C\overline{OC\underline{O(R)B}}F_2]\}^-$, where L_nM = Cp(OC)Fe, *cis*-$(OC)_4$Mn or *cis*-$(OC)_4$Re; R = Me or ^{i}Pr, i.e. (**17**).[146]

The He(I) photoelectron spectrum has been recorded for B_2O_2. Comparison of this with *ab initio* m.o. calculations shows conclusively that the molecule is linear ($D_{\infty h}$) O=B–B=O.[147]

The hitherto-unknown $KNa_2[BO_3]$ has been prepared. It crystallises in the orthorhombic system (space group Pmmn), and its crystals are very sensitive to atmospheric moisture.[148] Solubility and refractive indices were measured for the systems H_3BO_3-MNO_3-H_2O, where M = Li, Na or K.[149] The solubility of H_3BO_3 was also studied in aqueous solutions of alkali metal and ammonium dichromates,[150] and of $SrCl_2$.[151]

^{11}B n.m.r. and i.r. studies show that H_3BO_3 is extracted from aqueous solutions by 2-ethylhexanol as tris(2-ethylhexyl)-borate.[152] Boric acid, H_3BO_3, reacts with lactic acid, $CH_3CH(OH)COOH$, to form anionic complexes, with both 1:1 and 1:2 stoichiometries. The boron is four-coordinate in each case.[153] $[B(PO_2F_2)_4]^-$ is formed from H_3BO_3 and $P_2O_3F_4$ in HPO_2F_2 solution; it was characterised by ^{11}B, ^{19}F and ^{31}P n.m.r.[154]

$Ba_3[BCo(H_2O)W_{11}O_{39}].26H_2O$ forms tetragonal crystals, space group P4/mmc. The anion $BM_{12}O_{40}H_2{}^{6-}$ (where M = $Co_{1/12}W_{11/12}$) has the Keggin, α-$PW_{12}O_{40}{}^{3-}$, structure, and tetrahedrally-coordinated boron.[155]

Raman spectra of vitreous B_2O_3 were measured in the temperature range 8-700K and (at room temperature) at pressures up to 8 kbar. At room temperature the structure comprises equal proportions of boroxol (B_3O_6) rings and BO_3 triangles. Near glass transition temperatures, the B_3O_6 rings break up.[156] I.r. spectra were reported for the mixed alkali diborate glasses $(Li,Na)_2O.2B_2O_3$ and $(Li,K)_2O.2B_2O_3$. The B-O stretch and B-O-B deformation modes exhibit non-linear shifts in wavenumber with changing composition.[157]

Phase relationships have been elucidated in the systems Li_2O-B_2O_3-Ga_2O_3,[158] Li_2O-B_2O_3-Nb_2O_5,[159] and PbO-Bi_2O_3-B_2O_3.[160] Bismuth borate, BiB_3O_6, forms monoclinic crystals, space group C2. The anions are sheets built up of BO_3 triangles and BO_4 tetrahedra (ratio 2:1). This is a new type of phylloborate.[161]

The enthalpy of solution of $Na_2B_4O_7.10H_2O$ in HCl and NaOH solutions was used to calculate the standard enthalpy of formation of crystalline $Na_2B_4O_7.10H_2O$: -6286.4 ± 1.5 kJ.mol^{-1}.[162]

$Rb[B_5O_6(OH)_4].2H_2O$ forms orthorhombic crystals (space group Aba2), while crystals of $Cs[B_5O_6(OH)_4].2H_2O$ are monoclinic ($P2_1/c$). However, both contain isolated $B_5O_6(OH)_4$ units.[163,164]

(FBS), $(FBS)_2$ and $(FBS)_3$ are produced by pyrolysis of various sulphur fluorides over boron. They are unstable, but He(I) photoelectron spectra were obtained. Ab initio m.o. calculations were consistent with their identification, and assisted in the assignment of the spectra.[165]

CS_2 and $NaBH_4$ react in THF, MeCN or DMF according to equation (15). The reaction involves stepwise insertion to the B-H bonds

$$5NaBH_4 + 4CS_2 \rightarrow Na_5[B(S\text{-}CH_2\text{-}S)_4] + 2B_2H_6 \qquad \ldots(15)$$

of BH_4^-, and H^- transfer from BH_4^- to the intermediates.[166]

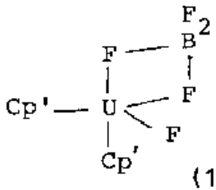
$Ag_6B_{10}S_{18}$ is prepared from stoichiometric amounts of Ag_2S, B and S at 700°C, with annealing at 580-460°C. The structure contains "super tetrahedra" $B_{10}S_{20}$ made up of 10 parallel, corner-sharing BS_4 tetrahedra. The $B_{10}S_{20}$ groups are linked via corners to give a layer-like arrangement, $(B_{10}S_{16}S_{4/2}{}^{6-})_n$. The mean B-S bond length is 191.5pm. Five i.r. bands ($610\text{-}760cm^{-1}$) are thought to be associated with νB-S.[167]

3.1.8 Boron Halides

Electron-impact fragmentation studies have been performed on $BF_3(g)$. The appearance potentials for BF_2^+, BF^+, B^+ are 16, 24, 30eV respectively. The appearance potential for BF_2^+ is only 0.2eV greater than the ionisation potential of $BF_3(g)$.[168] Ab initio (SCF-MO-LCAO) calculations on $LiBF_3^+$ suggest a preferred planar, unidentate structure of C_{2v} symmetry. The C_{3v} (terdentate) structure is unstable with respect to $Li^+ + BF_3$.[169]

There is F.T.i.r. evidence for the formation of weakly-bound complexes $BF_3.CO$ and $BF_3.N_2$ by co-condensation on to a cold CsI window.[170] Solid-liquid equilibria were studied in the systems $XF_5\text{-}BF_3$, where X = Cl or Br.[171]

Hydrolytic equilibria were studied in the system $LiBF_4\text{-}H_2O\text{-}\gamma$-butyrolactone.[172] $ClO_2^+BF_4^-$ forms monoclinic crystals, space group Cc. All four fluorines of BF_4^- form van der Waals contacts with Cl atoms of neighbouring ClO_2^+ ions.[173] $[UCp_2'(\mu\text{-}BF_4)(\mu\text{-}F)]_2$ has a pair of bridging bidentate BF_4^- ligands, and a $(\mu\text{-}F)_2$ arrangement. Mean U-FB, U-F and B-FU bond lengths were 241, 231, 134pm respectively, with B-F(terminal) 138 and 123pm. In solution, the dimer is in equilibrium with a monomer. N.m.r. data suggest that the structure of this is (18),[174] where



(18)

Cp' = η-$C_5H_3(SiMe_3)_2$.[174] Variable-temperature ^{19}F n.m.r. spectra of $[Re(CO)_3(tmen)(OH_2)]^+BF_4^-$ in CD_2Cl_2 solutions show the presence of equilibrium (16), where tmen = N,N,N',N'-tetramethylethan-1,2-diamine.[175]

$$Re(CO)_3(tmen)FBF_3 + H_2O \rightleftharpoons [Re(CO)_3(tmen)(OH_2)]^+ + BF_4^- \quad ...(16)$$

Trimethyl- and triethylsilyltrifluoromethanesulphonates (triflates) form strongly-polarised BX_3 (X = Cl, Br) complexes. ^{29}Si and ^{11}B chemical shifts indicated four-coordinate boron, and a partial positive charge on Si, involving O-coordination of the triflates with BX_3.[176]

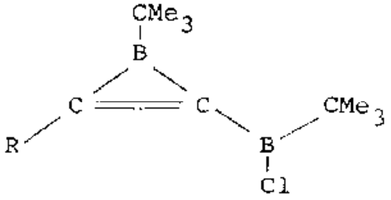
While passing BX_3, where X = Cl or Br, through an r.f. discharge to form B_2X_4 and B_4Cl_4, evidence was found for the intermediate formation of BX.[177] $Na_2B_6H_6$ and X_2 (where X = Cl, Br or I) react in aqueous alkaline solution to give $B_6X_6^{2-}$. ^{11}B n.m.r. spectra confirmed their octahedral structures, and revealed that the chemical shifts were in the sequence H < Cl < Br < I. I.r. and Raman spectra were also consistent with O_h symmetry, and showed that B_6 modes were insensitive to changing X.[178]

3.1.9 Boron-containing Heterocycles.

The simplest boron compounds with aromatic character have been prepared, (19; R = ^tBu, $SnMe_3$). Cyclic delocalisation of the two π-electrons, (20), was detected by n.m.r. measurements.[179]

A three-centre π-bond and a BC double bond were predicted in the $C_2B_2H_4$ isomer, (21). This is the parent of the first B=C bonded compound, (22).[180]

The first 1,3-diboretanes were formed by the reaction of (22)



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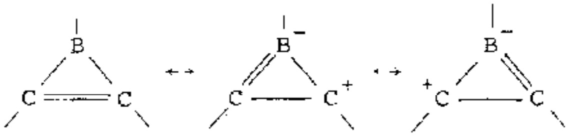

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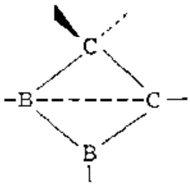

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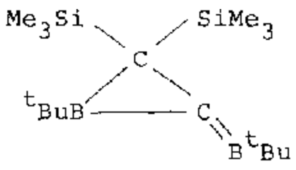
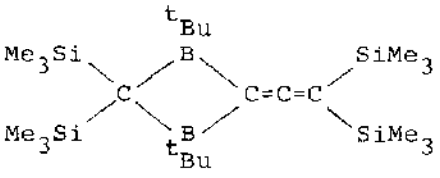


(22)

with, for example $Me_3SiC{\equiv}CSiMe_3$, giving (23).[181]



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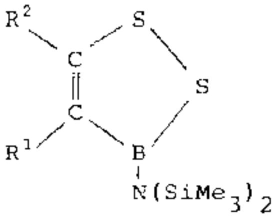

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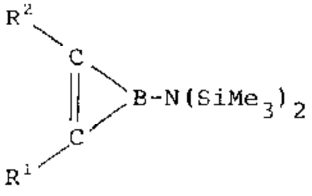

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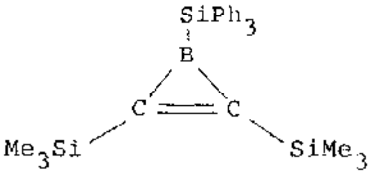
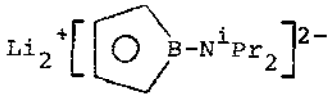


(26)

The 1,2,3-dithiaboroles, (24), where R^1 = H, R^2 = ^nPr, ^nBu, Ph; R^1 = Me, R^2 = ^nPr; R^1 = R^2 = Et, react with sodium, undergoing ring contraction to form the hitherto unknown 1-[bis(trimethylsilyl)amino]borirenes, (25).[182] A carbene- or nitrene-analogous boron species Ph_3SiB: is generated by photolysing $RB(SiPh_3)_2$ or $B(SiPh_3)_3$. It cyclo-adds to -C≡C- bonds to give borirenes such as (26).[183]



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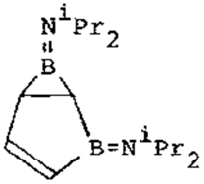

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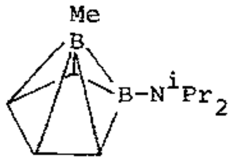
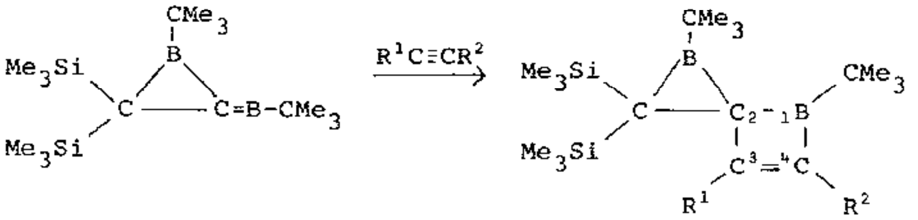


(29)

It has been possible to prepare both "classical" and "non-classical" derivatives of $C_4B_2H_6$. Depending upon the pattern of substitution, the borole dianion, (27), can be converted to the classical 2,6-diborabicyclo[3.1.0]hex-3-ene derivative, (28), or the *nido*-carbaborane, (29).[184]

Quantum-mechanical calculations show that 1,2-dihydroborete, (30), should have a puckered form, as shown, like the cyclobutenyl cation. A relatively strong 1,3-interaction was predicted, with potential homoaromatic character.[185] This prediction was borne out when the first 1,2-dihydroboretes were prepared, equation (17), where $R^1 = R^2$ = Me or Ph; R^1 = H, R^2 = CMe$_3$. Experimental evidence was found for a strong 1,3-interaction, hence they can be formulated as homoborirenes.[186]



