Coordination Chemistry Reviews, **34 (1981) 74–153**
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

Chapter 3

ELEMENTS OF GROUP 3

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3.1 BORON

3.1.1 Boranes

A note has appeared relating the styx rules for boranes to the Wade electron counting rules for such compounds.[1]

Ab initio molecular orbital calculations on the hypothetical polymeric boron hydride $[BH_2]_n$ show that it is unstable with respect to monomeric species, unlike the $[BeH_2]_n$ analogue.[2]

The potential surface of the shortest reaction path for equation (1) has been calculated using the Roothaan method, with the double-zeta basis of Roos and Siegbahn: $(7s3p)_B + (4s)_H$.[3] The

$$BH + H_2 \longrightarrow BH_3 \qquad \ldots(1)$$

wave functions were calculated and the nature of redistribution of electron density analysed for the "shortest" path of reaction (1) using the same methods as in the previous paper.[4]

Gaseous H_3BCO reacts with sulphide-activated nickel to form $Ni(CO)_4$ and B_2H_6, with 87% conversion of H_3BCO. Gaseous F_3PBH_3 reacts similarly, at 50°C, over 46h to give 98% conversion to $Ni(PF_3)_4$ and B_2H_6.[5]

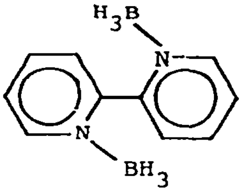
Studies of the acid-catalysed hydrolysis of $NH_3.BH_3$ confirm the trend: $k_2(NH_3.BH_3) > k_2(MeNH_2.BH_3) > k_2(Me_2NH.BH_3 > k_2(Me_3N.BH_3)$, where $k_2 = -(1/[H^+])d\ln[R_3N.BH_3]/dt$. The results are consistent with a previously suggested mechanism by which cis-displacement of BH_3 occurs via electrophilic attack of the proton of a general acid at the amino nitrogen (the nitrogen-boron electron pair).[6]

Binding energies (including valence-shell electron correlation) have been calculated for B_2H_6, BH_3CO, and BH_3NH_3, using the many-body perturbation theory. The binding energies were 35, 21 and 30 kcal.mol^{-1} respectively. Correlation effects account for 48, 62 and 32% of the binding energy. The calculated enthalpy of the association reaction $2BH_3 \longrightarrow B_2H_6$ agrees with the experimental value (-34 kcal.mol^{-1} at 300°C) to ±5%.[7]

Addition of 5% SF_6 to B_2H_6 increases the laser-induced conversion and formation efficiencies by a factor of 2-3 (CO_2CW laser operating on the P-16, 947.75 cm^{-1}, line). Yields for the formation of $B_{10}H_{14}$ were found to be as high as 23%.[8]

B_2H_6 impurity can be removed from SiH_4 by irradiating with a CO_2 TEA laser. Diborane decomposes more rapidly under the severe breakdown conditions, to give an unidentified solid.[9]

The reactions of B_2H_6 with chelating ligands, 2,2'-bipy, N,N,N',N'-tetramethyl-o-phenylenediamine (TMPD) and 1,8-bis(dimethylamino) naphthalene (BDN), have been examined. Bipy reacts with excess B_2H_6 to form the stable, ether-insoluble (1). TMPD with equimolar B_2H_6 produces (2), while with excess B_2H_6 it gives the air-sensitive $B_2H_7^-$ salt of the same cation. BDN reacts extremely slowly with excess B_2H_6 to give (3)[10].



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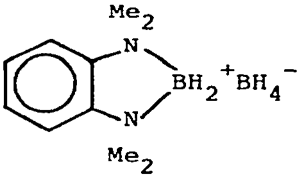

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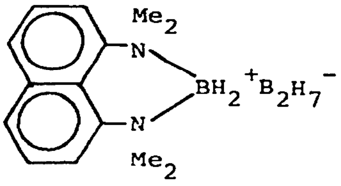

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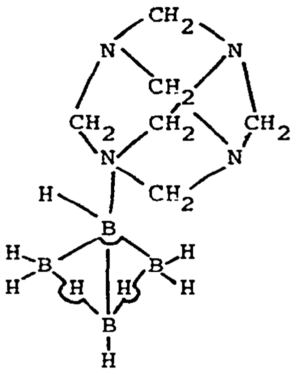
Low-resolution mass spectra of B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12}, B_8H_{12}, B_9H_{15} and $B_{10}H_{14}$ were recorded on a conventional spectrometer and compared with data obtained from a molecular beam sampling mass spectrometer. A method was developed for continuous quantitative analysis of borane mixtures in the gas phase. The thermolyses of B_2H_6 at 100°C or 120°C were compared with those of B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10} and B_6H_{12} at 75°C. The suggested order of thermolytic stability was: $B_{10}H_{14}$, $B_5H_9 \gg B_2H_6 > B_6H_{10} \gg B_6H_{12} > B_5H_{11} \gg B_4H_{10} \ggg \{B_4H_8\}, \{B_3H_7\}, \{BH_3\}$.[11]

The co-thermolyses of B_4H_{10} with B_2H_6, B_5H_9, B_5H_{11}, B_6H_{10} or B_6H_{12} at 75°C were studied by a mass-spectroscopic method. $\{B_4H_8\}$ appears to be a reactive intermediate of major importance.[12]

Hexamethylenetetramine reacts with B_2H_6, $B_3H_7.THF$, B_4H_{10} or B_5H_{11} in chloroform solutions to give $(CH_2)_6N_4.4BH_3$, $(CH_2)_6N_4.2B_3H_7$, $(CH_2)_6N_4.2B_3H_7.2BH_3$, $(CH_2)_6N_4.B_4H_8$ respectively. The products were characterised by ^{11}B and ^{1}H n.m.r. The proposed structure for the B_4H_8 adduct is (4).[13]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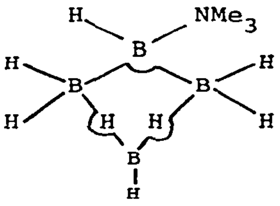
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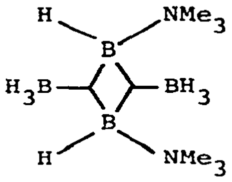
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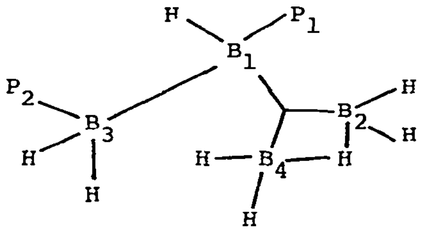
The trimethylamine adduct of tetraborane(8), $Me_3N.B_4H_8$, has been prepared for the first time, by the reaction of NMe_3 with alkyl sulphide-B_4H_8 adducts. Reaction with NMe_3 at low temperatures produces a bis-adduct $B_4H_8.2NMe_3$. ^{11}B and ^{1}H n.m.r. were consistent with the structures (5) and (6).[14]

Pentaborane(11) reacts with excess trimethylphosphine to give a new member of the B_4 *hypho*-class boranes: $B_4H_8.2PMe_3$. This reacts with HCl to form $Me_3P.B_3H_7$ and $Me_3P.BH_2Cl$. The $B_4H_8.2PMe_3$ can also be prepared by the reaction of $B_5H_9.2PMe_3$ with HCl in tetrahydrofuran at -80°C. The structure of the new adduct was not established definitively, but could be (7) or (8).[15]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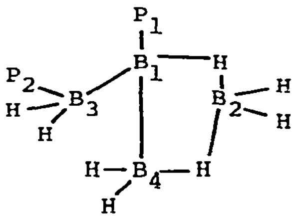
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An empirical relationship has been found between B-B and B-H bond lengths and bond enthalpies for *nido*- and *arachno*-boranes, B_nH_{n+4} and B_nH_{n+6}. For B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10} and $B_{10}H_{14}$ the calculated ΔH_{atom} values are very close to those found experimentally.

For B_8H_{12}, B_9H_{15}, $B_{13}H_{19}$ and $B_{18}H_{22}$ the calculated ΔH_{atom} values were quoted (no experimental values are available).[16]

Specific procedures have been developed for producing methyl-substituted boranes. Thus, 3-MeB_6H_{11} is formed by the addition of BH_3 to 1-$MeB_5H_7^-$, followed by protonation with HCl. This compound can be used to form methyl derivatives of small boranes. Thus, with NH_3 it forms $[BH_2(NH_3)_2]^+[3\text{-}MeB_5H_9]^-$ by cleavage of the bridge system. Protonation (by HCl) of the anion yields 3-MeB_5H_{10}. A repetition of the same sequence gives 1-MeB_4H_9. A directive effect seems to apply during the cleavage reactions - the boron atom furthest from the methyl group splits off from the framework. All of the methyl compounds produced are more stable than the parent boranes.[17]

Specific syntheses have been devised for 1,2'- and 2,2'-$(B_5H_8)_2$. Thus, a Friedel-Crafts catalysed reaction of 2-BrB_5H_8 with B_5H_9 gives the 1,2'-isomer, while metathesis of $K^+B_5H_8^-$ with 2-BrB_5H_8 gives 2,2'-$(B_5H_8)_2$. Both were characterised by ^1H and ^{11}B n.m.r., infrared and high-resolution mass-spectrometry.[18]

Eleven possible geometric isomers exist for bis(nido-decaboranyl) $(B_{10}H_{13})_2$. Four of these should exist as enantiomeric pairs, i.e. there are fifteen distinct structures. Five geometrical isomers were isolated and characterised, while there was some evidence for three others.[19]

The structure of one of the isomers of $B_{20}H_{26}$ formed by thermolysing nido-decaborane in the presence of tetrahydrothiophen has been shown to be 6,6'-bis(nido-decaboranyl). $^1H\text{-}\{^{11}B\}$ n.m.r. spectroscopy was used in conjunction with "partially-relaxed" ^{11}B and $^{11}B\text{-}\{^1H\}$ n.m.r.[20]

One of the isomers of $B_{20}H_{26}$ obtained by photolysis of $B_{10}H_{14}$ has been shown, by single crystal X-ray diffraction, to be 2,2'-bis(nido-decaboranyl). The two-centre, two-electron apical-apical B-B σ-bond is 1.692(3)Å long, compared to 1.74(6)Å for the analogous linkage in $(B_5H_8)_2$.[21]

Gamma-irradiation of $B_{10}H_{14}$ also produces several isomers of $B_{20}H_{26}$. The crystal structure of the most abundant isomer shows that it is 1,5'-bis(decaboran(14)yl): this is made up of a 1-decaboran(14)yl group linked by a two-centre B-B bond to a 5-decaboran(14)yl. The linking B1-B'5 bond is very similar in length to that in the 2,2'-isomer, 1.698(3)Å.[22]