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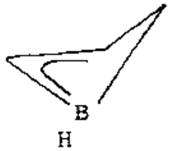

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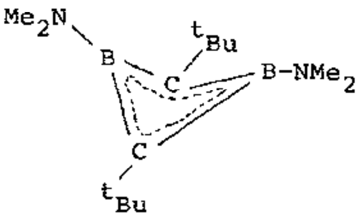
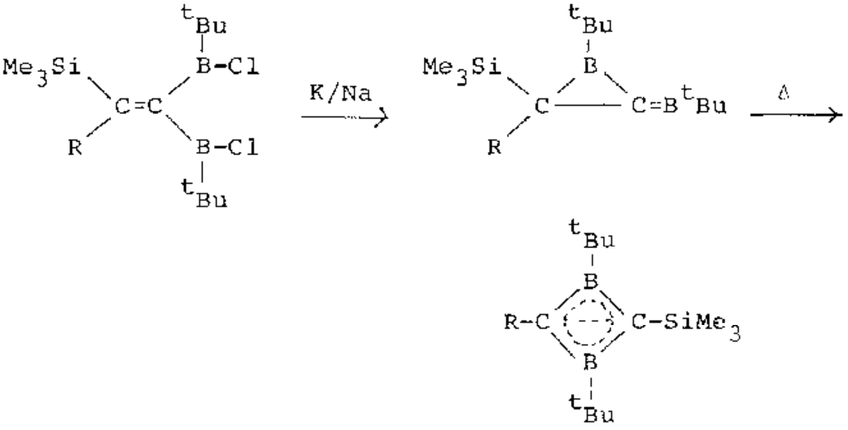


(31)

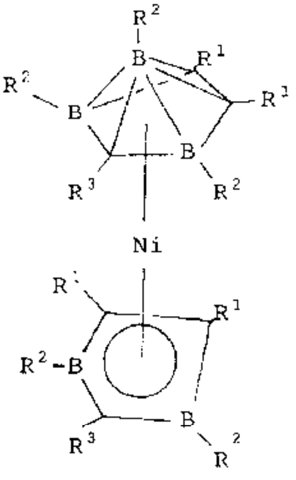
A non-planar B_2C_2 skeleton was found in the 1,3-dihydro-1,3-borete, (31), prepared by dehalogenation of the 1,2-diborylethene, $Me_2N(Cl)B-C(^tBu)=C(^tBu)-B(Cl)NMe_2$. The ring BC bonds are rather short, and the C-C ring distance is 181pm.[187] Other non-planar



...(18)

1,3-dihydro-1,3-boretes were prepared as in (18), where R = $SiMe_3$ or neopentyl.[188]

Carbaboranylnickel complexes have been reported which contain the novel η^5-2,3,5-tricarbahexaboranyl ligand, including (32) and (33), where $R^1 = R^2 = Et$, $R^3 = Me$; $R^1 = R^2 = Me$, $R^3 = H$; $R^1 = Et$, $R^2 = Me$, $R^3 = H$.[189]



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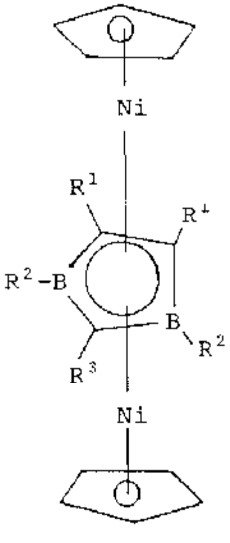

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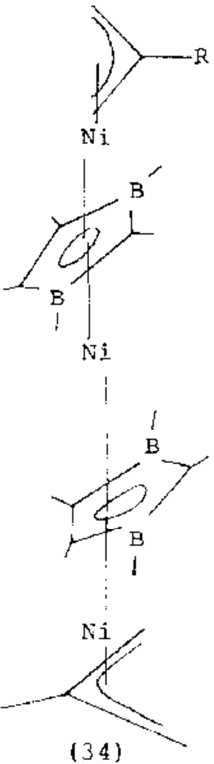
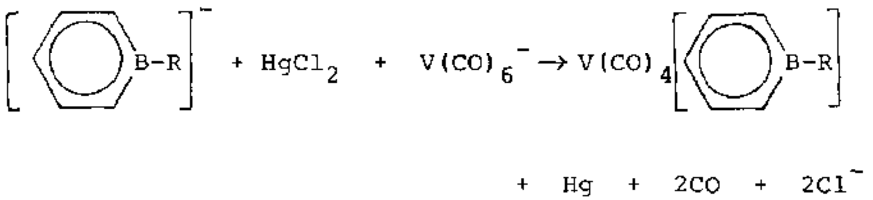


(34)

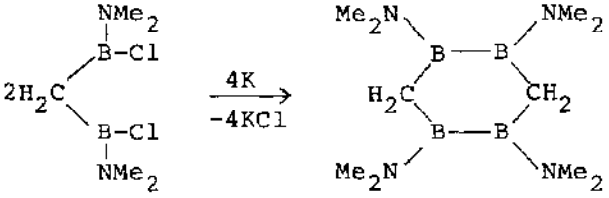
The first η^3-allyl tetradecker sandwich complexes, (34, R = H or Me) have been prepared from reactions between bis(allyl)nickel complexes and alkyl derivatives of 2,3-dihydro-1,3-diborole.[190]

$M(C_5H_5BR)$, where M = Na or K, R = Me or Ph, react with VCl_3 to give paramagnetic sandwich complexes, $V(C_5H_5BR)_2$. Reaction (19) produces $V(CO)_4(C_5H_5BR)$. The crystal structure of this (R = Me) shows that the $V(CO)_4$ is rotated by 10.4° from an ideal eclipsed conformation.[191]



...(19)

A B_4C_2 skeleton has been stabilised for the first time in a classical B-C compound, by introducing electron-rich NMe_2 groups, (20). Crystals of this compound contain molecules in the chair-conformation. Replacing NMe_2 by H or alkyl produces carbaborane systems.[192]



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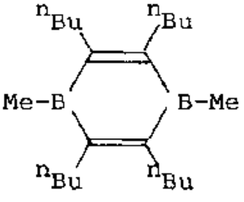
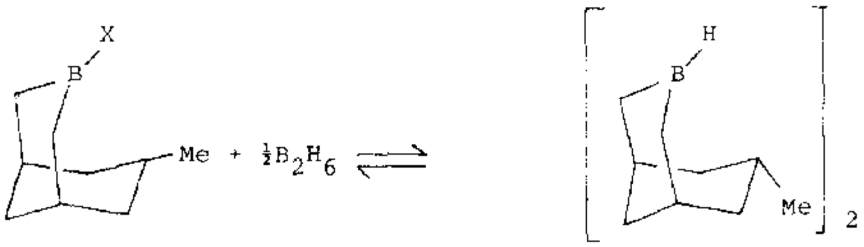


(35)

The methylborylene-generating system $2C_8K/MeBBr_2$ reacts with di-n-alkylacetylenes to form, for example, (35).[193] The dimer of 7-methyl-3-borabicyclo[3.3.1]nonane was prepared by the reaction of diborane with 3-methoxy(or chloro)-7-methyl-3-borabicyclo[3.3.1]nonane, equation (21, X = OMe or Cl).[194]



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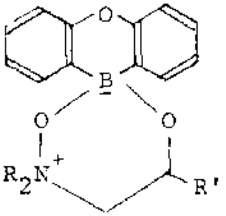
Various diarylboron chelates of the cyclic *B*,*N*-betaine type, e.g. (36, where R_2N = Et_2N, piperidino, morpholine; R' = Me or Ph), have been synthesised from N-(2-hydroxyalkyl)-*N*,*N*-dialkylamine-*N*-oxides and diarylboron reagents.[195]



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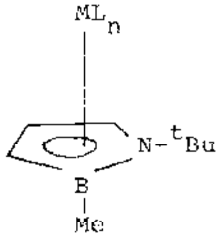
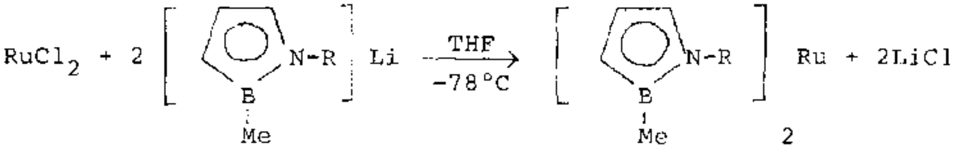


(37)

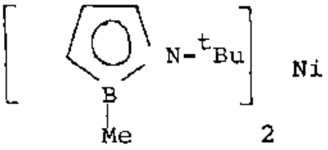
New Mn and Mo carbonyl complexes of the 1-*t*-butyl-2-methyl-η-1,2-azaborolinyl ligand have been prepared, (37, ML_n = $Mn(CO)_3$ or $Mo(CO)_2(\eta^3\text{-allyl})$). The chirality of the azaborolinyl ring leads to formation of enantiomers - present as a racemate in crystals of the molybdenum complex.[196] Bis(η^5-1,2-azaborolinyl)ruthenium sandwich complexes are prepared as in equation (22, R = Me_3C or Me_3Si). Each complex has two isomers - with clockwise and anticlockwise conformations of the azaborolinyl rings.[197]



...(22)

(38) is prepared from $NiBr_2$ and 1-*t*-butyl-2-methyl-1,2-azaborolinyl-lithium in THF at -78°C. The azaborolinyl is for the first time shown to be acting as an η^3- rather than an η^5-ligand. Only

the carbon atoms are effectively coordinated to the metal.[198]



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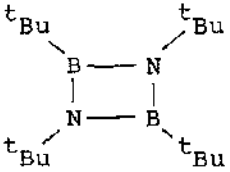
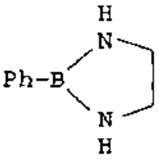


(39)

The iminoborane ${}^{t}BuB{=}N{}^{t}Bu$ is formed from the aminoborane $Cl({}^{t}Bu)B{-}N({}^{t}Bu)SiMe_3$ by elimination of Me_3SiCl in the gas phase at 530°C. The monomer slowly dimerises to (39). X-ray diffraction shows that the monomer has a linear CBNC chain (B-N 125.8pm), but that the dimer has a non-planar B_2N_2 ring, due to the presence of the bulky ligands.[199]

Mass spectra of derivatives of 2-phenyl-1,3,2-diazaboracycloalkanes, (40) and (41), contain peaks due to tropylium, boratropylium, cyclopentadienyl and boracyclopentadienyl ions.[200]



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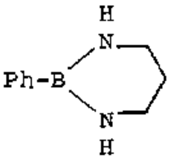

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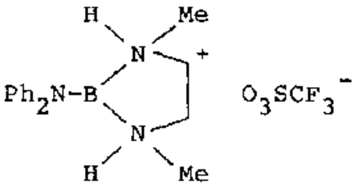
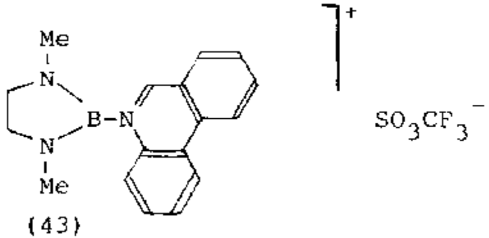


(42)

Three-coordinate boron is found in the cation (42), i.e. there is no interaction between B and the anion in the solid state. All three B-N bond lengths are different (138.6, 141.2, 154.7 pm).[201] N.m.r. data suggest that pyridine, but not phenanthridine, react with 2-chloro-1,3-dimethyl-1,3,2-diazaborolidine to form an ionic compound. However, phenanthridine and 1,3-dimethyl-2-trifluoromethanesulphonato-1,3,2-diazaborolidine give (43).[202]

(44), where Y = Me, Ph, Cl or Br, react with AlX_3 or GaX_3 to form (45), where Y = Me, E = Al, Ga, X = Cl, Br or I; Y = Ph, E = Ga, X = Cl; Y = Cl, E = Al, X = Br; Y = Cl, E = Ga, X = Cl; Y = Br, E = Al, X = Br. The B-N bond involving the four-coordinate nitrogen is much longer, but that to three-coordinate nitrogen is shorter than in the original heterocycle.[203] Alkyl-



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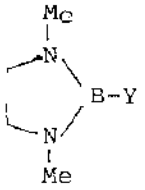

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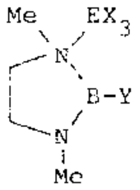
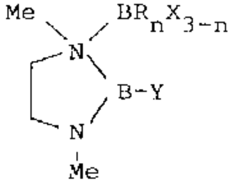