3.1.2 Borane Anions and Metallo-derivatives

Detailed permutational analysis of the reaction sequence (2) suggests that in aqueous solution the reaction could proceed via

$$[BH_4]^- + H^+ \rightarrow BH_5 \rightarrow BH_3 + H_2 \qquad ...(2)$$

a rigid C_s BH_5 intermediate containing an H_2 subunit. The anhydrous process ($NaBH_4 + H_2SO_4$) on the other hand could proceed via a trigonal-bipyramidal intermediate. For $NaBH_4$ + HF a non-rigid BH_5 intermediate (of unknown structure) is probable.[23]

Molecular-orbital calculations, using basis sets of minimal and double-zeta quality, have been performed on YXH_4, where Y=Li or Na; X=B or Al. The geometries of the minima and saddle-points were calculated, as well as the energy barriers on the potential energy surface. The XH_4 group suffers quite different distortions in the four hydrides studied.[24]

BH_4^- in acetonitrile is converted, in the presence of acetic acid, into $BH_3(OCOCH_3)^-$. Previous work on the hydrolysis of "BH_4^-" in such solutions actually referred to $BH_3(OCOCH_3)^-$. Kinetic data suggest that the acetic acid substrate complex formed in the hydrolysis of $BH_3(OCOCH_3)^-$ is $BH_3OC(CH_3)O.HOCOCH_3$.[25] The nature of the $BH_3(OCOCH_3)^-$ has been studied by H/D isotope experiments. These suggested that the intermediate is derived from a transient complex of CH_3COOH with BH_4^- itself.[26]

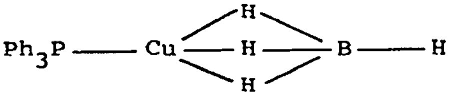
Crystals of $(t\text{-}BuO)_4Be_3(BH_4)_2$ are monoclinic, belonging to the space group A2/a. Each of the BH_4 groups in linked by two hydride-bridges to a Be atom. The three beryllium atoms are in a linear arrangement, each linked by two bridging t-BuO groups.[27]

$ZnCl_2$ reacts with $M(BH_4)_2$ (M=Mg or Ca) in ether solutions to give $Zn(BH_4)_2$ as ether addition compounds. The following derivatives were obtained: $M[Zn(BH_4)_3]$.n sol (where M=Li,Na,K,Rb or Cs; sol = Et_2O, THF or diglyme; $M[Zn(BH_4)_4]$.nsol. (where M=2Li, Mg, Ca or Ba). The i.r. spectra show that the BH_4 is bidentate with a solvated cation.[28]

A normal coordinate analysis has been carried out for $Zr(BH_4)_4$, assuming T symmetry.[29]

Bis(triphenylphosphine)copper(I) boranes react with B_2H_6 leading to ligand removal via formation of $Ph_3P.BH_3$. CuB_3H_8 and $Cu_2B_{10}H_{10}$ were prepared from reactions of $(Ph_3P)_2CuB_3H_8$ and $[(Ph_3P)_2Cu]_2B_{10}H_{10}$ with B_2H_6 in dichloromethane at 0^oC. CuB_3H_8 was previously unknown. There was some evidence for an intermediate species

$Ph_3P.CuB_3H_8$. $(Ph_3P)_2CuBH_4$ reacts at -78°C with excess of B_2H_6 in $CHCl_2$ giving $Ph_3P.CuBH_4$, which decomposes rapidly above -10°C. The most probable structure for the latter is (9).[30]



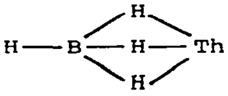
(9)

Preliminary X-ray studies have been reported on a new crystalline modification of $U(BH_4)_4$ i.e. $U(BH_4)_4$(II). The results were very incomplete.[31]

Infrared spectra were published for $U(BH_4)_4$ and $U(BD_4)_4$ vapours, and for the molecules in low-temperature matrices and thin films. Some assignments were proposed.[32]

$U(BH_4)_4$ and $U(BD_4)_4$ undergo complex degradation reactions when subjected to broad band u.v. radiation. The primary products appear to be $U(BH_4)_3$, B_2H_6 and H_2 (or the deuterio-analogues). $U(BD_4)_4$ undergoes a related decomposition under the influence of CO_2 laser irradiation at 924.97 cm^{-1}.[33]

The compounds $ClM[N(SiMe_3)_2]_3$, where M=Th or U, react with $LiBH_4$ to give $(BH_4)M[N(SiMe_3)_2]_3$. Infrared spectra suggest that the tetrahydroborate ligand is terdentate, and this was confirmed by X-ray studies, since when M=Th, the M-B bond distance was 2.61Å, corresponding to a unit (10).[34]



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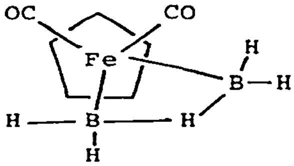


(11)

Stable crystalline complexes $(Ph_3P)_nMH_3BCO_2R$ (n=2,R=Me,Et or H, M=Cu; n=3, R=Et or H, M=Ag) have been prepared. As suggested by the formulae the (carboxy) trihydroborato ligand is bidentate in the copper complexes but unidentate in those of silver. This was confirmed by infrared and ^1H n.m.r. data. No evidence was found for interaction of $\geq$C=O with the metals.[35]

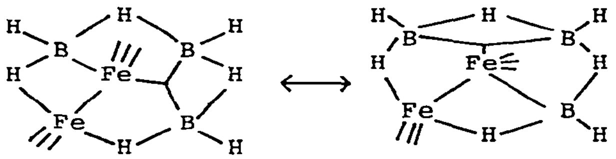
Diborane reacts with K $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ in dimethyl ether at -78°C, giving $(\eta^5\text{-}C_5H_5)(CO)_2Fe(\eta^2\text{-}B_2H_5)$, (11). This can be regarded as a very close analogue of the metal-olefin complex $(\eta^5\text{-}C_5H_5)(CO)_2Fe(\eta^2\text{-}C_2H_4)^+$.[36]

A survey of the reducing ability of aqueous NaB_3H_8 has revealed that under some conditions the $B_3H_8^-$ ion is more selective a reductant than BH_4^-.[37] The action of NaD on $THF.B_3D_7$ gave samples of NaB_3D_8 which were approximately 97% pure (in D).[38]

$B_3H_7^-$ is hydrolysed by HCl in $MeOH/H_2O$ mixtures at -78°C to give H_2 and a solution of B_3H_7: formulated as $B_3H_7OH_2$. Warming the latter to -45°C leads to complete hydrolysis (to $B(OH)_3$ and H_2). If OH^- is added to $B_3H_7OH_2$ at -78°C, $B_3H_7(OH)^-$ is formed.[39]

Infrared, Raman and inelastic neutron scattering spectra of CsB_3H_8 have been reported and the internal modes of $B_3H_8^-$ assigned together with some librational modes in the crystal. Energies of activation for exchange of one hydrogen were calculated to be 27 kJ mol^{-1} (via ν_{26}) or 45kJ mol^{-1} (via ν_{27}).[40]

$B_3H_7Fe_2(CO)_6$ is prepared, although only in about 1% yield, from the reaction of B_5H_9 with $Fe(CO)_5$ and $LiAlH_4$. The crystal structure was determined, which suggested two alternative interpretations of the bonding. By analogy with B_5H_9 it could be written as (12), or alternatively as a complex of $B_3H_7^{2-}$ (isoelectronic with the allyl ion, $C_3H_5^-$) with $Fe_2(CO)_6^{2+}$, (13). The π-electrons of the pseudo-allyl system bond to one iron atom, with 2 σ-bonds from the terminal boron atoms to the other iron.[41]



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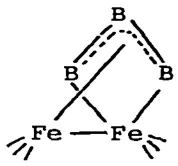
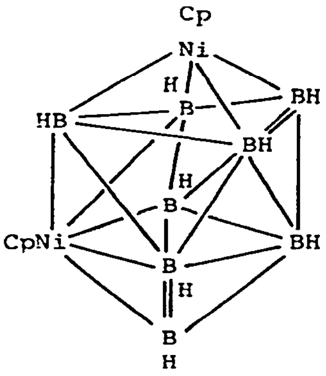


(13)

X-ray structural studies on the closo-, six-vertex metalloboron cluster 1,2-$(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$ show that the Co_2B_4 forms a distorted octahedral unit. The Co atoms are at adjacent vertices, and each Co is coordinated to an $(\eta^5\text{-}C_5H_5)$ ligand, as suggested by n.m.r. data. The two hydrogen atoms in face-bridging positions are approximately over the centres of Co_2B triangular faces: this is the first time that the positions of such hydrogen atoms have been refined. The bridging hydrogen atoms lead to a very long Co-Co distance, 2.557(1)Å.[42]

Single crystal X-ray diffraction measurements have been made on the related tetracobalt tetraboron cluster $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$. The Co_4B_4 skeleton forms an eight-vertex closo-polyhedron, whose symmetry is very close to D_{2d}. The Co atoms are at five-coordinate vertices, the borons at four-coordinate vertices. The compound violates Wade's electron-counting rules, as there are 16 skeleton electrons compared to the 18 expected. Several steric factors accounting for this were discussed.[43]

Two to four nickel atoms can be inserted into polyborane cages by reaction of $B_5H_8^-$ or $Me_2C_2B_4H_5^-$ with a number of metal-containing species. Thus NaB_5H_8 with $NiBr_2$ and NaC_5H_5 (followed by air oxidation) gives closo-1,6-$(\eta^5\text{-}C_5H_5)_2Ni_2B_8H_8$, closo-1,7-$(\eta^5\text{-}C_5H_5)_2Ni_2B_{10}H_{10}$. NaB_5H_8 will react with $(\eta^5\text{-}C_5H_5)_2Ni$ and sodium amalgam to produce closo-$(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$ and nido-$(\eta^5\text{-}C_5H_5)_4Ni_4B_5H_5$. The new compounds were characterised by ^{11}B and ^1H n.m.r., infrared, low- and high-resolution mass spectrometry, together with X-ray structural determination on $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$. The proposed structure of 1,6-$(\eta^5\text{-}C_5H_5)_2Ni_2B_8H_8$ is (14), while that established for $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$ is (15). The latter possesses a closo-, D_{2d}, cage geometry, despite having 20 valence electrons, from which a nido-structure would have been predicted. The nickel atoms occupy low-coordination positions, unlike the cobalt atoms in $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$. The Ni-Ni distance, 2.354(1)Å, is consistent with localised Ni-Ni bonding.[44]



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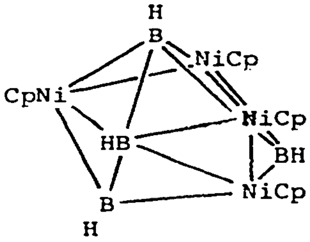
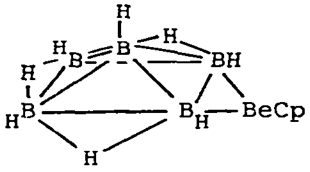


(15)

KB_5H_8 in pentane reacts with excess C_5H_5BeCl to give high yields of μ-$[(\eta^5$-$C_5H_5)Be]B_5H_8$. The structure was determined by single crystal X-ray diffraction. The cyclopentadienyl beryllium group is in a non-vertex bridging position between two adjacent basal boron atoms in a square pyramidal framework, (16). This should be compared with 2-$[(\eta^5$-$C_5H_5)]$-2-BeB_5H_{10} in which the same group is incorporated as a vertex in a six-atom nido-framework.[45]



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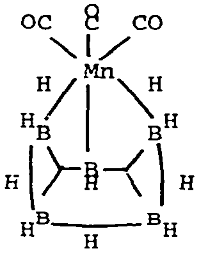
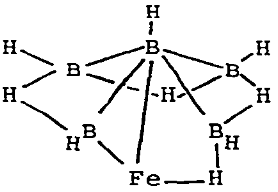


(17)

PRDDO-SCF molecular orbital calculations have been performed on the nido-beryllaboranes $B_5H_{10}BeX$ (where $X=BH_4$, B_5H_{10}, CH_3 or C_5H_5). These show that the bonding within the B_5H_{10} unit stays remarkably similar for all X, but that about Be is significantly different from the other compounds in $B_5H_{10}BeC_5H_5$.[46]

Pentaborane(9) reacts with $HMn(CO)_5$ (or H_2+$Mn_2(CO)_{10}$) at high-temperature (140°C) to give 2,2,2-$(CO)_3$-2-MnB_5H_{10}. The spectra are consistent with C_s symmetry, structure (17). The compound reacts with Br_2 to give an apically substituted (1-Br) derivative.[47]

Pyrolysis of B_5H_9 in the presence of $Fe(CO)_5$ in a hot-cold reactor produces $B_5H_9Fe(CO)_3$. ^{11}B and ^1H n.m.r. spectra are consistent with a pentagonal pyramidal structure, (18), in which the $Fe(CO)_3$ occupies a basal vertex site. The bridge hydrogen between the iron and a basal boron atom is fluxional.[48]



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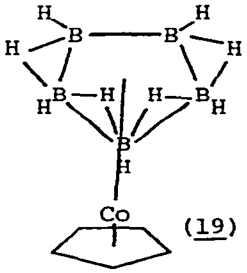

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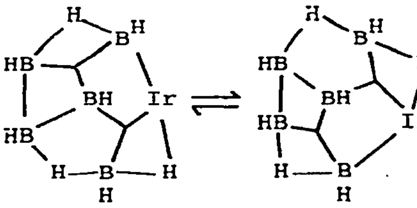
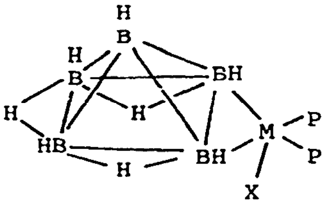
$B_5H_8^-$, Fe^{2+} and $C_5H_5^-$ react in THF at -78°C, and on working up the products in air 2-(η^5-C_5H_5)FeB_5H_{10}, 2-(η^5-C_5H_5)$FeB_{10}H_{15}$, ferrocene and traces of other ferraboranes are produced. ^{11}B and ^1H n.m.r. spectra of the first complex show that it has a pentagonal-pyramidal structure, with the iron at the base and five bridging hydrogen atoms (3 B-H-B, 2Fe-H-B) on the open face. Heating it to 175-180°C causes isomerisation to 1-(η^5-C_5H_5)FeB_5H_{10} (with an apical Fe). Both isomers are electronic analogues of B_6H_{10} and ferrocene, while the latter is a direct structural analogue of ferrocene. 2-(η^5-C_5H_5)$FeB_{10}H_{15}$ is an eleven-vertex icosahedral fragment.[49]

Direct reaction of B_5H_9 with (η^5-C_5H_5)$Co(CO)_2$ using hot-cold reaction methods leads to two new cobaltaborane species: 1-(η^5-C_5H_5)CoB_5H_9 and 2-(η^5-C_5H_5)CoB_9H_{13}. The former, (<u>19</u>), is isoelectronic with ferrocene, while it shows a dynamic behaviour that is closely reminiscent of B_6H_{10}.[50]

KB_5H_8 reacts with $Ir(CO)Cl(PPh_3)$ at low temperatures to form $Ir(B_5H_8)(CO)(PPh_3)_2$, crystals of which are monoclinic, space group $P2_1/c$. The molecular structure is most unusual. The transition metal atom is inserted into the polyhedral pentaborane cluster in such a way as to form a pentagonal pyramid, with a basal iridium atom. N.m.r. data suggest that in solution an equilibrium is set up (<u>20</u>).[51]



(<u>20</u>)



(<u>21</u>)

^1H-{^{11}B}, ^{11}B, ^{11}B-{^1H} and ^{31}P- ^1H n.m.r. spectra were studied for $[M(B_5H_8)X(dppe)]$, where M=Ni or Pd, X=halogen, dppe = bis(diphenylphosphino)ethane. All have a static metallo-<u>nido</u>-pentaborane structure with the metal atom bridging between two basal boron atoms.[52]

An attempt has been made to evaluate the fluxional behaviour of $B_8H_8^{2-}$ by carrying out molecular orbital calculations using the PRDDO method. A low-energy path connects the D_{2d} and C_{2v} geometries (the former being more stable), the barrier being less than 4kcal.mol^{-1}. There was no computational evidence for a stable D_{4d} structure. The effects of solvation and ion-pairing were also calculated. Li^+ seems to stabilise square faces in $Li^+B_8H_8^{2-}$, but addition of a second Li^+ gives the stability order: $D_{2d} > C_{2v} > D_{4d}$.[53]

Four or five-coordinate iridium(I) cations, Ir(dppe)$_2^+$ or Ir(CO)(dppe)$_2^+$ react with $B_{10}H_{14}$, 6-$ClB_{10}H_{13}$ or $B_{10}H_{13}^-$ to form several new ionic compounds. Thus [Ir(dppe)$_2$]Cl and $B_{10}H_{13}X$ (X=H or 6-Cl) produce [Ir(III)Cl(dppe)$_2$H][$B_{10}H_{12}X$]. [Ir(CO)(dppe)$_2$]Cl and $B_{10}H_{13}^-$ in methanol, on the other hand, give[Ir(I)(CO)(dppe)$_2$][$B_{10}H_{13}$], which undergoes methanolic degradation to [Ir(III)(dppe)$_2H_2$][B_9H_{14}]. The crystal structure of the last compound was determined, but the $B_9H_{14}^-$ ions were grossly disordered.[54]

Empirically based calculations of bond enthalpies for $B_nH_n^{2-}$, based upon B-B and B-H bond lengths, have been carried out. The results shed some light on the relative stabilities of the clusters, and on the distribution of their skeletal bonding electrons. The following stability sequence was suggested:[55]

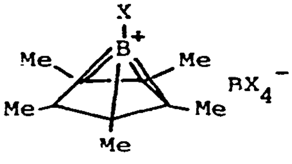
$$B_{12}H_{12}^{2-} > B_{10}H_{10}^{2-} > B_6H_6^{2-} > B_9H_9^{2-} > B_8H_8^{2-}$$

Detailed analysis of the valence electron density in the space around the molecule for electron-deficient polyhedral molecules such as $B_{12}H_{12}^{2-}$ and the isomers of $C_2B_{10}H_{12}$ has been performed. The main electron charge resides within the sphere inscribed in the polyhedron defined by the network atoms. A significant proportion of this electron density was found at the centre of this sphere. The bonding is therefore said to be characterised by "volume conjugation".[56]

Solubility was studied at 25°C in the $Cs_2B_{12}H_{12}$-Cs_2SO_4-H_2O system. The solubility of Cs_2SO_4 is very low over a wide range of $Cs_2B_{12}H_{12}$ concentrations, allowing pure $Cs_2B_{12}H_{12}$ to be obtained.[57]

3.1.3 Carba- and other Non-metal Heteroboranes

Dihalogeno(pentamethyl cyclopentadienyl)boranes, $C_5Me_5BX_2$, (X=Cl,Br or I), undergo halide abstraction reactions with BX_3 to form 1-halogeno-2,3,4,5,6-pentamethyl-2,3,4,5,6-pentacarba-*nido*-hexaborane(6) cations, (22). These complete the series of pentagonal pyramidal *nido*-carbaboranes, and the structure was confirmed by n.m.r. (^1H, ^{13}C, ^{11}B) data.[58]



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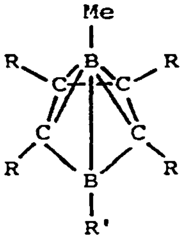

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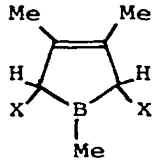


(24)

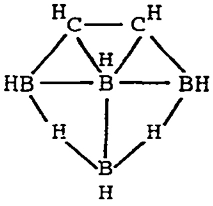
Nido-2,3,4,5-tetracarbahexaborane(6) derivatives, (23), where R=R'=Me; R=R'=Et; R=Et, R'=Me, have been prepared for the first time, from 1-stanna-4-bora-2,5-dimethylcyclohexadiene or 3-diethylboryl-1-stanna-cyclopentadiene with $MeBBr_2$. The 1-bora-3-cyclo-pentene derivative (24), X=B(Me)Br, is an intermediate with the former reagent.[59]

Geometry-optimised *ab initio* molecular orbital calculations for 2,3,4,5-*nido*-hexaborane(6) give a structure in agreement with that found experimentally. Bonding between neighbouring atoms in the basal plane is very strong, while that between the apical boron and the basal plane is weak. The electronic structure of the apical BH is in some respects similar to that of $Mn(CO)_3$ in $CpMn(CO)_3$.[60]

The He(I) photoelectron spectra of 2-X-1,6-$C_2B_4H_5$ and 2,4-X_2-1,6-$C_2B_4H_4$ (where X=Cl, Br or I) have been reported. The effects of halogen substitution on the spectrum of the parent *closo*-carbaborane could be described in terms of a three-parameter model. The major effect is a π-type interaction between surface orbitals of the cage and the filled halogen p-orbitals.[61]

The adducts $B_5H_9 \cdot 2L$ (L=NMe_3 or SMe_2) react with 2-butyne or phenylacetylene *in situ* at or below room temperature to form carbaboranes $RR'C_2B_4H_6$, derivatives of (25), which were isolable by vacuum fractionation. The best results were obtained for

L=NMe_3, with B_5H_9 in excess, and simultaneous addition of trimethylamine and alkyne to the borane of the B_5H_9 is generated in situ from $B_3H_8^-$ salts, this constitutes a "one-pot" conversion of $B_3H_8^-$ to $C_2B_4H_8$ derivatives.[62]



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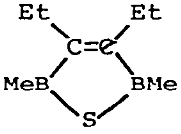