(45)

halogenoboranes, R_nBX_{3-n} (n = 0-2), and 1,3-dimethyl-1,3,2-diazaborolidines also form stable 1:1 addition compounds, (46), where Y = Me, n = 1,2, X = Cl, Br, I; Y = Me, n = 1,2, X = Br, R = Me; Y = Ph, n = 0, X = Cl; Y = Cl, n = 0, X = Cl, Br; Y = Cl, n = 1, X = Cl, R = Ph; Y = Cl, n = 2, X = Br, R = Ph; Y = Br, n = 0, X = Br. For the BCl_3 adduct (Y = Cl) there are two enantiomers in the asymmetric unit, an envelope ring conformation, and strong π-bonding between the boron and non-coordinated N atoms.[204]



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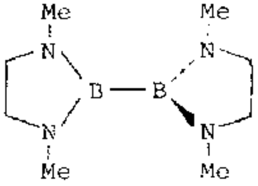

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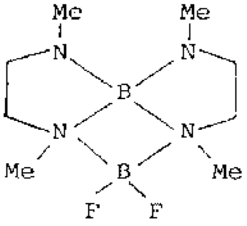

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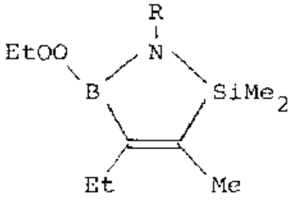
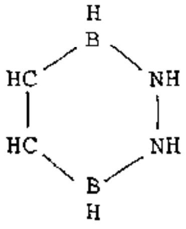


(49)

(47) forms 1:1 and 1:2 adducts with the trihalides EX_3 (E = B, Al or Ga; X = Cl, Br or I). The $AlCl_3$ and $GaCl_3$ 1:1 adducts show fluxional behaviour, unlike the 1:1 BBr_3 adduct and all of the 1:2 adducts. The diazaborolidine ring changes from the planar to the envelope form an adduct formation.[205] 2-Fluoro-1,3-dimethyl-1,3,2-diazaborolidine dimerises in an anomalous fashion, to the fluxional tricyclic species (48).[206]

(49), where R = Me, Ph or CH_2Ph, contain a thermally-stable ethylperoxyboron unit. They are prepared by the simple addition of O_2 to the corresponding Et-B heterocycle.[207]

Minimal STO-nG (n = 3,4 or 6) basis set non-empirical HF-SCF-MO calculations were carried out on the topologically related (50) and (51). The 2,5-diaza derivative is 48 kJ.mol^{-1} less stable than the 2,3-analogue.[208]



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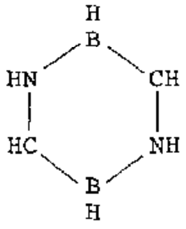

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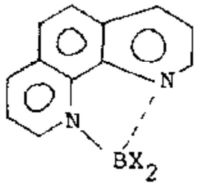
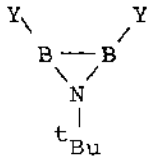


(52)

^{11}B n.m.r. data and crystal structure determinations were reported for (52, X = F, Br or I). They contain a five-membered NBNCC heterocycle, with two different B-N bonds (B-N 149(2)pm; B---N 158(2)pm).[209]



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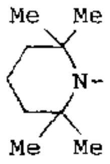

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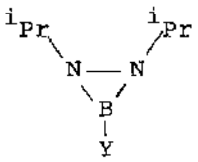
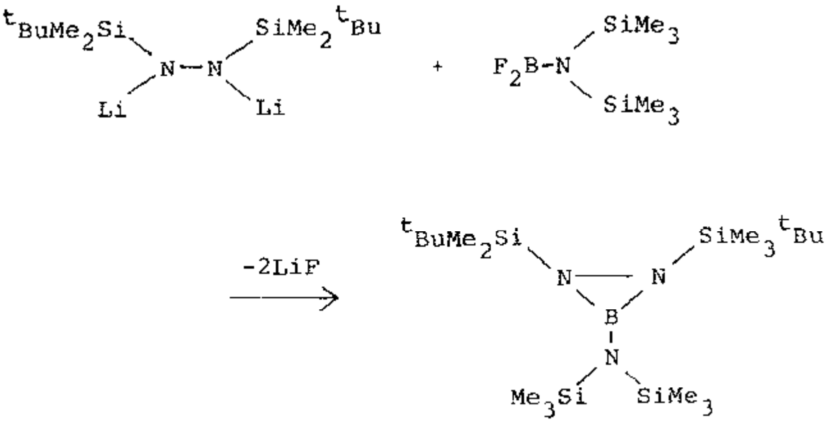


(55)

N.m.r. data on 1-t-butyl-2,3-bis(2,2,6,6'-tetramethylpiperidino)-1-aza-2,3-diboririne, (53, Y = 54), are consistent with a 2π-electron system. For (55), however, non-planar nitrogen coordination is suggested.[210] A new BN_2 ring compound is formed by reaction (23).[211]

Iminoboranes, $RB{\equiv}N^tBu$, where R = Me, Et or ^{i}Pr, undergo catalytic cyclodimerisation at -10°C to -20°C to (56). At 50°C cyclotrimerisation to (57) is preferred. For R = Bu the dimer is kinetically stable with respect to the trimer, but it can form the trimer by reaction with excess monomer.[212]

$(Me_3CNHBF_2)_2$ forms orthorhombic crystals, space group Pbca. The dimers, (58), have an exactly planar B_2N_2 ring (B-N 159.5pm; BF 135.5, 136.6pm).[213] A number of cations containing three-



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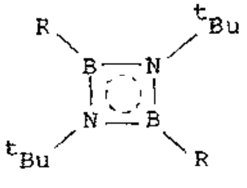

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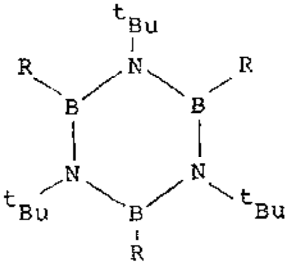

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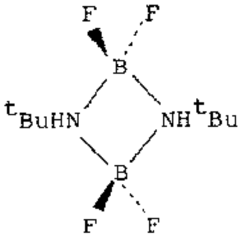
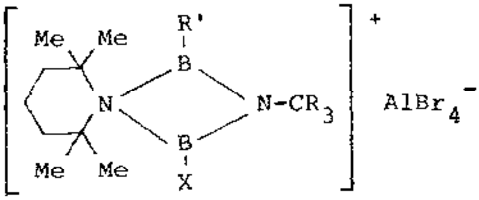


(58)

coordinate boron have been prepared, e.g. (59), where R' = X = Br; R' = Me, X = Br; R' = Ph, X = Cl; R = Me.[214]



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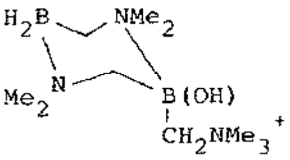

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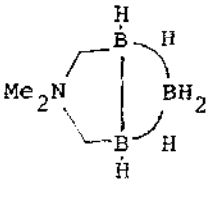
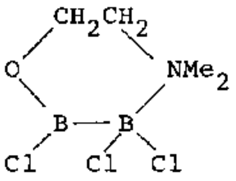


(61)

Hydrolytic and cleavage reactions of two B-C-N sequenced boranes led to characterisation of a volatile hydroxylated species

(60), and the triborane (61). The B-C-P species $Me_2P(CH_2BH_2)_2H$ and $BH_2CH_2Me_2PCH_2BH_2NMe_2$ were also prepared.[215]



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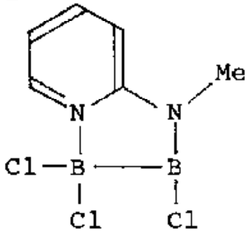

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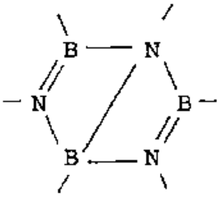
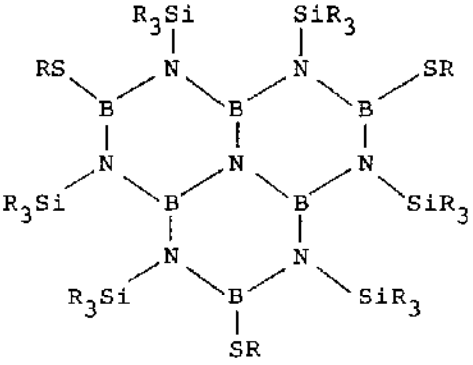


(64)

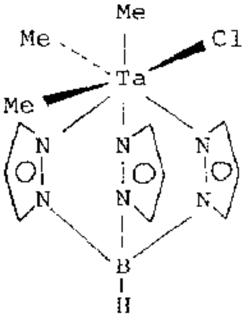
$Cl_2B\text{-}BCl_2$ reacts with suitable bifunctional bases to form molecules containing directly-bonded boron atoms with different coordination numbers, e.g. (62), (63) etc.[216] $^{i}PrB{\equiv}N^{t}Bu$ (metastable at -78°C) trimerises at higher temperatures to $(^{i}PrBN^{t}Bu)_3$, which has a Dewar-borazine type of structure, with two short peripheral BN double bonds (136,138pm) and an extra-long B-N single bridge bond (175pm), (64).[217]



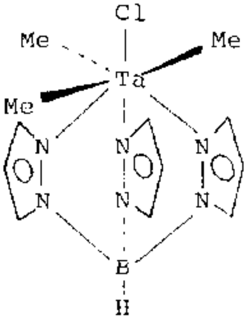
(65)

A novel compound with annelated BN 6-membered rings, (65), is formed in good yield from $B(SR)_3$ and $R_3SiN(SnR_3)_2$, where R = Me. Because of steric strain it is non-planar.[218] Pyrazaboles, $H_2B(\mu\text{-}pz)_2BRR'$, where pz = pyrazolyl; R = R' = H; R = H, R' = pz; R = R' = pz, are prepared by the reaction of pyrazol-1-ylborate ions with $Me_3N.BH_2I$. Analogous species containing 3,5-Me_2pz were also reported.[219]

$TaMe_3Cl_2$ and poly(pyrazolyl)borate ligands $[HB(pz)_3]^-$ or $[HB(3,5\text{-}Me_2pz)_3]^-$ react to form $[HB(pz)_3]TaMe_3Cl$ or $[HB(3,5\text{-}Me_2pz)_3]TaMe_3Cl$, which are remarkably stable for alkyl-

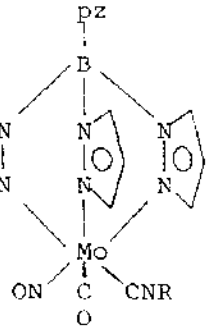


(66)



(67)

tantalum species. The [HB(pz)$_3$]-derivatives show the presence of two isomers, (66) and (67) in solution.[220]



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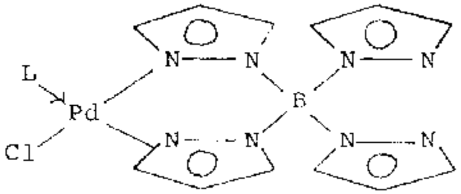
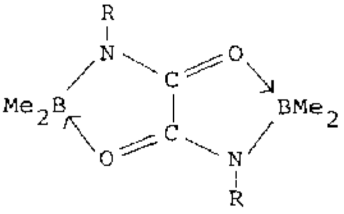


(69)

The syntheses of enantiomeric and diastereomeric forms of (68, M = Mo or W, R = Et, CH$_2$Ph or CHMePh) have been described.[221] PdCl(Bpz$_4$)L, where L = PEt$_3$ or P(OEt)$_3$, (69), show fluxional behaviour of the Bpz$_4$ ligand, leading at high temperature to spectroscopic equivalence of all four pyrazolyl groups.[222]



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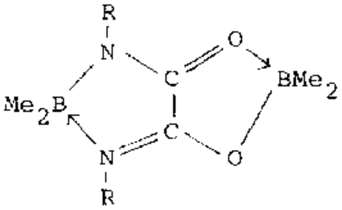
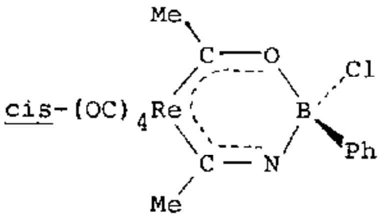


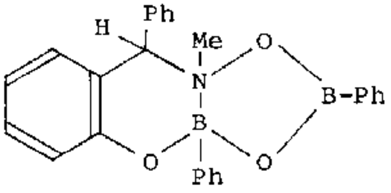
(71)

Reactions of symmetrically substituted *N*,*N'*-dialkyl(diaryl)-ethandiamides and Me_2BBr give a variety of products, depending on the substituents and conditions. Thus, in 1:2 ratio (**70**, R = Me, Et, ^nPr, ^iPr, ^nBu) are formed, with smaller amounts of (**71**).[223]