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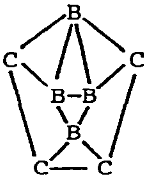
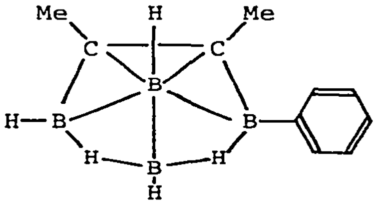


(27)

Reaction of (26) with potassium in tetrahydrofuran forms K_2S and the C_4B_4 carbaborane $(EtC)_4(BMe)_4$, whose structure is believed to involve the skeleton (27). [63]

The nido-carbaborane anion $[2,3\text{-}Me_2C_2B_4H_5]^-$ reacts with anhydrous $HgCl_2$ in tetrahydrofuran at room temperature producing $\mu,\mu'\text{-}[Me_2C_2B_4H_5]_2Hg$. The mercury atom is bound to two carbaborane ligands by B-Hg-B three-centre, two-electron bridge bonds. Heating in benzene to 180°C gives quantitative loss of mercury and formation of the B-B linked nido-carbaborane $5,5'\text{-}[Me_2C_2B_4H_5]_2$ as a single isomer. Aerial oxidation of this in benzene solution led to cleavage of the B-B bond and oxidative addition of C_6H_6, giving $4\text{-}Ph\text{-}2,3\text{-}Me_2C_2B_4H_5$ (28). This is a stable derivative of nido-2,3-$C_2B_4H_8$. $B_5H_8^-$ reacts with $HgCl_2$ in THF to form $\mu,\mu'\text{-}(B_5H_8)_2Hg$,



(28)

a stable white solid in which the mercury atom is bridged to two pentaborane ligands.[64]

Isomers of $(B\text{-}CH_3)_x\text{-}2,4\text{-}C_2B_5H_{7-x}$ (x=1 to 4) reach equilibrium at 300°C. The methyl group prefers positions in the order:

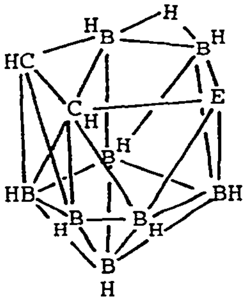
3>1,7>5,6. The mechanism of the interconversions involves either a diamond-square-diamond (dsd) or a triangle rotation cage rearrangement. If the thermal rearrangement of 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ is carefully controlled, the 1,5-dimethyl isomer forms before the 1,3-, the 3,5- or the 1,7-isomers. Also, the 3,5-isomer is formed faster from the 1,5- than is the 1,3-, even though the latter is more stable. The methyl positional preferences are exactly the opposite to those observed in the kinetically-controlled, "electrophilic" methylation of $C_2B_5H_7$. The increased B-methyl preference under equilibrium conditions probably involves a simple electrostatic polarisation model in which the methyl group is more effective in dispersing the charge when located on the more positively charged boron atoms.[65]

Reaction of trimethylborane with *nido*-2,3-$C_2B_4H_6$ at 220-230°C produces a two-boron cage expansion, yielding 2,3,4,5,6,8-Me_6-*closo*- 1,7-$C_2B_6H_2$, in addition to the previously known one-boron cage expansion (to 1,3,5,6,7-Me_5-*closo*-2,4-$C_2B_5H_2$). The cage expansion product from the reaction of *closo*-1,6-$C_2B_4H_6$ with excess trimethylborane at 550-600°C is B-Me_2-*closo*-2,4-$C_2B_5H_5$.[66]

The crystal structure of the cobaltocenium ion salt of $Me_4C_4B_8H_9{}^-$ has been determined. The anion is a thirty-electron, twelve-vertex cage, with an open, basket-like, geometry and four C-Me groups contiguous on an open face. One C-Me unit is coordinated to only two framework atoms, and the "extra" hydrogen atom is coordinated to this bridging carbon. This structure, together with the previously known geometry of neutral $C_4Me_4B_8H_8$, was used to propose a mechanism for the formation of the dianion $Me_4C_4B_8H_8{}^{2-}$ and its fluxional character.[67]

$AsCl_3$ and zinc dust (in refluxing diethyl ether) react with sodium undecahydro-5,6-dicarba-*nido*-decaborate to give a low yield of $B_8C_2{}^{7,8}As^9H_{11}$. The phosphorus analogue is made by a similar reaction using PCl_3, and their structures are believed to be (**29**, E=P or As). The arsenic compound reacts with TlOH to give $B_8C_2{}^{1,2}Tl^3As^4H_{11}$.[68]

$B_9H_{11}CNMe_3$ reacts with sodium hydride, and subsequent treatment with NaC_5H_5 and $CoCl_2$ gives $(C_5H_5Co)B_9H_9CNMe_3$. This is a fluxional *closo*-, eleven-atom cage molecule at +70°C, but static at -40°C on the ^{11}B n.m.r. time scale. Heating the cobalt complex produces $B_9H_9CNMe_3$, which in turn reacts with sodium polyselenide giving a moderate yield of *nido*-$SeB_9H_9CNMe_3$, (**30**).[69]



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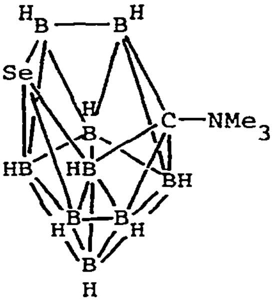

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Specifically-labelled deuterio- and brominated-derivatives of the general form 4,7-(ORO)-2,3-$(CH_3)_2$-2,3-$B_9C_2H_7$, where R= a divalent radical bridging two adjacent B-O units, e.g. C_6H_4, have been prepared. The ^{11}B n.m.r. spectra of these were used to assign the spectra of 2,3-$(CH_3)_2$-2,3-$B_9C_2H_9$ and 4,7-$(OH)_2$-2,3-$(CH_3)_2$-2,3-$B_9C_2H_7$. For example, the former gave four doublets (relative intensities 4:2:2:1) assigned to B(4,5,6,7), B(8,9), B(10,11) and B(1) respectively.[70]

Gas-phase electron-diffraction data were used to obtain structural parameters for the p-phospha- and p-arsa-carbaboranes, 1,12-$XCHB_{10}H_{10}$ (X=P or As). When X=P; r(B-X) was 2.049(5)Å, and when X=As, 2.137(3)Å.[71].

A number of new stibaboranes have been prepared. Thus $B_{10}H_{12}As^-$ reacts with $SbCl_3$ and trimethylamine in tetrahydrofuran to give 1,2-$B_{10}H_{10}AsSb$. The reaction mixture $B_{10}H_{14}/SbCl_3/NMe_3/Zn$ in THF gave $B_{10}H_{10}Sb_2$, while the chief product of the reaction of $B_{11}H_{14}^-$ with $SbCl_3/NMe_3$ in THF was $B_{11}H_{11}Sb^-$. Treatment of 1,2-$B_{10}H_{10}AsSb$ or 1,2-$B_{10}H_{10}Sb_2$ with piperidine gave unstable eleven-particle icosahedral fragments (not characterised further). These could be stabilised by adding $CoCl_2$ and cyclopentadiene, to form CpCo(7,8-B_9H_9AsSb) or CpCo(7,8-$B_9H_9Sb_2$).[72]

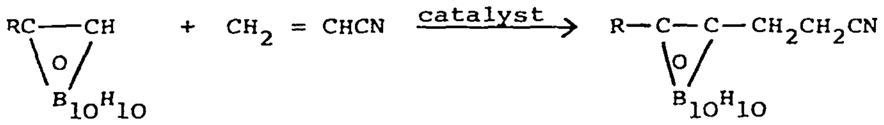
O-carbaborane phosphino-derivatives, $R_2P[B_{10}H_{10}C_2]PR'R''$, where R=Ph, R'=R''=$NMe_2$ or F; R=Ph,R'=F,R''=NMe_2; R=R'=NMe_2, R''=F, have been prepared, and characterised by mass-,infrared- and n.m.r.-(^1H,^{19}F,^{31}P) spectroscopy.[73]

The crystal structure of 9-trimethylamine-6-thiadecaborane(11) has been determined. This is the first such study of a non-metallated, nido-, ten-vertex thiaborane, and it showed that the NMe_3 is attached to the thiaborane cage in an exopolyhedral fashion at B(9), with $r(B-N)=1.600(4)$Å. The sulphur atom, at position 6, is bound to three boron atoms, with an average S-B distance of 1.927(8)Å.[74]

$NaB_{11}H_{14}(dioxan)_{2.5}$ reacts with ammonium polyselenide to give a low yield of $B_{11}H_9Se_3^{2-}$. X-ray diffraction was used to determine the molecular structure of this unusual species - it is derived from $B_{11}H_{11}^{2-}$, with an Se_3 chain bonded to two adjacent boron atoms of the <u>closo</u>-cage, <u>exo</u> to the boron polyhedron.[75]

Gas-phase isomerisation of 3-aryl-o-carbaboranes in vacuo at 550-600°C yields equal amounts of 2- and 4-aryl-<u>m</u>-carbaboranes. These were separable by column chromatography.[76]

The CH group of <u>o</u>-carbaboranes reacts with acrylonitrile in the presence of an alkali catalyst, according to (3), to form β-cyanoethylcarbaboranes.[77]



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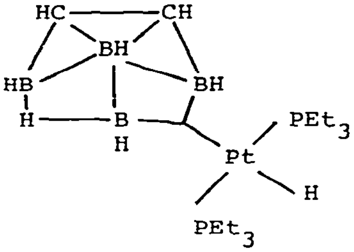
3.1.4 Metallo-heteroboranes

A single-crystal X-ray diffraction study of $[2,3\text{-}Me_2C_2B_4H_4]_2FeH_2$ showed that the structure has a sandwich-form, with two pentagonal pyramidal carbaborane ligands face-bonded to the iron atom. The "extra" hydrogen atoms probably occupy bridging positions on the FeB_2 polyhedral faces.[78]

A new series of cobaltcarbaboranes has been prepared from the coupled carbaboranes $(2,4\text{-}C_2B_5H_6)_2$ and $[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$. Heating $(\eta\text{-}C_5H_5)Co(CO)_2$ with a mixture of $(2,4\text{-}C_2B_5H_6)_2$ isomers led to direct metal insertion, forming several multimetal complexes. Six of these were of the general formula $(\eta\text{-}C_5H_5)_2Co_2B_{10}H_{12}$. ^{11}B and ^{1}H n.m.r. spectra showed that <u>both</u> cobalt atoms are in one cage: there is a $1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ unit attached to an unmetallated $C_2B_5H_6$ cage. The isomers differ in the points of attachment of the two cages. All of the compounds underwent a series of rearrangements. Deprotonation of an isomeric mixture of $[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$ by NaH, followed by treatment with sodium cyclopentadienide and $CoCl_2$, gave three sets of products, including several isomers of $(CH_3)_2C_2B_4H_5\text{-}(CH_3)_2C_2B_3H_4Co(\eta\text{-}C_5H_5)$ and of $(CH_3)_2C_2B_4H_5\text{-}(CH_3)_2C_2B_4H_3Co(\eta\text{-}C_5H_5)$, as well as $4,5'\text{-}[(CH_3)_2C_2B_4H_3Co\text{-}(\eta\text{-}C_5H_5)]_2$.[79]