The crystal structure of the β-ketoiminato complex $[\textit{cis}\text{-}(OC)_4Re(CH_3\overline{CO)(CH_3C\underline{NH)]B}}(Cl)Ph$ confirms the coordination of the rhena-β-ketoiminato moiety to boron as a bidentate, chelating ligand. The electron density in the rhena-chelate ring appears to have a delocalised π-electron structure (**72**).[224]

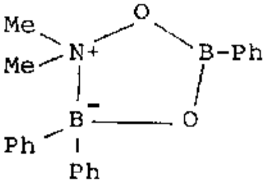


(**72**)

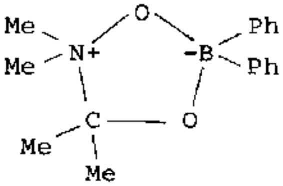


(**73**)

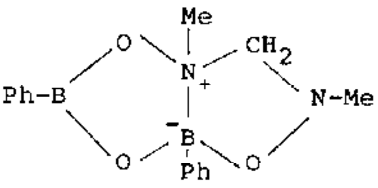
The preparation and crystal structure of (**73**) has been reported. Three fused rings are present, and the longest B-N bond yet recorded (176pm).[225] Other compounds recorded as having unusually long B-N bonds are (**74**), (**75**),[226] and (**76**).[227]



(**74**)

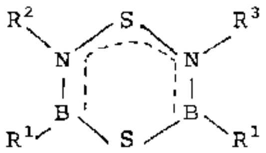


(**75**)

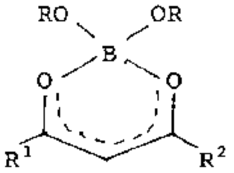


(**76**)

The new B-N-S ring compounds (**77**, R^1 = Me, R^2 = $SiMe_3$, R^3 = $SiMe_3$, ^tBu; R^1 = Me, R^2 = R^3 = ^tBu; R^1 = NEt_2, R^2,R^3 = $SiMe_3$, ^tBu; R^1 = $N(SiMe_3)_2$, R^2 = R^3 = $SiMe_3$) are prepared by the reaction of 3,5-dialkyl-substituted-1,2,4-trithia-3,5-diborolanes with 1,3-disubstituted sulphur di-imides.[228]

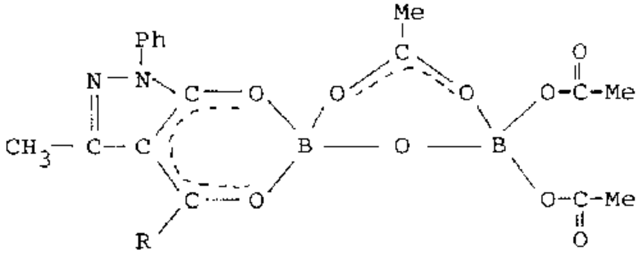


(**77**)



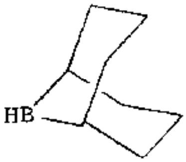
(**78**)

U.v. and visible spectra were reported for the substituted 1,3-diketoborates, (78, $(RO)_2$ = oxalyl; R^1 = R^2 = Ph, 4-ClC_6H_4, 4-MeC_6H_4, 4-$(MeO)C_6H_4$, 2-naphthyl; R^1 = Me, Ph, 2-naphthyl, R^2 = Me).[229]



(79)

New β-diketone derivatives of boron, $B_2O(OAc)_{4-n}[OC(R)\overline{C=CON(Ph)-N=C}CH_3]_n$, where n = 1 or 2, R = Me, Et, Ph or p-ClC_6H_4, were prepared by reactions of oxy-bis(diacetatoborane) and substituted pyrazolones. For n = 1, one acetate is bridging, the other two are unidentate, (79).[230] Pivalic acid and (80, = HB⊂) react to form (81), which contains an almost planar six-membered ring with a three-centre, two-electron B-H-B bond.[231]



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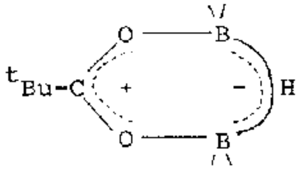

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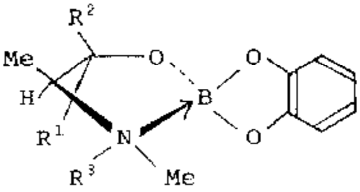
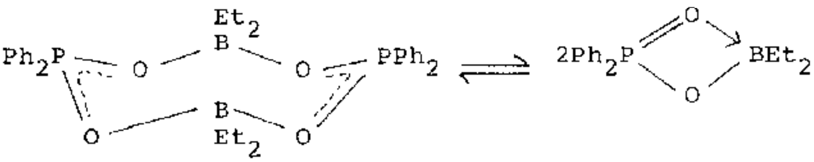


(82)

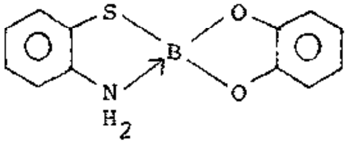
The novel spiroborates, (82, R^1 = H, R^2 = Ph, R^3 = H or Me; R^1 = Ph, R^2 = H, R^3 = H or Me) are formed by the reaction of catecholborane with ephedrine-type amino-alcohols. They are useful models for the study of intramolecular N→B coordination by ^1H, ^{11}B and ^{13}C n.m.r.[232]



(83)

Diorgano(phenylphosphinoyloxy)boranes, $R_2BOP(=O)C_6H_5(R')$, where R = Et, R' = Ph, H, etc., are characterised by ^1H, ^{11}B, ^{13}C and ^{31}P n.m.r. In solution, monomer⇌dimer equilibria are set up as a result of $\equiv\overset{+}{P}-O-\overset{-}{B}\equiv$ coordination, e.g. (83).[233]

The existence of various intermediates in the formation of boron heterocycles such as (84) has been established by n.m.r.[234] The crystal structure of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl-4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane, (85), shows that the rings make up an almost planar system. The molecular symmetry approximates to D_{2h}.[235]



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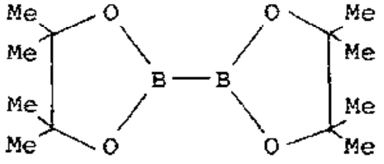

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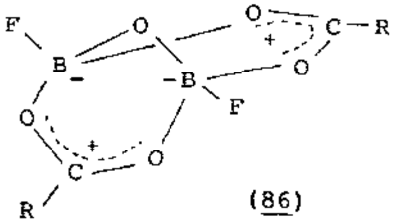
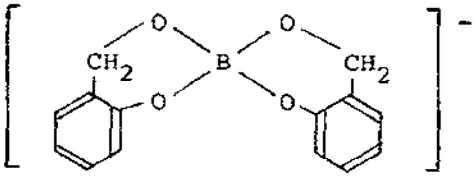


(86)

Trimeric alkoxydifluoroboranes, $(F_2BOR)_3$, and carboxylic acid anhydrides react to form bicyclic acyloxy fluoroboranes, (86). An X-ray crystal structure determination was carried out for R = Me.[236]

Salts of two anionic complexes of boron with 2-hydroxybenzyl alcohol (H_2A) have been prepared, BA_2^-, (87), and $[B(OH)_2A]^-$.[237]



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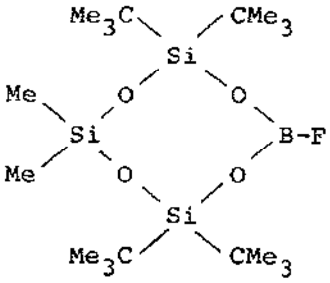


(88)

(88) has been prepared from a 1,3,5-trisiloxane-1,5-diol derivative and BF_3. The crystal structure of the cyclic compound was obtained. The Si_3O_4 and O_2BF planes are tilted by 15.8° with respect to each other. There was some evidence for B----F interaction.[238]

Treatment of [*fac*-$(OC)_3Re(CH_3CO)_2(RCO)]BX$, where R = Me, ^{i}Pr; X = F, Cl, with KH leads to proton removal from an acetyl ligand, producing anionic η^3-allyl complexes: {*fac*-$(OC)_3Re[\eta^3\text{-}CH_2COCO(R)]\text{-}(CH_3CO)BX\}^-$. Formation of these occurs by an interligand C-C bond formation between two of the original acyl-carbon donor atoms of the triacylrhenato ligand.[239]

3.1.10 Boron Carbide and Metal Borides

The symmetry and local bonding of C in the boron carbide $B_{12}C_3$ was studied by ^{13}C n.m.r. This showed that only C_3 chains are present, with no evidence for boron-substitution at the central carbon of this chain.[240]

The reaction of H_2 with YCo_4B, $GdCo_4B$ and YCo_3B_2 has been studied. Hydride phases based on these ternary borides have lower equilibrium pressures than those based on YCo_5.[241]

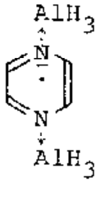
The material $Nd_2Fe_{14}B$ is promising for the construction of permanent magnets. Layers of puckered, sigma-phase-type nets of Fe atoms are sandwiched between triangular nets formed by Nd, Fe and B.[242]

Primitive tetragonal $ErRh_4B_4$ (space group $P4_2/nmc$) is isostructural with $CeCo_4B_4$.[243]

3.2 ALUMINIUM

3.2.1 Aluminium Hydrides

There is some i.r. evidence for the formation of aluminium hydride in the reaction of distilled water with aluminium powder activated by Ga, In or Sn.[244] E.s.r. studies of single-electron transfer reactions between AlH_3 or AlD_3 and pyrazine or related species show the formation of binuclear radical anions of the type (89).[245]



(89)

CaH_2 and AlH_3 react in the presence of Et_2O and $LiMH_4$, where M = Al or B, to give $Ca(AlH_4)_2.0.5LiMH_4.nEt_2O$ (at temperatures below 34°C) or $Ca(AlH_4)_2.nEt_2O$ (above 34°C).[246] A detailed study has been made of reactions between $LiAlH_4$ and $MgMe_2$ in Et_2O and THF. In Et_2O, MgH_2 is produced, with soluble $LiAlH_nMe_{4-n}$ (n = 0-4). In THF, depending on the mole ratio, MeMgH + $LiAlMe_4$ or $MeMg_2H_3$ + $LiAlHMe_3$.[247] ZnI_2 interacts with $LiAlH_4$ and AlH_3 in the mixed solvent ether/toluene (3:7 by volume) to give $ZnH_2.nEt_2O$ (n = 0.1-0.3).[248]

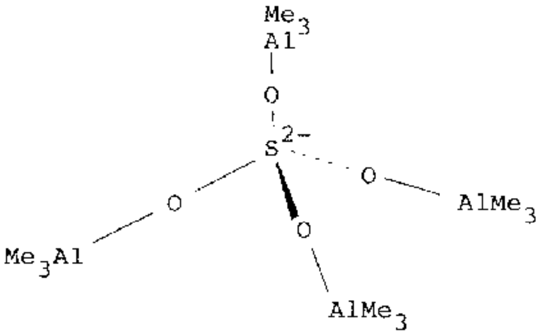
The structure of $NaAlH_4$ has been redetermined. It crystallises in the tetragonal system, space group $I4_1/a$. The Al-H distance is 161(4)pm, with Al-Na 355.0(1)pm.[249] The temperature dependence of the heat capacity of caesium tetrahydroaluminate has been measured, from 10K to 320K.[250] The double decomposition of $LiAlH_4$ and $AlCl_3$ in Et_2O gives a precipitate which is largely LiCl, with a variety of species in solution.[251]

The crystal structure of $Cp_2WH_2AlMe_3$ shows conclusively that there is a double hydride bridge linking W and Al (Al-H 196, 208 pm; W-H 122, 170pm).[252] The crystal structure of $Cp_2Ti(\mu\text{-}H)_2\text{-}AlCl_2.OEt_2$ shows that the aluminium is five coordinate, with Al-H_{br} 173pm, Al-Cl_t 216pm, Al-O 196pm.[253] I.r. spectra of adducts $Cp_2ReHAlH_nX_{3-n}$, where X = Cl, n = 0-3; X = Br, n = 0, show that there is a direct Re-Al bond in complexes with AlX_3 or $AlHCl_2$, but a bridging Re-H-Al unit for AlH_3 or AlH_2Cl complexes.[254] The crystal and molecular structure of $\{[(\eta^5\text{-}C_5H_5)Y(\mu_3\text{-}H)][(\mu_2\text{-}H)AlH_2.L]\}_2$, where L = OC_4H_8, shows the presence of a $Cp_2Y(\mu_3\text{-}H)YCp_2$ metallocycle, connected to an AlH_3.THF group *via* the μ_2- and μ_3-hydrogen atoms. The distance Yb-μ_3-H is *ca*. 220pm, Al-μ_3-H 200pm.[255] A report was also given of the analogous complex with L = NEt_3.[256]