Pt_2(μ-cyclo-octadiene)(PEt_3)$_4$ reacts with 2,3-dicarba-*nido*-hexaborane(8), 2,3-dimethyl-2,3-dicarba-*nido*-hexaborane(8) and monocarba-*nido*-hexaborane(9) to give (respectively): [*nido*-$\mu_{4,5}$-{*trans*-(Et_3P)$_2$Pt(H)}-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$], [*nido*-$\mu_{4,5}$-{*trans*-(Et_3P)$_2$Pt(H)}-$\mu_{5,6}$-H-2,3-Me_2-2,3-$C_2B_4H_4$] and [*nido*-$\mu_{4,5}$-{*trans*-(Et_3P)$_2$Pt(H)}-($\mu_{3,4}$-H)($\mu_{5,6}$-H)-2-CB_5H_6]. The molecular structure of the first complex was established by X-ray studies. The cage core atoms form a *nido*-pentagonal pyramidal geometry, with adjacent facial carbon atoms. Both pentagonal B-B links are bridged, one by hydrogen, the other by *trans*-(Et_3P)$_2$Pt(H). (*31*)[80]



(*31*)

Oxidative addition reactions of Pt(PEt_3)$_2$; Pt(*trans*-stilbene)(PR'_3)$_2$, R'=Et or Me; M(cod)(PMe_3)$_2$, M=Pt or Ni or Ni(cod)(PEt_3)$_2$ occur with *closo*-1,7-R_2-1,7-$C_2B_6H_6$ (R=H or Me), *closo*-4,5-R_2-4,5-$C_2B_7H_7$ or *closo*-1,6-$C_2B_8H_{10}$ to form the following new complexes: *closo*-[4,5-R_2-6,6-(PR'_3)$_2$-4,5,6-$C_2MB_6H_6$], where M=Pt, R=H, R'=Me; M=Pt,R=Me,R'=Me or Et; M=Ni, R=Me,R'=Me or Et; *nido*-[4,5-R_2-7,7-(PR'_3)$_2$-4,5,7-$C_2PtB_6H_6$], where R=H, R'=Me; R=Me,R'=Et; *nido*-[2,8-R_2-10,10-(PR'_3)$_2$-2,8,10-$C_2MB_7H_7$], where M=Pt, R'=Et, R=H or Me; M=Ni, R=H, R'=Et or R=R'=Me, and *nido*-[μ-(6,10)-{Pt(PMe_3)$_2$}-10,10-(PMe_3)$_2$-7,9,10-$C_2PtB_8H_{10}$] respectively. The last, with activated charcoal, forms *nido*-[10,10-(PMe_3)$_2$-7,9,10-$C_2PtB_8H_{10}$].[81]

The crystal and molecular structure have been determined for isomer V of (η^5-C_5H_5)$_2Co_2Me_4C_4B_6H_6$. The latter consists of two pentagonal pyramidal (η^5-C_5H_5)$CoMe_2C_2B_3H_3$ units, partially fused together along their C_2B_3 faces. The pairs of carbons on the two pyramidal units are separated by non-bonding distances. The shape is a severely-distorted icosahedron with a large opening on one side, and its central cage system is very similar to that in the mono-cobalt complex (η^5-C_5H_5)$CoMe_4C_4B_7H_6$(OEt). ^{11}B and ^1H n.m.r. spectra were used to suggest structures for three isomers

(V,VI and VII) of $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$.[82]

The severe polyhedral distortions found in, for example, $(\eta^5\text{-}C_5H_5)_2Co_2Me_4C_4B_6H_6$ can be explained in terms of the preferred valence structures of the idealised $(C_2B_4H_6)_2$ system from which it can be derived. These valence structures can be related to the $C_2B_4H_8$ framework.[83]

Platinathiaboranes have been prepared by the reaction of L_4Pt, (where $L{=}PMe_2Ph$, PEt_3 or PPh_3), with $1\text{-}SB_9H_9$ in ethanol. X-ray diffraction results were not able to differentiate between the possible thiaborane ligands SB_8H_8 and SB_8H_{10}. Mass- and ^1H n.m.r. -spectra, however, showed the complexes to have the general formula $L_2Pt(SB_8H_{10})$. Thus, the framework electron count corresponds to the nido skeletal structure found crystallographically, i.e. the structure is not the "unexpected" one found for other d^8 or d^9 metalloheteroboranes. In addition to 3 $9,9\text{-}L_2\text{-}6,9\text{-}SPtB_8H_{10}$ compounds, $8\text{-}(OEt)\text{-}9,9\text{-}(PPh_3)_2\text{-}6,9\text{-}SPtB_8H_9$ was also characterised, and the relationship between these four and the previously-known $L_2M(SB_9H_9)$, (M=Pd or Pt), was discussed. The synthetic method for the new compounds is a degradative insertion, and even treatment of $SB_{11}H_{11}$ with L_4Pt leads to the kinetically stable $L_2Pt(SB_8H_{10})$.[84]

Several new nido-metallocarbaboranes with four skeletal carbon atoms have been prepared and characterised. $Me_4C_4B_8H_8$ reacts with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ under u.v. irradiation to give isomer I of $(\eta^5\text{-}C_5H_5)CoMe_4C_4B_7H_7$, and isomers I and II of $(\eta^5\text{-}C_5H_5)CoMe_4C_4B_6H_6$. The same CoC_4B_7 isomer resulted from the oxidative fusion of ligands in closo, nido-$[Me_2C_2B_4H_4]Co[Me_2C_2B_3H_5]^-$, followed by reaction with O_2, $Na^+C_5H_5^-$ and $CoCl_2$. The proposed structures were based on ^{11}B and ^1H F.T. n.m.r., infrared and low- and high-resolution mass spectrometry.[85]

Crystals of $[Et_4N]^+[(C_5H_5)Co(C_2B_8H_{10})Co(C_2B_8H_{10})]^-$ are monoclinic, and belong to the space group $P2_1/c$. The two $C_2B_8H_{10}$ units have different geometries: the central cage resembles a distorted dodecahedron, while the terminal cage shows greater distortion (shortening of B-C, lengthening of two facial B-B distances) as an eleven-vertex polyhedron. The angle between the two ligating faces of the central cage is close to 120°, as expected for an ideal truncated dodecahedron.[86]

X-ray spectra have been reported for $Cs^+[(1,2\text{-}B_9C_2H_{11})_2M]^-$, where M=Fe, Co or Ni, and for $(1,2\text{-}B_9C_2H_{11})_2Ni$ and $(1,7\text{-}B_9C_2H_{11})_2Ni$.

The orbitals largely derived from metal 3d-orbitals lie at lower energy for Ni(III) than for Fe(III) or Co(III). The two isomeric Ni(IV) complexes differ significantly in the effective charges of the Ni atom.[87]

Reactions of electrochemically generated Co(I)π-complexes, based on $CpCo(B_9C_2H_{11})$, $CpCo(B_9C_2H_8Br_3)$ or $Co(B_9C_2H_{11})_2$, with phenol in non-aqueous solvents were studied by d.c. polarography, cyclic voltammetry, differential pulse polarography and bulk electrolysis.[88]

Two new carbaborane complexes having catalytic activity have been prepared: $3,3\text{-}(PPh_3)_2\text{-}4\text{-}C_5H_5N\text{-}3,1,2\text{-}RhC_2B_9H_{10}$ and its carbonyl derivative $3\text{-}(PPh_3)_2\text{-}3\text{-}(CO)\text{-}4\text{-}C_5H_5N\text{-}3,1,2\text{-}RhC_2B_9H_{10}$. The crystal structure of the latter has been determined. Comparing the bond distances from Rh to the C_2B_3 face $[(Rh\text{-}C)_{ave} - (Rh\text{-}B)_{ave} = 0.031Å]$ suggests that the structure can be classified as <u>closo</u>. This conclusion is also supported by the small value (0.02Å) of the slip parameter Δ, and the C-C bond length (1.630(7)Å). The $Rh(CO)(PPh_3)$ unit is in an unexpected conformation, rotated ca. 90° from the expected orientation, possibly because of steric interaction with the pyridine ring.[89]

HNO_3 or NO_2/N_2O_4 reacts with $[3,3\text{-}(PPh_3)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ to form the nitratorhodacarbaborane: $[3\text{-}(PPh_3)\text{-}3,3\text{-}(NO_3)\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$. A crystal structure was determined for the latter, which showed that the nitrato-group is symmetrically bidentate (Rh-O = 2.20(1)Å).[90] A crystal structure determination on $3,3\text{-}(Ph_3P)_2\text{-}3\text{-}(HSO_4)\text{-}3,1,2\text{-}RhC_2B_9H_{11}OEt_2$ showed that the HSO_4^- is bonded to the rhodium via an Rh-O bond. The rhodium atom is at the apex of the $RhC_2B_9H_{11}$ icosahedral cluster. Solution n.m.r. data, $^{31}P\text{-}\{^1H\}$, suggested that a form in which the HSO_4 is bidentate is present.[91]

New d^{10} metallacarbaboranes have been prepared as follows, equations (4) and (5), while $Na[B_9C_2{}^{7,8}(NC_5H_5){}^9H_{10}]$ reacts with

$$\{HgCl_2(PPh_3)\}_2 + Tl[B_9C_2{}^{1,2}Tl{}^3H_{11}] \rightarrow B_9C_2{}^{1,2}[Hg(PPh_3)]{}^3H_{11} \quad \ldots(4)$$

$$HgMe(O_2CMe) + K[B_9C_2H_{12}]/KOH \rightarrow [B_9C_2{}^{1,2}(HgMe){}^3H_{11}]^- \quad \ldots(5)$$

$AuCl(PPh_3)$, $\{CuCl(PPh_3)\}_4$ and $HgCl_2$ to form $B_9C_2{}^{1,2}[Au(PPh_3)]{}^3\text{-}(NC_5H_5){}^4H_{10}$, $B_9C_2{}^{1,2}[Cu(PPh_3)]{}^3[NC_5H_5]{}^4H_{10}$ and $3,3'\text{-}\{Hg[B_9C_2{}^{1,2}\text{-}(NC_5H_5){}^4H_{10}]\}_2$ respectively. The structure of the first is shown in Figure 1, i.e. the mercury is coordinated almost linearly by

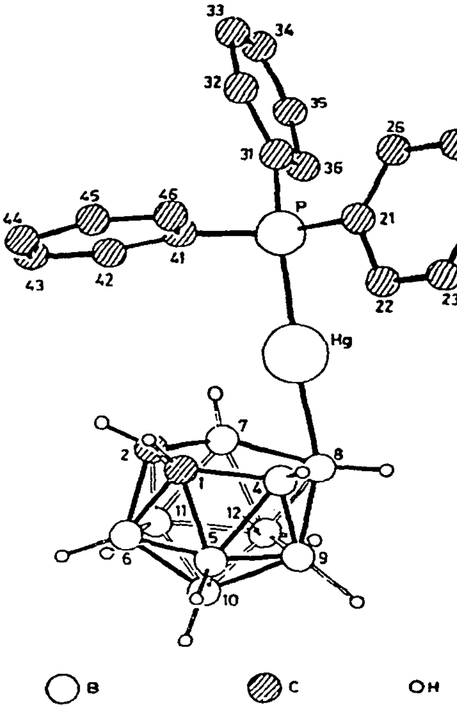


Figure 1. Molecular structure of $B_9C_2{}^{1,2}[Hg(PPh_3)]^3H_{11}$. Phenyl hydrogen atoms are omitted. (Reproduced by permission from J.Chem.Soc., Dalton Trans., (1979) 619.)