3.2.2 Compounds containing Al-C Bonds

M.o. calculations on the units Al_4CO and Al_4NH_3 were used to simulate the adsorption of the ligands at an 'on-top' site of the Al(III) surface. For NH_3 it seems that the electrostatic attraction of the effective dipoles of the metal and ligand makes an important contribution to the bonding.[257] $Al(CO)_2$ is produced in an Ar matrix by co-condensation of Al and CO. It was shown by e.s.r. to have a bent OC-Al-CO structure, and some back-bonding from the Al p_π orbital to the antibonding π^* CO orbitals.[258]

Matrix i.r. spectra were reported for monomeric $AlMe_3$,[259] monomeric and dimeric $AlMe_3$, $AlEt_3$ and $GaEt_3$.[260] The interpretation of the spectra was aided by a normal coordinate analysis. Vapour pressure/temperature relationships were established for trialkylaluminium and alkylaluminium chlorides: R_3Al (R = Me, Et, ^nPr, ^iBu), Et_2AlCl, $EtAlCl_2$, $Me_3Al_2Cl_3$ and $Et_3Al_2Cl_3$.[261] Stoichiometric amounts of $AlMe_3$ and K_2SO_4 react in aromatic solvents to form a liquid clathrate, $K_2[Al_4Me_{12}SO_4]$.n(aromatic). In toluene, n = 0, and this forms monoclinic crystals, space group $P2_1/c$. Four $AlMe_3$ units are bonded to separate oxygens of the SO_4^{2-} group, (90). The Al-O distances average 190(2)pm.[262]

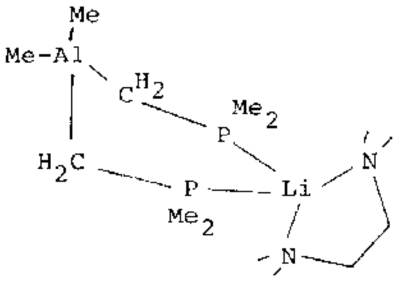


(90)

$AlMe_3$ and Cp_2TiCl_2 form $Cp_2Ti(CH_3)Cl.Al(CH_3)_2Cl$. Further $AlMe_3$ gives $Cp_2TiCH_2AlMe_2Cl$.[263] The reactivity of alkynylaluminium compounds, $(Me_2AlC\ CR)_2$, towards alkynylation of ketones is in the sequence: R = Et < Me < Ph.[264]

Anionic aluminates, $[Me_xAl(CH_2PMe_2)_{4-x}]^-$, have been synthesised, and shown to coordinate to Li^+. X-ray structure determination shows that $Me_2Al(CH_2PMe_2)_2Li(Me_2NCH_2CH_2NMe_2)$ contains a six-membered $Al(C-P)_2Li$ ring, (91).[265] "Anthracenemagnesium" reacts with dialky;aluminium hydrides or aluminium hydride to form (92, where R = Me, Et, ^sBu or H). An X-ray structural determination for R = Et shows that the Al and Mg occupy 9 and 10 positions in a 9,10-dihydro-9,10-anthrylene system.[266]

Monomeric bis(dimethylmetal(III)glyoximato)metallates(II), where metal(III) = Al, Ga or In; metal(II) = Ni, Pd, Pt, Cu: $Me_2M^{III}[M^{II}(R_2C_2O_2N_2)_2]$, where R = H or Me, were prepared from



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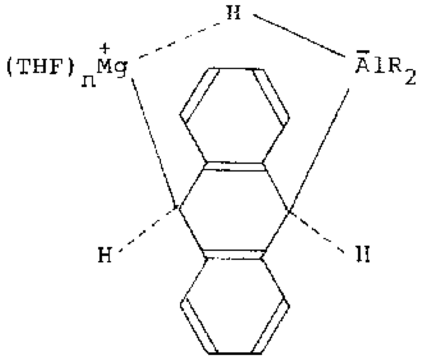


(92)

$M^{III}Me_3$ and $[R_2C_2N_2(O)OH]_2M^{II}$.[267] Several alkylaluminium adducts of cyclopentadienylrhodium compounds were prepared, e.g. $CpRhL_2(AlMe_3)$, where L = PMe_3, PMe_2Ph or PEt_3, $CpRh(PMe_3)_2(AlEt_3)$, $CpRh(C_2H_4)(PMe_3)(AlMe_3)$ and $CpRh(PMe_3)_2(Al_2Me_4Cl_2)$. The structure of the last compound shows that it can be regarded as an $Rh\text{-}AlMe_2^+$ cation, with a weakly associated $AlMe_2Cl_2^-$ anion.[268]

$NaAlMe_4$ and $NaAlEt_4$ in benzene solution containing HMPA undergo alkyl group exchange to give a statistical distribution of alkylaluminate ions. Rate constants were followed by ^{27}Al heteronuclear decoupled ^1H n.m.r. The reaction is thought to proceed via contact ion pairs, with two aluminates occupying coordination sites at the same Na^+.[269]

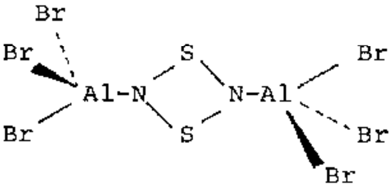
The reaction of Al_2Me_6 with ReH_7P_2 and ReH_5P_3 (P = PMe_2Ph or $PMePh_2$) results in methane elimination and formation of ReH_6AlMe_2P, $ReH_4AlMe_2P_3$ respectively. The structure of $ReH_6AlMe_2(PMePh_2)_2$ shows the presence of an ReH_6P_2 dodecahedron, with two hydrogens bridging to $AlMe_2$.[270]

3.2.3 Compounds containing Al-N Bonds

Raman spectra of the $AlCl_3\text{-}H_2O\text{-}CH_3CN$ system showed that there were four types of CH_3CN molecule present, two of which involve Al: $CH_3CN\text{---}Al^{3+}$ and $CH_3CN\text{---}HO\text{---}Al^{3+}$. In the absence of H_2O there was evidence for $AlCl_3.2CH_3CN$, $[AlCl(CH_3CN)_5]^{2+}$ and $AlCl_4^-$.[271]

The HeI and HeII photoelectron spectra of the $AlEt_2(L)^{\cdot}$ radical, where L = $^tBuN{=}CH{-}CH{=}NBu^t$, are qualitatively in agreement with MNDO calculations. The radical electron resides mainly in the ligand π^*-orbital.[272]

$S_2N_2.2AlBr_3$ is prepared from S_4N_4 and $AlBr_3$ in 1,2-dibromoethane at room temperature. The crystals are monoclinic, space group $P2_1/n$. The complex is centrosymmetric, (93), with the Al-N 196.8pm.[273]



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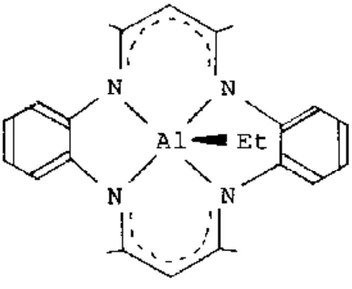


(94)

The Al-C bond in (94) is unusually stable, and is only broken under rather extreme conditions.[274] Crystal and molecular structures were determined for Al(Pc)Cl and Ga(Pc)Cl, where Pc = phthalocyaninato dianion. Both were triclinic, space group $P\bar{1}$, and both contain square-pyramidally coordinated Al or Ga.[275]

The molecular structure of $[Cp_2TiAlH_4]_2NMe_2C_2H_4NMe_2$ shows that 2 units of $Cp_2TiH_2AlH_2$ are linked by a tetramethylethylenediamine (rAl-N = 211pm). The aluminium is five-coordinate (trigonal bipyramidal), with $rAl-H_{br}$ 180, 160pm; $rAl-H_t$ 160pm.[276] Bis(morpholine)aluminium trichloride, $Al(C_4H_9NO)_2Cl_3$ forms triclinic crystals, space group $P\bar{1}$. Discrete molecules are present, with slightly distorted trigonal bipyramidal geometry, and equatorial Cl atoms.[277]

3.2.4 Compounds containing Al-O, Al-S or Al-Se Bonds

Ab initio (Hartree-Fock-Roothaan) m.o. calculations on AlOMe, MeAlO, AlOOH, HOAlO, AlOLi, LiAlO, FAlO, AlOF, ClAlO and AlOCl showed that the ground-state isomers are AlOMe, HOAlO, AlOLi, FAlO and ClAlO. On the potential surfaces for the unimolecular XAlO→AlOX reactions there is a high potential barrier separating the ground from the excited states, except for X = Li or F.[278] Vibrational force-field calculations were reported for orthorhombic $SmAlO_3$ and $EuAlO_3$.[279]

A series of aluminium alkoxides, $[Al(OR)_3]_n$, was investigated by ^{27}Al n.m.r. Three types of structure were found, dependent on R: (i) dimers: very bulky R; (ii) tricyclic tetramers: sterically non-demanding n-alkyls; (iii) linear trimers: mediumsized α-branched alkyls.[280]

High-field ^{27}Al n.m.r. spectra of highly alkaline aluminate solutions show that generally only $Al(OH)_4^-$ is present. Only in some sodium aluminate solutions is there evidence for species related to those formed on crystallisation from the solutions.[281]

Decomposition of lithium hydroxocarbonatoaluminate was investigated by i.r. spectroscopy, TGA, X-ray phase analysis and mass-spectrometry.[282]

The tetraisopropoxyaluminate of copper with various alcohols or acacH produced $Cu[Al(OR)_4]_2$, where RO = methoxy, ethoxy, 2,2,2-trifluoroethoxy-, 1,3-dibromo-2-propoxy-, _n_-butoxy, _t_-butoxy or acetylacetone.[283] Similar reactions were reported for Ni(II) tetraisopropoxyaluminate.[284] Crystal structure determinations were carried out for $[Al(OR)_2(acac)]_n$, where R = $SiMe_3$ (a symmetric polymer with both tetrahedral and octahedral aluminium coordination) or $SiPh_3$ (a distorted tetrahedral monomer).[285]

^{1}H n.m.r. studies of hydrated aluminium, gallium and indium vanadates show that they are best represented as: $\{[Al(OH_2)_{1.3}VO_4](H_2O)_2\}.xH_2O$; $\{[Ga(OH_2)_{0.9}VO_4](H_2O)_2\}.xH_2O$; $\{[In(OH_2)_{0.7}VO_4]H_2O\}.xH_2O$.[286] I.r. spectra were reported for $M_3^{II}[M^{III}(OH)_6]_2$, where M^{II} = Ca or Sr; M^{III} = Al or Ga. Assignments were helped by H/D substitution, which confirmed that OH, not H_2O was present.[287] ^{19}F n.m.r. was used to show that hexacoordinated solvates of Al^{3+} and Ga^{3+} in methyl, ethyl or _n_-propyl alcohols form outer-sphere complexes with F^-.[288]

The crystal structures of $(NH_4)_3[M(C_2O_4)_3].3H_2O$, where M = Al or Ga, show that the anion geometries are as expected, with three bidentate oxalato geoups. The average Al-O distance is 190(1)pm, Ga-O 197(1)pm.[289] A dynamic ^{1}H n.m.r. study has been made of the fluxional behaviour of tris(trifluoro-2,4-pentanedionato) chelates of Al(III) and Ga(III). Isomerisation processes occur _via_ a one-bond rupture mechanism.[290] Quite detailed vibrational assignments have been proposed from Raman spectra of single crystals of Al(III), Ga(III) and In(III) β-diketonates: $M(L\text{-}L)_3$, where L-L = acetylacetonate, trifluoroacetylacetonate, dipivaloylmethanate, hexafluoroacetylacetonate or dibenzoylmethanate.[291]

Solubility was studied in the systems $Al(OH)_3$-$Sr(OH)_2$-H_2O and $GaO(OH)$-$Sr(OH)_2$-H_2O at 25°C,[292] and in the $LiHCOO$-$Al(HCOO)_3$-H_2O system at 25,50 and 100°C.[293] $Al(HCOO)_3.3H_2O$ was prepared from aluminium chloride and NaOOCH in aqueous HCOOH or from freshly-precipitated $Al(OH)_3$ and HCOOH. The trihydrate reacts with water at 100°C to form $Al(OH)(HCOO)_2$.[294] I.r. and ^1H n.m.r. spectra were reported and assigned for crystalline $Al(IO_3)_2NO_3.6H_2O$ and $Al(IO_3)_3.2HIO_3.6H_2O$. ν_3 of AlO_6 was *ca.* $590cm^{-1}$ in each case.[295]