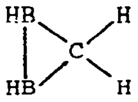
PPh_3 and the unique boron atom of the C_2B_3 face, implying a direct Hg-B σ-bond (Hg-B distance, 2.20Å, Hg-P, 2.39Å).[92]

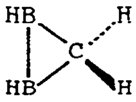
Crystals of $[NMe_4][\eta^5\text{-}C_5H_5)CoCB_{10}H_{11}]$ are orthorhombic, and belong to the space group Pbcm. The anion is an icosahedron in which the pairs of atoms C(2), C(5); C(3),C(4); BC(1)-BC(7); B(4)-B(8); B(5)-B(12); B(6)-B(11) are related by a mirror plane. The cobalt is coordinated to the pentagonal face (BC(1)-B(3)-B(7)-B(11)-B(6)).[93]

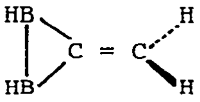
Temperature-dependent magnetic susceptibilities have been measured for $(Et_4N)_2[Cr(II)(C_2B_{10}H_{12})_2]$. The magnetic data also reported for $Cs[Cr(III)(C_2B_9H_{12})_2]$ ($g=1.98, \theta = -1.5K$) were in agreement with e.p.r. results.[94]

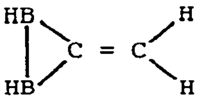
3.1.5 Compounds containing B-C bonds

Ab initio m.o. calculations on a number of compounds containing three-membered BBC rings suggest that the most favoured structures will be those which appear to violate all of the normal conventions!


(32a)


(32b)


(33a)


(33b)

Thus, for the methane and ethene derivatives, (32a) and (33a) were calculated to have much lower energies than (32b) and (33b), with similar results for allene and butatriene derivatives. Delocalised bonding schemes could account for this. Note that no close analogues of any of these systems have yet been prepared.[95]

A detailed study has been made of the H/D and $^{10}B/^{11}B$ isotopic shifts in the infrared and Raman spectra of $B(CH_3)_3$ and $B(CD_3)_3$. Normal coordinate analysis gave a set of force constants able to reproduce observed shifts. Infrared and Raman spectra were also obtained for $M^+B(CH_3)_4^-$ (M=Na,K or Rb), and assignments proposed. A normal coordinate analysis was carried out using a comparable potential field to that for $B(CH_3)_3$.[96]

Microwave spectra of $CH_3{}^{11}BF_2$, $CH_3{}^{10}BF_2$ and $^{13}CH_3{}^{11}BF_2$ in the ground torsional state were analysed to give the following structural parameters: r(C-H) 1.102 ± 0.007Å, r(C-B) 1.564 ± 0.005Å, r(B-F) 1.315 ± 0.005Å, ∠HCB 110.4° ± 0.5°, ∠FBF 116.8° ± 0.5°. The structure of the BF_2 group in this and related compounds is relatively invariant, in comparison with the isoelectronic NO_2 group.[97]

Infrared and Raman spectra were reported for CH_3BCl_2 and CD_3BCl_2, the latter for the first time. $^{10}B/^{11}B$ and H/D shifts were used to generate a fairly complete force field.[98]

Addition of one molar equivalent of BR_3 (where R is an alkyl group) to a solution of lithium trimethoxyaluminohydride in tetrahydrofuran at room temperature gives rapid formation of polymeric $Al(OMe)_3$, leaving $Li^+BR_3H^-$ in quantitative yield. This process is applicable to a very wide range of alkyl groups.[99]

Me_3SnCF_3 reacts with boron trifluoride in a 3:1 ratio to give $CF_3BF_3^-$ and also, by reactions (6),(7) and (8), the hitherto unknown ion $(CF_3)_2BF_2^-$ (as the main product). Potassium and

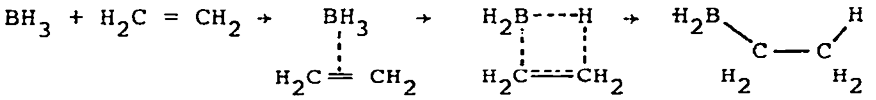
$$Me_3SnCF_3 + BF_3 \rightarrow [Me_3Sn][CF_3BF_3] \qquad \ldots (6)$$

$$[Me_3Sn][CF_3BF_3] \rightleftharpoons CF_3BF_2 + Me_3SnF \qquad \ldots (7)$$

$$CF_3BF_2 + Me_3SnCF_3 \rightarrow [Me_3Sn][(CF_3)_2BF_2] \qquad \ldots (8)$$

caesium salts were isolated, and infrared and Raman spectra obtained. These were assignable using a molecular symmetry of C_{2v}. ^{19}F n.m.r. parameters were also reported.[100]

Calculations have been performed to obtain information about the path of the hydroboration reaction. The molecular structures of the reactants, intermediates and products were calculated by

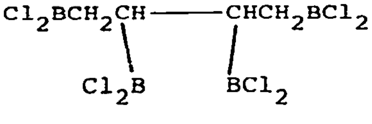
 ...(9)

$$BH_3 + H_2C=CH_2 \rightarrow \underset{H_2C=CH_2}{\overset{BH_3}{\vdots}} \rightarrow \underset{H_2C=\!=\!=CH_2}{\overset{H_2B\text{----}H}{\vdots\quad\vdots}} \rightarrow H_2B\text{—}CH_2\text{—}CH_2\text{—}H \qquad \ldots (9)$$

the partial retention of diatomic differential overlap (PRDDO) method. Equation (9) summarises the suggested mechanism.[101]

A detailed vibrational assignment of dimethylvinylborane, $Me_2BCH = CH_2$, based on infrared and Raman spectra of gaseous, liquid and solid samples, has been presented. These data, together with ^1H and ^{13}C n.m.r. spectra at low temperatures, show clearly that the heavy atom skeleton is planar. This disproves a theoretical calculation (N.L. Allinger and J.H. Seifert, J.Am. Chem.Soc., 97 (1975) 752) which had suggested that the vinyl group should be twisted out of the molecular plane.[102]

One molecule of B_2X_4 (X=Cl or F) adds on to 1,3-butadiene to form 1,4-bis(dihalogenoboryl)-2-butene, $X_2BCH_2CH = CHCH_2BX_2$. If X=Cl, a second B_2Cl_4 molecule can be added to the butene



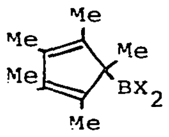
$$\underset{Cl_2B}{Cl_2BCH_2CH}\text{——}\underset{BCl_2}{CHCH_2BCl_2}$$

(34)

double bond, forming (34). B_2X_4 can cause polymerisation of methyl-substituted conjugated or cumulated di- or polyenes.[103]

N,N,N',N'-Tetramethylethylenediamine (TMED) forms air-stable adducts with numerous monoalkylboranes: $TMED.BH_2R$ and $TMED.2BH_2R$. They can be stored safely for long periods, but addition of BF_3 to the adducts rapidly precipitates the highly insoluble $TMED.2BF_3$ and regenerates the monoalkylborane. The TMED adducts are therefore convenient for storage of BH_2R compounds in a stable form.[104] For dialkylboranes, a similar adduct is found by ethylenediamine: en. $2BHR_2$, which also regenerates BHR_2 on treatment with BF_3.[105]

The (pentamethylcyclopentadienyl)boranes, (35, X=Cl,Br or I) can be prepared from trimethyl(pentamethylcyclopentadienyl)germane and BX_3. These compounds, and others where X_2 = $(NMe_2)_2$ or (Me)Cl, are all fluxional, due to sigmatropic rearrangements of the BX_2 groups, the speeds of which increase with increasing Lewis acidity of the boron atom (i.e. much slower when $X=NMe_2$).[106]



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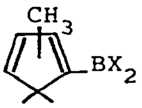

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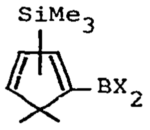

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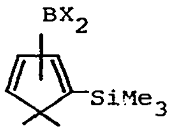

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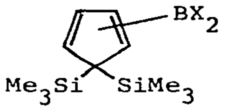
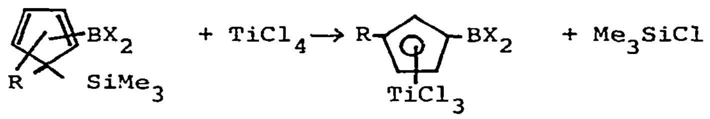


(39)

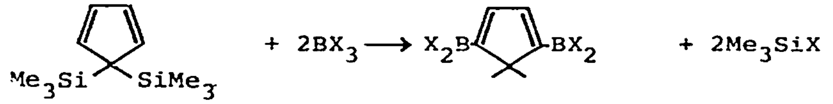
A wide range of cyclopentadienylboranes, (36-39, X=Cl or Br) can be prepared by the reaction of halogenoboranes with e.g. cyclopentadienyltrimethylsilanes. The products were characterised chiefly by n.m.r. spectroscopy (^1H, ^{11}B, ^{13}C). 5-trimethylsilylcyclopentadienylboranes show a dynamic behaviour due to sigmatropic rearrangements.[107]

η^5-Borylcyclopentadienyltitanium(IV) trichlorides have been prepared, according to equation (10).[108]



... (10)

Bis(trimethylsilyl)cyclopentadiene reacts with two equivalents of BX_3 (X=Cl,Br or I) to form bis(dihalogenoboryl)cyclopentadienes,



... (11)

equation (11). These in turn react with $SnMe_4$, NMe_2H or AsF_3 to give respectively, derivatives with X=Me, NMe_2 or F.[109]

3.1.6 <u>Aminoboranes and other Compounds containing B-N Bonds</u>

The adduct $H_3N.BH_3$ reacts with boron trihalides at low temperatures in an ether solvent at various molar ratios to give products identified by n.m.r. spectra. BCl_3 gave the new compounds $H_3N.BH_2Cl$ and $H_3N.BHCl_2$, together with $H_3N.BCl_3$, $Et_2O.BH_2Cl$ and $Et_2O.BHCl_2$.BBr_3 formed $H_3N.BH_2Br$, $Et_2O.BH_2Br$, $Et_2O.BHBr_2$, and also cleavage products. BF_3, on the other hand, gave only $H_3N.BF_3$ and $(\mu\text{-}H_2N)B_2H_5$.[110]

Tris(dichloroboryl)amine and a number of bis(dichloroboryl)-silylamines have been prepared by reaction (12) and (13). All

$$N(SnMe_3)_3 + 3BCl_3 \longrightarrow N(BCl_2)_3 + 3Me_3SnCl \quad \ldots (12)$$

$$RN(SnMe_3)_2 + 2BCl_3 \longrightarrow RN(BCl_2)_2 + 2Me_3SnCl \quad \ldots (13)$$

$$(R = SiCl_3,\ SiCl_2Me,\ SiClMe_2 \text{ or } SiMe_3).$$

are colourless liquids, with a very high thermal stability (e.g. $N(BCl_2)_3$ survives for 2 hours at 200°C), but they are very sensitive to hydrolysis.[111]

The new compounds $R(Me_3Si)NBH_2$, where R=Me_3Si or t-Bu, have been prepared by the sequence of reactions (14)-(16). ^{11}B n.m.r.