The formation of complexes of Al(III) with hydroxycarboxylic acids (e.g. citric, tartaric, gluconic etc. acids) was studied potentiometrically. Al(III) has a very strong tendency to displace protons from the hydroxyl groups of such acids - a property which had hitherto not been fully recognised.[296]

^{27}Al n.m.r. data showed that if acetate ions are added to aluminium salt solutions, they are protonated by the strong acid $Al(H_2O)_6{}^{3+}$, which itself dimerises to $[(H_2O)_4Al(\mu\text{-}OH)_2Al(OH_2)_4]^{4+}$. This can lose 2 further protons. No evidence was found for a tridecameric cation. Excess acetate ion coordinates to the aluminium dimer cation.[297]

Equilibrium studies of complex formation by Al(III), Ga(III) or In(III) with mercaptoacetate, 3-mercaptopropionate and 2-mercaptobenzoate show that Al^{3+} forms only hydroxo-complexes, while Ga^{3+} and In^{3+} give quite stable complexes involving simultaneous coordination of carboxylate and the deprotonated mercapto group.[298] A potentiometric study has been made of chelation of Al^{3+} by succinic, aspartic or glutamic acids, or histidine. For Al^{3+}/glutamic acid (H_2A), $Al(HA)^{2+}$ and $Al(OH)(HA)^+$ are formed, while for Al^{3+}/histidine(HA), $Al(OH)(HA)^{2+}$ and $Al(OH)A^+$ are formed.[299]

Dehydroxylation of alumina above 673K gives an i.r band at $1020\text{-}1050cm^{-1}$ (sensitive to $^{16}O/^{18}O$ substitution). This was assigned to a surface vibrational mode of alumina.[300] Na_2O and α-alumina form three new sodium-rich aluminates: $Na_7Al_3O_8$ (infinite double chains of Al_6O_{16} rings linked by O-bridges); $Na_{17}Al_5O_{16}$ (discrete Al_5O_{16} chains of corner-sharing AlO_4 tetrahedra); and Na_5AlO_4 (isolated AlO_4 tetrahedra).[301]

There is crystallographic evidence for two distinct phases in the $BaAlO_2\text{-}Al_2O_3$ system.[302] Phase relationships have been elucidated for the following systems: $BaO\text{-}Y_2O_3\text{-}Al_2O_3$;[303] $Al_2O_3\text{-}V_2O_3\text{-}SiO_2$, $Fe_2O_3\text{-}Al_2O_3\text{-}SiO_2$, $Fe_2O_3\text{-}V_2O_3\text{-}Al_2O_3\text{-}SiO_2$;[304,305] and $MoO_3\text{-}TeO_2\text{-}Al_2O_3$.[306]

The kinetics of thermal dissociation of $M_2(SO_4)_3$, where M = Al, Ga or In, were measured.[307] The equilibrium diagram of the Na_2SO_4-$Al_2(SO_4)_3$ system has been refined, and the i.r. spectrum of $Na_3Al(SO_4)_3$ reported.[308] Addition of KOH to $Al_2(SO_4)_3$ solution at 20°C gave precipitates of alunite, $KAl_3(OH)_6(SO_4)_2$, or the amorphous basic sulphate $2Al_2O_3.SO_3.nH_2O$ - the former at lower, the latter at higher pH.[309] NaOH addition to solutions containing Al and Mg sulphates gave sodium alunite, $Na_2SO_4.Al_2(SO)_4)_3.4Al(OH)_3$, aluminium hydroxide sulphates, $Al(OH)_{3-n}(SO_4)_{0.5n}$, and a double magnesium aluminium hydroxide of variable composition: $Mg_mAl_n(OH)_p(SO_4)_q.\ell H_2O$, where $m = 0.6$-1.2, $n = 1$, $p = 3.5$-5.0, $q = 0.2$-0.3, $\ell = 2.0$-4.0.[310] $Al_2(SO_4)_3$ is extracted by the complex primary amine "Primine JMT" as hydrolysed complexes. A complex containing three amines per metal is formed in the organic phase.[311] Solubility relationships were found in the system $Al_2(SO_4)_3$-$In_2(SO_4)_3$-H_2O at 25°C.[312]

Seven types of oligomeric and polymeric alkali-aluminium and alkali-iron phosphates have been formed, including (for the first time) $M^IAl_2^{III}[(H_2P_3O_{10})(P_4O_{12})]$, where M^I = Li, Na, K, Rb, Cs or NH_4.[313] $Al_2(NH_4)(OH)(PO_4).2H_2O$ is isomorphous with $GaPO_4.2H_2O$. Columns of Al-centred corner- and edge-shared octahedra are linked <u>via</u> PO_4 tetrahedra to form channels approximately parallel to the <u>b</u> axis.[314] Ammonium tripolyphosphate reacts with $Al(NO_3)_3$ in aqueous solution to form a double salt: $NH_4Al_3(P_3O_{10})_2.xH_2O$ (where x = 16-18).[315] $Al_3P_3O_{11}(OH)_2$ forms a clathrate compound with ethylene diamine.[316]

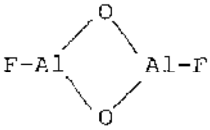
Neutron-diffraction on natrolite, $Na_2Al_2Si_3O_{10}.2H_2O$ at 20K shows that the crystals are orthorhombic, space group Fdd2. The tetrahedral sites have complete Al_2Si_3 order.[317] ^{27}Al magic-angle spinning (MAS) n.m.r. studies on calcium aluminates show that the technique is useful for investigating the kinetics of hydration of cement pastes.[318] ^{27}Al and ^{29}Si MAS n.m.r. were recorded for a series of polycrystalline 2:1 phyllosilicates. The spectra distinguish clearly between tetrahedral and octahedral Al.[319] The dependence of gel-formation in aluminosilicate solutions on the cation present and an alkali concentration has been studied.[320,321] Extra-lattice tetrahedral aluminium species in zeolites were investigated by ^{27}Al MAS n.m.r.[322] Similar experiments were reported for amorphous silica/alumina gels (in Na^+, NH_4^+ forms);[323] and the calcium hydrogen silicate C-S-H(Di,poly).[324] The latter showed that both tetrahedral and octahedral Al were present, with more octahedral species at higher CaO:SiO_2 ratios.

Barium aluminate, $Ba_{0.75}Al_{11}O_{17.25}$, has a structure close to that of sodium aluminate.[325] The aluminate sodalite, $Ca_8[Al_{12}O_{24}](WO_4)_2$, forms orthorhombic crystals, space group Aba2. The sodalite framework is composed entirely of AlO_4 tetrahedra.[326] Characteristic i.r. wavenumbers were established for the cation $[GeO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{8+}$ (450-990cm^{-1}), by analogy with those for $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$.[327] Solid-state n.m.r. studies were reported for $Na[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}](EO_4)_4.13H_2O$, where E = S or Se, and the mineral zunyite, $[AlO_4Al_{12}(OH,F)_{16}F_2][Si_5O_{20}]Cl$.[328] Neutron powder diffraction was used to study the structures of dealuminated Linde Y-zeolites: $Si_{173.1}Al_{18.9}O_{384}$ and $Si_{139.7}Al_{52.3}O_{384}$. There was evidence for the presence of AlO_4 units at the centre of the sodalite unit in each case.[329] $Na_{13}Al_{24}Si_{13}P_{11}B_{96}.16H_2O$ has a structure based on that of analcime, with alternation of 24Al and (13Si+11P) over tetrahedral sites.[330]

Single crystals were obtained in the systems $MAlS_2$-SnS_2 (M = Cu or Ag). The composition $[M_{1-x}\square_x Al_{1-x}Sn_{1-x}]S_4$ was found for these non-stoichiometric phases.[331] I.r. and Raman spectra of AlSX and AlSeX (X = halide) were assigned in terms of dimeric structures with planar four-membered Al_2S_2 or Al_2Se_2 rings and short, terminal Al-X bonds. The aluminium is coordinatively saturated by further X---Al interactions, giving chain structures.[332]

3.2.5 Aluminium Halides

Trapping AlF in an inert-gas matrix produces an $(AlF)_2$ dimer, for which a cyclic D_{2h} structure was shown by matrix i.r. and *ab initio* m.o. calculations. The matrix reaction of this dimer with O_2 produces $(OAlF)_2$. For this the antisymmetric νAlF wavenumber, $^{16}O/^{18}O$ wavenumber shifts and *ab initio* m.o. calculations are consistent with the structure (95).[333]



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Analysis of phases in the system CaF_2-AlF_3 gave evidence for the following: Ca_2AlF_7, β-$CaAlF_5$, CaF_2 and AlF_3. α-$CaAlF_5$ can be produced by heating β-$CaAlF_5$ to 973K.[334] Single crystals of $KCuAlF_6$ have been obtained for the first time. They are orthorhombic, space group Pnma, and isotypic with $CsAgFeF_6$.[335] Phase relationships were investigated in 4 internal sections of the 3Li,3Na¦¦3F,3Cl,AlF_6 system.[336] Liquidus curves were determined for the system Na_3AlF_6-MgF_2. The results suggest that MgF_4^{2-} is formed.[337]

The phase diagram of the NaCl-$AlCl_3$ system has been determined accurately near the equimolar composition. The freezing point of $NaAlCl_4$ is at 156.7±0.1°C. Also, the effects of added oxides on the phase diagram were examined. For added AlOCl, the species $(AlOCl)_2.AlCl_4^-$ is thought to be present.[338] Density, conductivity and electrolytic studies were made of liquid phases in the systems MCl/$AlCl_3$/SO_2, where M = Li or Na.[339] 25°C solubility isotherms were constructed for 14 systems: $AlCl_3$-H_2O-organic solvent.[340]

^{27}Al spin-lattice relaxation measurements were used to determine the relative numbers of chloroaluminate species present in the molten 1-n-butylpyridinium chloride-$AlCl_3$ system.[341] I.r. emission spectra (50-1500cm^{-1}) of alkali chloroaluminates and related melts were recorded, with at least 3 atmos. vapour pressure above the sample. The perturbation of the $AlCl_4^-$ ion follows the expected series: $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$. In $Al_2Cl_7^-$ systems only Li^+ is able to stabilise a bent Al-Cl-Al bridge (the others are linear).[342]

Mo(NO)$(CO)_4$($ClAlCl_3$) and $AlEtCl_2$ in CH_2Cl_2 give the new species Mo(NO)$(CO)_4$($ClAlCl_3$)[Al(Et)Cl_2], with νNO 1758cm^{-1}, νCO 2085cm^{-1}, compared to 1713, 2065cm^{-1} in the original complex.[343]

Crystalline $NbAlCl_8$ can be prepared from Al_2Cl_6 and Nb_2Cl_{10} at ca. 200°C in evacuated, sealed glass ampoules. Dinuclear $Cl_4NbCl_2AlCl_2$ is present, i.e. an $AlCl_4$ tetrahedron sharing a common edge with a distorted $NbCl_6$ octahedron. Al-Cl bond lengths are 207.8, 220.0pm. Polarised Raman spectra of $NbAlCl_8$ single crystals were assigned by factor group analysis. Raman spectra of melts of $AlCl_3$ + $NbCl_5$ at 235°C contain bands due to Al_2Cl_6, Nb_2Cl_{10} and $NbAlCl_8$. In gas-phase Raman spectra, bands at 369 and 418cm^{-1} are due to $NbAlCl_8$.[344]

Mass spectra were presented for aluminium bromide clusters containing up to 30 atoms. Mass spectral peaks for $(AlBr_3)_n^+$ are particularly strong for n = 2,4 or 6.[345] I.r. spectra have been obtained for aluminium bromide and iodide, and gallium chloride vapours. Seven of the eight i.r.-active modes of the M_2X_6 dimers (D_{2h} symmetry) were assigned, and all three i.r.-active modes of the MX_3 monomers (D_{3h} symmetry).[346]

3.2.6 Other Aluminium-containing Species

The new compound $Ca_{14}AlSb_{11}$ forms tetragonal crystals (space group $I4_1/acd$). The structure includes Sb^{3-} ions, $AlSb_4^{9-}$ and linear Sb_3^{7-} units.[347] In Ca_3AlSb_3 there are $AlSb_4$ tetrahedra, linked into chains by sharing corners. In $Ca_5Al_2Bi_6$ there are $AlBi_4$ tetrahedra linked by corners and Bi_2 groups to give double chains.[348]

Interaction of alloys of the Al-Ca-Mg system with H_2 was investigated. The intermetallic compound $CaAl_2$ reacts with H_2 at 300°C to form CaH_2 and Al.[349] $BaAl_2$ is formed in the Ba-Al system at 30kbar and 1000°C. It is metastable at S.T.P. after quenching, and crystallises with the $MgCu_2$ structure.[350] The new compound $CaZn_2Al_2$ forms tetragonal crystals (space group I4/mmmm); the structure can be described as an "inverse" $ThCr_2Si_2$-type.[351] $Na_7Al_2Sb_5$ forms monoclinic crystals (space group $P2_1/m$); $AlSb_4$ units are linked by corners, edges and Sb_2 groups to form anionic sheets.[352]

3.3 GALLIUM

3.3.1 Gallium Hydrides

A historical review has been given of the discovery of gallium, with a brief survey of its most important compounds.[353]

The isotropic e.s.r. spectrum of $GaH_3^{\overline{\cdot}}$ has been observed. The gallium hyperfine splitting shows that the out-of-plane angle is similar to that in $AlH_3^{\overline{\cdot}}$.[354]

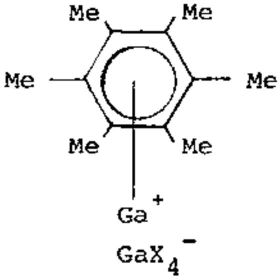
Electron diffraction was used to determine the gas-phase structure of $Me_3N.GaH_3$. rGa-H is 149.7(1.5)pm, rGa-N 212.4(0.7) pm, and the GaNC angle 109.9°.[355]

3.3.2 Compounds containing Ga-C Bonds

The synthesis and physical properties have been reported for bis(tropolonatodimethylgallium), $[(C_7H_5O_2)GaMe_2]_2$. The dimer contains five-coordinate Ga atoms with irregular trigonal bipyramidal geometry, and a planar, four-membered Ga_2O_2 ring.