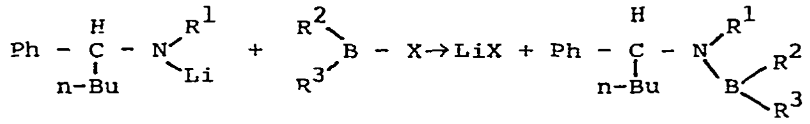
$$2Me_2S.BH_3 + Br_2 \xrightarrow[\text{benzene}]{25^{\circ}C} 2Me_2S.BH_2Br + H_2 \quad \ldots (14)$$

$$R(Me_3Si)NH + n.BuLi \xrightarrow[\text{hexane}]{0^{\circ}} LiN(R)SiMe_3 + n\text{-}C_4H_{10} \quad \ldots (15)$$

$$Me_2S.BH_2Br + LiN(R)SiMe_3 \xrightarrow[\text{hexane}]{25^{\circ}} R(Me_3Si)NBH_2 + LiBr + Me_2S \quad \ldots (16)$$

spectra confirm that the products are monomeric at room temperature. This is probably due to steric resistance to dimerisation, or to decreased availability of the nitrogen lone pair typical of silylamines.[112]

Unsymmetrical mono-, bis- and tris-aminoboranes can be prepared by reacting halogenodiorganylboranes with the adduct of Schiff

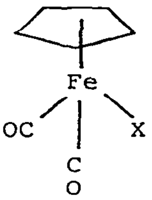


...(17)

bases with n-BuLi, (17, for numerous R^1, R^2, R^3).[113]

Indirect ^{10}B - ^{11}B coupling has been detected in $(Me_2N)_2B-B(NMe_2)_2$, where $^1J(^{11}B-^{10}B)$ 25 ± 2Hz.[114]

Two new stable complexes of $CpFe(CO)_2$ have been obtained, (40, where $X=CNBH_3^-$ or $CNBH_2NMe_3$). Shifts in $\nu(CN)$ on coordination were interpreted in terms of N-coordination, and Fe X back-bonding.[115]



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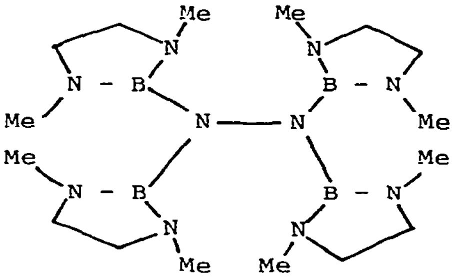


(41)

Bromoborane adducts, $L.BH_2Br$, where L = 3- or 4-methylpyridine, isoquinoline or quinoline, and boronium bromide salts, $L_2BH_2^+Br^-$ (L = 3- or 4-methylpyridine) are prepared by the reaction of $Me_2S.BH_2Br$ with an appropriate ratio of the nitrogen-containing heterocycle. The more stable $L_2BH_2^+PF_6^-$ salts were also prepared. All were characterised by ^1H and ^{11}B n.m.r., and infrared spectra.[116]

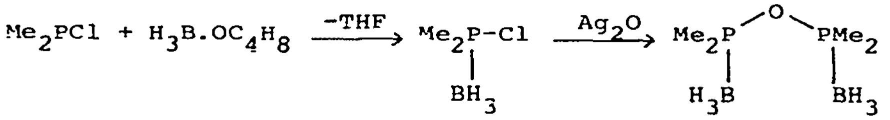
N,N,N'-Tris- and N,N,N',N'-tetrakis(1,3-dimethyl-1,3,2-diazaborolidinyl)hydrazine, (41), were prepared via N,N'-lithiated N,N'-bis(1,3-dimethyl-1,3,2-diazaborolidinyl)hydrazine. The N-N bond is rather long (1.464Å), and the ring B-N bonds are shorter than the B-N bonds to the hydrazine i.e. there is preferential electronic saturation of the boron via ring B-N π-bonding.[117]

3.1.7 Compounds containing B-P Bonds

Normal coordinate analyses have been carried out on $Ph_3P.BH_3$, $Ph_3P.BD_3$ and $(C_6D_5)_3P.BH_3$. Comparison with $F_3P.BH_3$ and $H_3P.BH_3$ reveals a linear relationship between $J(^{31}P-^{11}B)$ in the n.m.r. spectra and the P-B stretching force constants.[118]

The η^1-cyclopentadienyl- or -methylcyclopentachenyl-fluorophosphines, $(\eta^1-RC_5H_4)_nPF_{3-n}$, (R=H or Me; n=1 or 2), have been prepared. They form straightforward adducts with BH_3, containing a direct P→B coordinate bond, e.g. in $CpPF_2.BH_3$, νBH bands are at 2435 and 2402 cm^{-1}, with νPB at 535 cm^{-1}.[119]

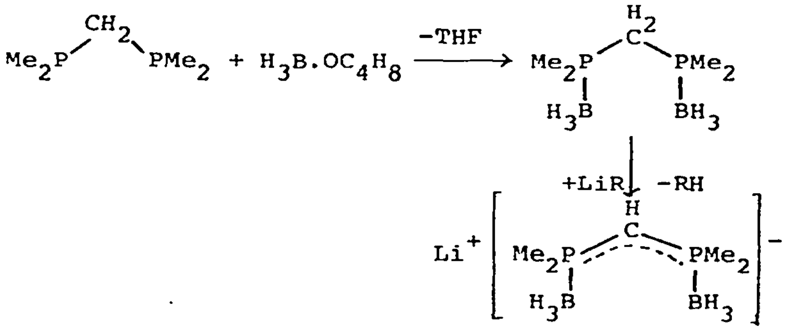
A number of stable $Me_2(H_3B)P$- compounds have been prepared which show remarkable analogies to the isoelectronic Me_3Si-compounds. They open up a number of possible synthetic routes. Equation (18) summarises the preparation for the analogue of hexamethyldisiloxane.[120]



... (18)

$$Me_2PCl + H_3B.OC_4H_8 \xrightarrow{-THF} Me_2P(BH_3)-Cl \xrightarrow{Ag_2O} Me_2P(H_3B)-O-PMe_2(BH_3)$$

A closely related species is the anion $[H_3B(Me)_2P{=}CH{=}P—(Me)_2BH_3]^-$. This is prepared by the reactions shown in (19). X-ray diffraction



... (19)

shows that the "central" P-C bonds are equal, and shorter than the "terminal" P-C bonds, in agreement with the formulation shown.[121]

^1H, ^{11}B, ^{19}F and ^{31}P n.m.r. spectra of $B_4H_8.PF_2NMe_2$ show that two isomers are present in solution. The low-temperature ^{19}F n.m.r. spectra suggest that these isomers are geometrical (i.e. endo- or exo-placement of the ligand). At about-125°C, rotation about the P-B bond in one isomer is slow on the experimental time scale, even though rapid in the second isomer. At approximately-80°C the two isomers interconvert rapidly on the n.m.r. time scale.[122]

3.1.8 Compounds containing B-O Bonds

$B(HSO_4)_3$ can be prepared by the reaction of liquid SO_3 on boric acid, while treatment of boron trichloride with H_2SO_4 forms $B(SO_4)(HSO_4)$. Both were characterised by infrared spectroscopy and thermography.[123]

Complete vibrational analyses have been proposed for the adducts $BF_3.MeOH$ and $BF_3.2MeOH$. In both complexes OBF_3 groups are associated via a dipole-dipole interaction. The 1:1 complex is additionally associated by hydrogen-bonding. In the 1:2 complex the second methanol molecule is bound to the first by a strong hydrogen-bond. Both complexes dissociate to ions in the liquid phase; BF_4^- and $MeOH_2^+$ were both identified.[124]

Trisilyl borate, $(H_3SiO)_3B$, can be prepared by the reaction of tris(tributyltin)borate and silyl bromide at 195K. Infrared (gas-phase) and Raman (solid), and n.m.r. spectra were consistent with the formulation given. The new compound is extremely sensitive to decomposition in the liquid phase.[125]

X-ray diffraction of single crystals of $La_2O_3.B_2O_3.2MO_3$ (where M = Mo or W) shows that both contain infinite chains of BO_3 triangles. These chains are linked by La^{3+} ions to form infinite corrugated layers, between which MO_4 tetrahedra are found.[126]

EuB_2O_4 forms orthorhombic crystals, belonging to the space group Pnca. They are isostructural with CaB_2O_4, and contain endless chains of BO_3 groups, i.e. $(BO_2)_\infty$, along the c-axis. The Eu^{2+} ions are eight-coordinated (dodecahedral) by oxygen atoms.[127]
Single crystals of $Na_4B_2O_5$ have been obtained for the first time: they are monoclinic, space group C2/c (C_{2h}^6). The crystal contains discrete $B_2O_5^{4-}$ anions.[128]

Raman spectra of polyborate ions in aqueous solution have been obtained over a wide range of pH values. Wavenumbers could be assigned to a number of species. $B(OH)_3$ was the predominant species for pH<5, and $B(OH)_4^-$ for pH>11. In the intermediate region there was evidence for: $B_5O_6(OH)_4^-$ (small amounts, pH 5-7); $B_3O_3(OH)_4^-$ (dominant species, pH 7-8); $B_4O_5(OH)_4^{2-}$ (fairly large amount, pH 8-10) and $B_3O_3(OH)_5^{2-}$ (small amount, pH∿10). The B_5 and B_4 species seemed to have the same structures as in the solid state.[129]