The Ga-O$_{eq}$ distance is 197.2pm; Ga-O$_{ax}$ 202.5, 255.1pm, and Ga-C 195pm.[356]

The new compound KGa$(CH_2SiMe_3)_2H_2$ is prepared from Ga$(CH_2SiMe_3)_2$Br and excess KH. It reacts with further Ga$(CH_2SiMe_3)_2$Br in benzene to produce Ga$(CH_2SiMe_3)_2$H. This decomposes at room temperature to Ga, H_2 and Ga$(CH_2SiMe_3)_3$, probably <u>via</u> GaH_3.[357]

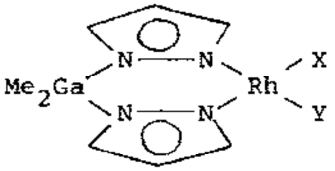


(<u>96</u>)

Reactions of Ga_2X_4 (X = Cl or Br) with C_6Me_6 in toluene produce (<u>96</u>), the first monoarene complexes of Ga(I). They can be regarded as π-complexes or as <u>nido</u>-clusters.[358,359] Ga_2Cl_4 in hot mesitylene, however, gives crystals of $[C_6H_3Me_3]_2Ga^+GaCl_4^-$ on cooling. The cation has a sandwich structure, with the arene rings inclined by <u>ca</u>. 40°C to each other. The anion forms Ga^{III}-Cl-Ga^{I} bridges to form a chain-like coordination polymer.[360]

3.3.3 <u>Compounds containing Ga-N, Ga-P or Ga-Sb Bonds</u>

The dirhodium species $[MeGa(N_2C_3H_3)_3]_2Rh_2(\mu\text{-}CO)_3$ has been prepared for the first time. The overall symmetry is close to D_{3h}, with rGa-C 194pm, rGa-N 192-195pm.[361] Synthesis and characterisation was reported for the bidentate pyrazolylgallate complexes (<u>97</u>, X = Y = CO, PPh_3; X = CO, Y =PPh_3; or XY = cyclo-octadiene). In the solid phase, the Ga-$(N\text{-}N)_2$-Rh ring is in the boat conformation.[362]



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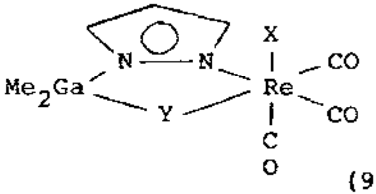


(<u>98</u>)

Complexes, (98), with symmetrical and unsymmetrical chelating pyrazolylgallate ligands were prepared and characterised, where $Y = N_2C_3HR_2$, R = H, X = CO, PPh_3 or $N_2C_3H_4$; $Y = N_2C_3HR_2$, R = Me, $X = PPh_3$, $N_2C_3H_4$; Y = OH, X = CO, PPh_3, R = H, Me.[363]

Detailed vibrational assignments, and a normal coordinate analysis, were reported for the adducts $H_3N.GaX_3$ and $H_3P.GaX_3$ (X = Cl or Br). νGa-N is in the range 480-500cm^{-1}, νGa-P 280-305cm^{-1}.[364] Similar data were also given for $Ph_nPH_{3-n}.GaCl_3$, where n = 1,2 or 3. νGa-P (strongly coupled with P-Ph stretches) was at 316, 260, 182cm^{-1} for n = 1,2,3 respectively.[365] The covalent derivatives $[Et_2M\text{-}PEt_2]_3$, where M = Ga or In, can be prepared from the Lewis acid-base $Et_3M.PEt_2H$ by alkane elimination. Mass spectra show that they are indeed trimeric.[366]

The molten Ga-Sb and In-Sb systems were studied by ultrasonic techniques.[367]

3.3.4 Compounds containing Bonds between Ga and Group 6 Elements

$KNa_4(GaO_4)$ is prepared from binary oxides or from $KGaO_2/Na_2O/$-K_2O. The hitherto unknown $CsK_4(GaO_4)$ is prepared from the reaction of $K_2O + CsGaO_2$ + excess Cs_2O in a closed gold tube at 580°C. Both belong to the $Na_5(GaO_4)$ structure type.[368]

Raman spectra of oriented single crystals of $CsM(SO_4)_2.12H_2O$, where M = Ga or In, gave a complete assignment of skeletal modes for $M(OH_2)_6{}^{3+}$. The $\nu_sM\text{-}O$ modes are at higher wavenumber than previously thought (537cm^{-1} (Ga) or 505cm^{-1} (In)).[369] The formation kinetics of a 1:1 GaIII complex with tropolone in acidic aqueous media were studied spectrophotometrically (stopped flow technique). Evidence was found for a dissociative-interchange mechanism.[370]

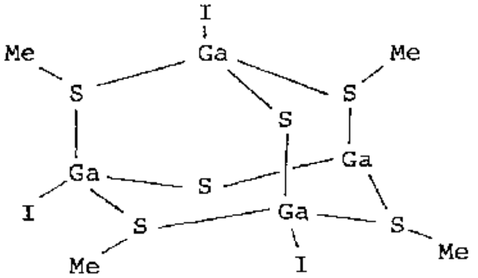
The vibrational spectra of α-Ga_2TiO_5 and H-Ga_2TiO_5 were reported and analysed. The data were not wholly consistent with published structures.[371] The Ga_2O_3-Ga_2S_3 system was shown to be simple eutectic.[372] $M_2(MoO_4)_3$ can dissolve 10 (M = Al), 30 (In) or 40 (Fe) mole % of $(Ga_2O_3 + 3MoO_3)$.[373]

Triphenylgallane and alkyl- and aryl-thiols give the corresponding diphenylalkyl- and diphenylarylthiogallanes. The spectra of these were reported, together with an X-ray structure determination of $Ph_2(Et\ )Ga$.[374] $MeGaCl_2$ and silyl sulphides, Me_3SiSR, where R = Me, Et, ^{n}Pr, ^{i}Pr, Ph or CH_2Ph, in benzene give the hitherto unknown chloro(methyl)(organylthio)gallanes, Me(Cl)GaSR. These form stable adducts with NMe_3.[375] $GaPh_3$ and alkyl- or aryl-thiols in the molar ratios 1:2 or 1:3 form $PhGa(SR)_2$ (where R = Et, ^{n}Pr, ^{i}Pr, Ph, CH_2Ph), or $Ga(SR)_3$ (where R = Me, Et, ^{n}Pr, ^{i}Pr, Ph, CH_2Ph) respectively.[376]

Redox reactions between GaI_3 or $PhGaI_2$ and disulphides, MeSSMe or PhSSPh, give monoalkylthio- and monoarylthiogallanes: $MeSGaI_2$, $PhSGaI_2$ respectively. InI_3 does not react with the disulphides, but $PhInI_2$ does give $MeSInI_2$ or $PhSInI_2$. Ph_2GaI and Ph_2InI only give thioether adducts with the disulphides (not isolated).[377] Nucleophilic substitution reactions between Me_2GaCl and silyl sulphides Me_3SiSR, where R = Me, Et, ^{n}Pr, ^{i}Pr, Ph or CH_2Ph, produce moisture-sensitive dimethyl(alkylthio)- or dimethyl-(phenylthio)-gallanes, Me_2GaSR. When R = Me, Et, ^{n}Pr or ^{i}Pr, the compounds are trimeric in benzene solution; when R = Ph or CH_2Ph they are monomeric.[378] Phenyl- and methyl-di-iodogallane and alkyl- or aryl-thiols form corresponding di-iodoalkylthio- and di-iodoaryl-thiogallanes, $I_2Ga(SR)$, where R = Me, Et, ^{n}Pr, ^{i}Pr, Ph or CH_2Ph. From I_2GaMe, initially thiol-adducts are formed.[379]

$KGaS_2$ forms monoclinic crystals (space group Aa). It possesses a layer structure, with each layer built up of Ga_4S_{10} tetrahedral polyanions.[380] The first ortho-thiogallate, $Ba_5(GaS_4)_2$, has been prepared. It forms orthorhombic crystals (space group Cmca), and isolated GaS_4^{5-} tetrahedra are present (rGa-S = 226pm).[381] Crystal and molecular structures of tris(o-ethylxanthato)-gallium(III) and -indium(III), $M)S_2COEt)_3$, where M = Ga or In, show that the metal is six-coordinate, distorted octahedral. There are three chelating xanthates in each case.[382]

The first example of a neutral Ga/S cluster compound has been reported: $Ga_4I_4(SMe)_4S_2$, from Me_2S_2 and Ga_2I_4. The crystal structure reveals an adamantane-like cage, including both -S- and -SMe- bridging sulphur atoms, (99).[383]



(99)

X-ray and i.r. studies on spinel solid solutions, $Zn_{1-x}Ga_{0.67x}Cr_2Se_4$, where x = 0-0.6, gave no evidence for ternary $Ga_{0.67}Cr_2Se_4$.[384] (LaO)$GaSe_2$ forms orthorhombic crystals (space group $P2_1ab$). Alternating layers of (LaO) and ($GaSe_2$) built up the structure, parallel to the (001) plane. The structure is very different to that of $LaGaOS_2$.[385] The equilibrium diagram of the Yb-Ga-Te system was examined along the sections: Yb-GaTe; YbTe-Ga_2Te_3; YbTe-GaTe; $YbGa_2$-YbTe, and $YbGa_2$-GaTe. The compounds $YbGa_2Te_4$ and $Yb_3Ga_2Te_5$ were detected.[386] Equilibrium diagrams were constructed for Ga_2Te_3-FeTe and GaTe-Fe systems.[387]

3.3.5 Gallium Halides

A summary has been given of the available knowledge about phase diagrams of Ga, In and Tl with the halogens.[388]

X-ray diffraction studies on $GaCl_3$.1,4-dioxan show that five-coordinate gallium is present. Infinite chains of distorted planar $GaCl_3$ units are bridged by dioxan chairs.[389] Distribution of gallium between HCl solution and a macroporous copolymer of styrene and divinylbenzene, impregnated with tributylphosphate, have been examined.[390]

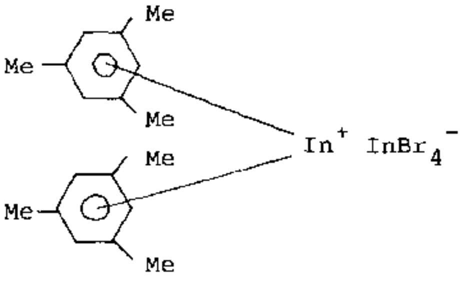
A review has been made of bromide complexes of Ga(III) and In(III).[391] Simple addition reactions give very stable adducts of gallium halides with chalcogenides, GaX_3.HYEt, where X = Br; Y = S or Se; X = I, Y = O, S, or Se.[392] $GaBr_4^-$, $Ga_2Br_7^-$ and Ga-Br-Sb(Bi) species were identified by i.r. and Raman spectrum of mixtures of gallium tribromide and other metal bromides.[393]

3.4 INDIUM

3.4.1 Compounds containing In-C Bonds

Hydrolysis of dimethylbis(t-butylamino)silane in the presence of $MeInCl_2$ forms crystals of the Lewis-base adduct $MeInCl_2.H_2N^tBu$. The indium is four-coordinate (tetrahedral), with In-N 221pm (i.e. very short), In-C 214pm and In-Cl 240pm.[394] The new compounds $Me_nIn(CH_2SnMe_3)_{3-n}$, where n = 0,1 or 2, and $(^tBu)_2InCH_2SnMe_3$ were prepared from Me_3SnCH_2Li and $InCl_3$, $MeInCl_2$ or R_2InCl (where R = Me or ^tBu).[395]

The electrolysis of MeMgCl or Me_2Mg in THF with an indium anode produces the adduct Me_3In.THF directly. Addition of excess L (= NEt_3, PMe_3 or PEt_3) to this forms Me_3In.L.[396]



(100)

$In[InBr_4]$ reacts directly with mesitylene to form the crystalline (100), the first arene complex of indium.[397]

3.4.2 Compounds containing Bonds between In and the Elements of Group 5

Crystal structures were determined for $MCl_3py_3.py$, where M = In or Tl. The coordination at M is close to octahedral, with a mer-arrangement of ligands. The molecular symmetry is approximately C_2.[398]

Visible/u.v., absorption, emission and excitation spectra of indium(III) tetraphenylporphyrin chloride, In(TPP)Cl, and indium(III) octaethylporphyrin chloride, In(OEP)Cl, reveal a strong interaction between In^{3+} and the porphyrin π-systems.[399]

Phase equilibria were established for the systems In-As-Bi;[400] InSb-InSe, $InSb-In_2Se_3$, $InSb-Sb_2Se_3$;[401] and In-Sb-Bi-Zn.[402]

3.4.3 Compounds containing In-O, In-S or In-Se Bonds

Solubilities were studied in the system $Zn(NO_3)_2-In(NO_3)_3-Na_2WO_4-H_2O$.[403] The inhibiting action of NO_3^- on the disproportionation of In(I) in aqueous solutions was investigated.[404]

In and Tl hydrogen sulphate monohydrates were studied by ^1H n.m.r., i.r. and X-ray diffraction.[405] Addition of KOH to aqueous $In_2(SO_4)_3$ solution led to precipitation of $KIn_3(OH)_6(SO_4)_2$ (final pH ≤ 3.2) or an amorphous basic sulphate, $2In_2O_3.SO_3.nH_2O$ (final pH ≥ 3.2).[406] The $CdSO_4-In_2(SO_4)_3-H_2O$ system reveals the existence of the congruently-soluble compound, $3CdSO_4.In_2(SO_4)_3.26H_2O$.[407] Stability constants for the complexes of In(III) with iminodiacetic, tartaric, aspartic, malonic, maleic, oxalic and picolinic acids were determined by potentiometric measurements.[408] Three indium(I) thiosulphates have been obtained as solids: $In_2S_2O_3.2H_2O$, $In_2S_2O_3.InOH.2H_2O$ and $In_2S_2O_3.2InNO_3.2H_2O$.[409]

Heating alkaline earth metal indates with H_2S produces the corresponding thioindates, MIn_2S_4, where M = Ca, Sr or Ba. $M_3In_2S_6$ compounds were also prepared.[410] $In_5Sn_{0.5}S_7$ forms monoclinic crystals, space group $P2_1/m$. It has the same structure on In_6S_7, with one In^+ replaced by $\frac{1}{2}Sn^{2+}$. Three In^{3+} ions have octahedral environments, while the two atoms of the In-In pair have four-fold coordination.[411]

Various physical techniques were used to study interactions in the InSe-PbTe system.[412] Phase relationships were investigated along the InSe-Sb and In_2Se_3-Sb sections of the $In-Sb-Se_4$ ternary system.[413]

3.4.4 Indium Halides

Binding energies for In d and Cl p core and valence levels were determined by photoelectron spectroscopy for $InCl_n$ (where n = 1, 1.5, 1.8, 2 or 3), $Cs_3In_2Cl_9$, PCl_4InCl_4, $Rb_2LiInCl_6$, $Cs_2InInCl_6$ and InY_2Cl_7. There was no evidence for the presence of mixed oxidation states.[414]

InX, where X = Cl, Br or I, in toluene/py or CH_2Cl_2/py insert into homonuclear R_nM-MR_n, where M = O, S, Se or Co, to form $(R_nM)_2InX$ as their bis-pyridine adducts. No such addition occurs for M = Sn, Pb, N, P, Te, Mn or Fe.[415]

Reaction between InX, where X = Cl, Br or I, and InY_3 (Y = Br or I) in toluene/CH_2Cl_2/tmen, where tmen = N,N,N',N'-tetramethylethanediamine, at temperatures below about 20°C produces In-In species $X(Y)InInY_2$, as bis-tmen adducts. There are no analogous products for InX + $InCl_3$.[416] The crystal and molecular structure of the bis(tmen) adduct of $In(Br)InInBr_2$ confirms the presence of an In-In bond (277.5pm in length).[417]

$KInBr_4$ forms orthorhombic crystals, space group Pnna. It is the first alkaline halo-indate with tetrahedral coordination (In-Br distances 249.4-252.0pm).[418] Electrode kinetic parameters were determined for the In(III)/In(I) couple in acidic 4M Br^- solution.[419] The initial stage of formation of colloidal In in aqueous InBr solutions was studied. The effects of $[In^I]$, $[F^-]$, $[Cl^-]$, pH etc. were examined.[420]

It is possible to obtain structural information on red α-InI_3

by forming mixed crystals α-$InI_{3-x}Br_x$ ($x \sim 1$). The phase diagram of InI_3-$InBr_3$ was determined.[421] "Indium di-iodide", $In^{I}In^{III}I_4$, forms orthorhombic crystals, space group Pnna. The In(I) is eight-coordinate by Cl as a slightly distorted dodecahedron (bond distances 359-367pm), while the In(III) is approximately regularly tetrahedrally coordinated.[422]

3.5 THALLIUM

3.5.1 Thallium(I) Compounds

Electron impact on thallium carboxylates produces the gaseous species $TlCO_2^+$. Mass spectra were consistent with the presence of a Tl-C bond.[423] $Tl[Au(CN)_2]$ forms orthorhombic crystals, space group Pbcn. Coordination about the Tl^+ is highly irregular.[424] The anion in $AsPh_4^+[\{Ru_6C(CO)_{16}\}_2Tl]^-$ consists of a bimetallic carbonyl cluster containing two distorted Ru_6 octahedra linked by two edge-related Ru atoms to the central Tl atom. The Tl is in approximately square-planar coordination, with Tl-Ru 278-288pm.[425]

I.r. spectra were reported for matrix-isolated ion-triplets $Tl_2^+SO_3^{2-}$ and $Tl_2^+S_2O_5^{2-}$.[426] The thermal decomposition of thallium(I) carboxylates, TlCOOR, where R = CH_3, CF_3, Ph or PhCH=CH, was studied by DTA and TGA.[427] A ^{205}Tl and ^{13}C n.m.r. study has been made of the Tl(I)-enniatin B complex. The ^{205}Tl chemical shift is consistent with the general relationship established between the chemical shift and the basicity of the functional group(s) used by the antibiotic in binding the metal ion.[428]

The structure of $Tl^{I}Mo_3P_{5.8}Si_2O_{25}$ contains MoO_6, PO_4 and Si_2O_7 units, forming an intersecting "tunnel" structure.[429] N.m.r. (^{203}Tl, ^{205}Tl) studies were used to investigate the Tl^+ ion mobility in the pyrochlore $TlNb_2O_5F$. There was evidence for both a jump from cavity to cavity, and motion between sites inside the same cavity of the rigid NbO_5F framework.[430] $Tl_4Nb_6O_{17}$ has a layer structure, isostructural with the orthorhombic K^+ and Rb^+ analogues. The ionic conductivity for the Tl^+ compound is less than that of the K^+ species.[431]

Polymorphic transformations in $TlLn(WO_4)_2$, where Ln = La, Ce-Lu or Y, were investigated just below their melting points.[432] Matrix-isolation i.r. spectra on ^{18}O-enriched samples of $TlReO_4$

established a C_{2v}, bidentate structure. Distortion of the ReO_4^- anion from T_d to C_{2v} is greater in the Tl^+ compound than in alkali metal derivatives. There was also evidence for ($TlReO_4$) dimers.[433]

Composition and stability constants were determined for Tl(I) complexes with dithiopropionic acid.[434] Phase equilibria were studied for the following systems: Tl_2S-GeS_2;[435] Tl_2S-Cu_2S;[436] $3Hg-Tl_2S$, $3Hg_5Tl_2-7Tl_2S$, $7HgS-2Hg_5Tl_2$.[437] Single crystals have been grown of $Tl_{2-x}Cd_xS$ and $Cd_{1-x}Tl_xS$ solid solutions.[438]

Thallium(I) alkylenedithiophosphates, $TlS_2P{<}^{O}_{O}{>}G$, where G = $-CH_2CMeCH_2-$, $-CH_2CEt_2CH_2$, $-CMe_2CH_2CHMe-$, $-CMe_2CMe_2-$ or $-CHMeCHMe-$, can be synthesised from Tl(OAc) or Tl_2CO_3 and the corresponding ammonium alkylenedithiophosphates in aqueous media.[439] Homogeneity ranges were determined for Tl_4SiS_4, Tl_2SiS_3 and $Tl_2Si_2S_5$.[440] Black crystals of Tl_2SnS_3 are monoclinic, space group C2/m. There are two types of Tl^+ ion, one at the centre of an irregular cube, the other a bicapped trigonal prism.[441] The isostructural compounds Tl_4MS_4, where M = Ti or Sn, and Tl_4TiSe_4 also form monoclinic crystals, space group $P2_1/c$. The Tl^+ ions are coordinated by 6-7 chalcogen atoms (rTl-S 293-398pm, rTl-Se 303-396pm; the nearest Tl---Tl distances are 346-365pm).[442]

Neutron time-of-flight diffraction studies were used to establish the crystal structures of Tl_3PSe_4 and Tl_3AsS_4. Both belong to the space group Pcmn.[443] Crystals of Tl_3SbS_3 are rhombohedral, space group R3m. The SbS_3 groups are strongly bound to three Tl atoms, through Sb-S-Tl bridges, producing Tl_3SbS_{12} groups.[444]

The formation of chloride complexes of Tl(I) was investigated potentiometrically at 298K. Stoichiometric stability constants were calculated for TlCl and $TlCl_2^-$.[445]

3.5.2 Thallium(III) Compounds

$Tl(CF_3)_3$ was prepared by condensing Tl atoms and CF_3 radicals on a cryogenic surface. There was some evidence for Al, Ga and In analogues, but they were less well-defined.[446] Measurements were made of Tl-H coupling constants in a series of mono- and di-arylthallium(III) derivatives, with alkyl groups *o*- or *p*- to the thallium atom. There was evidence for 'through-space' coupling in some of the *o*-alkylphenylthallium compounds.[447]

$TlBr_3py_2$ forms monoclinic crystals (space group $P2_1$), containing distorted trigonal bipyramidal molecules (Tl-Br distances 251.9-254.0pm; Tl-N, 241-244pm).[448] In crystals of $TlBr_3py_3$ (orthorhombic, space group $P2_12_12_1$) there are distorted octahedral molecules, with mer-geometry (Tl-Br distances 261.8-267.0pm, Tl-N 242.5-251.4pm).[449] The adduct $TlBr_3(OPPh_3)_2$ also contains discrete molecules, distorted trigonal bipyramidal (Tl-Br distances 249.7-251.5pm; Tl-O 238, 239pm).[450]

The kinetics and mechanism of oxidation of glycolic (Hga) and glyoxylic (Hgox) acid by Tl(III) have been studied.[451] $Tl(NO_3)_3.3H_2O$ forms rhombohedral crystals. The i.r. spectrum shows that the $Tl-NO_3$ interaction is essentially ionic.[452] K_5TlO_4 crystals were prepared by heating K_2O + Tl_2O_3 in a closed silver cylinder. They are orthorhombic (space group Pbca), and belong to the Na_5GaO_4 structure type.[453]

Genuine pentacoordinated $TlCl_5^{2-}$ can be prepared as a pyridinium salt in non-aqueous solutions, but not in aqueous solutions, as previously suggested.[454] Crystallisation from aqueous solutions of $CaCl_2$ + $TlCl_3$ produces colourless, hygroscopic crystals of $CaTlCl_5.7H_2O$. X-ray diffraction shows these to contain $[Ca(OH_2)_7]^{2+}$ and $Tl_2Cl_{10}^{4-}$ (with two bridging chlorines).[455]

Thallium(I) iodide, with I_2 and 3-methylpyridine-N-oxide, gives $TlI_3(MeC_5H_4NO)_2$ as monoclinic crystals (space group C2/c). The thallium is five-coordinated, as a slightly distorted trigonal bipyramid, the iodine atoms being in the equatorial plane.[456]

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