In a complementary report, Raman spectra were recorded for solid H_3BO_3, $Na_2[B_4O_5(OH)_4].8H_2O$, $K[B_5O_6(OH)_4].2H_2O$ and $Na[B(OH)_4]$ in the range 300-1500 cm^{-1}. Data were also obtained for borax in aqueous solution (as functions of concentration and pH) and for ammonium tetraborate in aqueous solution (as a function of pH). In solution, all of the lines in the Raman spectra were assigned, and depolarisation ratios measured. The Raman bands can be used to identify B-O modes in unknown borate or polyborate solutions.[130]

^{11}B n.m.r. spectra of Na^+, K^+ and $NH_4{}^+$ polyborates in aqueous solution (as functions of concentration and pH) gave evidence for the nature of hydrolysis equilibria. Two ^{11}B n.m.r. lines were seen in aqueous $M[B_5O_6(OH)_4]$, (M=Na, K or NH_4), but only one in $M_2[B_4O_5(OH)_4]$, (M=Na or NH_4).[131]

The new borates EuB_4O_7, EuB_2O_4 and $Eu_2B_2O_5$ have been synthesised. Their infrared spectra can be assigned in terms of a three dimensional network of BO_4 tetrahedra (EuB_4O_7), an infinite chain of BO_3 groups, $(BO_2)_\infty$, (EuB_2O_4), or isolated $B_2O_5{}^{4-}$ ions ($Eu_2B_2O_5$). EuB_4O_7 and $Eu_2B_2O_5$ are paramagnetic, but EuB_2O_4 is antiferromagnetic.[132]

A more accurate refinement has been carried out on the crystal structure of $Li_2B_4O_7$ (space group $I4_1cd$). The results were in agreement with earlier work (merely smaller standard errors).[133]

Phase relationships were studied in the systems $NH_4B_5O_8$ - NH_4X - H_2O, where X = Cl,Br or I; all are eutonic. It was suggested that interactions between the components are hindered by intramolecular π-bonding in the $B_5O_8{}^{4-}$ anion.[134] No new solid phases could be detected in an examination of the phase diagrams of the NaB_5O_8 - NaX - H_2O (X = Cl,Br or I) systems at 25°C.[135]

The crystal structure of $HoCo(BO_2)_5$ is built up from layer anions $(B_5O_{10})^{5-}$; this unit contains three BO_4 and two BO_3 fragments.[136]

The new phase $2Na_2O.3B_2O_3.H_2O$ can be made by isothermal sintering at 523K. It forms monoclinic crystals, belonging to the space group $P2_1/c$. The basic structural unit in these crystals is the new isolated borate polyanion $[B_{12}O_{20}(OH)_4]^{8-}$. This is built up from three tetrahedra and 3 triangles, doubled about the centre of symmetry. It could, alternatively, be described as a loop of six six-membered B-O rings. The structural formula is $Na_8[B_{12}O_{20}(OH)_4]$.[137]

Glasses can be formed in the SiO_2-B_2O_3 system by dehydration of the corresponding gels, followed by hot pressing. The process is much quicker than production by classical fusion methods. The glasses formed have a very low water content.[138]

A number of solid polyalcohol alkaliborate compounds have been isolated and characterised e.g., di-, tri-mannitol lithium borate; tri-fructose lithium borate, di-sorbital lithium borate, tri-galactose lithium borate, tri-mannitol sodium borate and tri-dulcitol sodium borate.[139]

3.1.9 Boron Halides

Calculations have been performed on the electronic structures of $N_2.BF_3$, $OC.BF_3$ and $Ar.BF_3$. The calculated energies of complexing of the donor molecules are 4.07, 4.34 and 0.01 kcal mol^{-1} respectively.[140]

$Sn(NR_2)_2$, where R=Me or Et, reacts with BF_3 to give a 1:3 adduct. Multinuclear n.m.r. and Mössbauer spectra showed that one BF_3 molecule is coordinated to the tin atom, and two to the amino-nitrogens. Spectra of solutions containing the reagents in 1:1 and 1:2 ratios showed that Sn-B coordination occurred first, then B-N.[141]

BF_3 reacts with $NiL_2(CO)_2$, where $L=Me_2NPF_2$, to give $NiL_2(CO)_2.nBF_3$, where n=1.44 at -128°C, 1.11 at 2°C. Infrared spectra suggest that the BF_3 is coordinated to the nitrogen atom of the Me_2NPF_2 ligands. Similar data were obtained for $NiL_4.nBF_3$.[142]

Potentiometric measurements have been made on aqueous solutions of HF and H_3BO_3 at 25°C. The measured stability constants of $[BF_3(OH)]^-$ and BF_4^- were $(2.7 \pm 1.3) \times 10^6$ and $(7.6 \pm 4.4) \times 10^8$ respectively, at an ionic strength of 0.2.[143]

pK values of HBF_4 were measured in a variety of solvents and these were used to estimate a value in water ($pK = -0.48 \pm 0.02$).[144]

Silver chloride reacts with elemental boron at 1133K to give a 77% yield of BCl_3 (based on boron consumption by excess AgCl, or 96% based on AgCl for excess boron.) The reaction is useful for the preparation of isotopically substituted BCl_3 i.e. $^{10}BCl_3$. $^{11}BCl_3$, $^{10}B^{35}Cl_3$, $^{11}B^{35}Cl_3$.[145]

Conductivity studies have been carried out on MCl_3-MeCN systems at 25°C (M=B,Al,Ga or In). BCl_3 is a non-electrolyte. For aluminium the process (20) was confirmed. For Ga and In the adducts are largely associated.[146]

$$2AlCl_3 + 4CH_3CN \rightarrow AlCl_2(CH_3CN)_4^+ + AlCl_4^- \qquad \ldots (20)$$

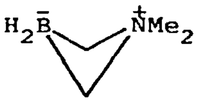
Reduction of BX_3 (X = Cl or Br) by H_2, followed by a flow method in the temperature range 1150-1470K, has been studied. The compositions of the vapour phase were monitored by infrared spectroscopy. BX_3 and BHX_2 are the only species with detectable concentrations in the vapour phase. The enthalpies of formation of BHX_2 molecules were calculated: $\Delta H^o(298)(BHCl_2) = -61.4 \pm 0.25$ kcal mol^{-1}; $\Delta H^o(298)(BHBr_2) = -30.6 \pm 0.6$ kcal mol^{-1}.[147]

Boron trichloride is converted to B_4Cl_4 under the influence of radiofrequency discharges (approx. 10MHz) significantly more rapidly than previously thought. The ^{11}B n.m.r. chemical shift of B_4Cl_4 shows that the boron nucleus is very deshielded. B_4Cl_4 is thermally more stable than $C,3-Me_2-1,2-C_2B_3H_3$ or $1,5-C_2B_3H_5$.[148]

Gas phase electron diffraction measurements on B_2Br_4 show that it has a staggered molecular conformation, of D_{2d} symmetry. The observed bond distances were: B-B, 1.689(16)Å; B-Br, 1.902(4)Å. The bond angles were: ∠BrBBr, 120.7(3)°; ∠BBBr, 119.8(2)Å. The barrier to rotation about the B-B bond was calculated as being 3.07 kcal mol^{-1}.[149]

3.1.10 Boron-containing Heterocycles

The new four-membered ring compound (42) was isolated from the products of reacting t-BuLi with the salt $Me_3NBH_2CH_2NMe_3{}^+Cl^-$. ^1H n.m.r. results suggest that this structure is inverting rapidly. The compound is stable, and soluble in water, but hydrolysed by dilute acid.[150]



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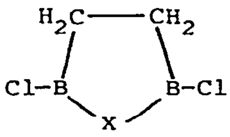

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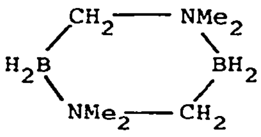
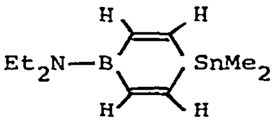


(44)

The five-membered ring compounds (43), where X=S or NMe, were prepared from $Cl_2BCH_2CH_2BCl_2$ and $(Me_3Si)_2X$. The analogous B-Me compounds were made from $MeClBCH_2CH_2BClMe$.[151]

Molecular-orbital calculations were carried out, using the IEHT and CNDO/2 methods, on 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane (44). Evidence was found for partial electron transfer from N to B. A normal coordinate analysis of the vibrations was also carried out, which showed values for the ring stretching force constants of 2.19 mdyn.$Å^{-1}$ (B-N), 3.33 mdyn.$Å^{-1}$ (B-C).[152]

^{1}H, ^{11}B, ^{13}C and ^{119}Sn n.m.r. data were reported for (45) and (46, R=Me,tBu,Et_2N or MeO).[153]



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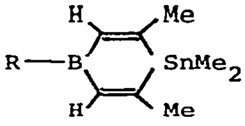
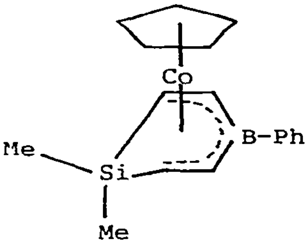


(46)

^{13}C and ^{11}B n.m.r. data were collected for 29 phenylboranes and nine boron-substituted aromatic heterocycles. Low-temperature ^{13}C n.m.r. and/or $^{13}C-\{^{11}B,^{1}H\}$ heteronuclear triple-resonance experiments were used to obtain ^{13}C chemical shifts of the boron-bonded carbon atoms.[154]

Several cationic borabenzene complexes have been described: $ML(C_5H_5BPh)^+$, where ML=CpCo, $Co(C_5H_5BPh)$, $Rh(C_5Me_5)$, $Ir(C_5Me_5)$ or $Ru(C_6H_6)$. All are much more electrophilic than the corresponding cyclopentadienyl complexes, $ML(C_5H_5)^+$.[155]

Photochemical reaction between $CpCo(CO)_2$ and $Me_2Si(CH=CH)_2BPh$ produces the new π-complex (47).[156]



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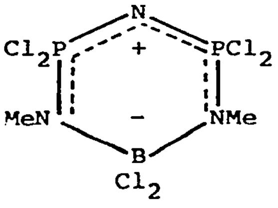
INDO-SCF molecular-orbital calculations have been carried out on the bis-borabenzene complexes $M(C_5H_5BR)_2$, where M=Cr,Mn,Fe or Co, R=H; M=Fe or Co, R=Me. The ordering of orbitals mainly derived from metal 3d levels corresponds to the one-electron energy sequence for metallocenes. The borabenzene ligand was found to be intermediate between $(\eta^5-C_5H_5)$ and $(\eta^6-C_6H_6)$ in bonding characteristics, but with an appreciably greater involvement of the ligand σ-orbitals.[157]

A number of new derivatives of 2,2,4,4,6,6-hexachloro-3,5-dimethyl-4-bora-2,6-diphospha-1,3,5-triazene, (48), have been prepared by substitution of the chlorine atoms. In most cases reaction occurs first at the boron-site. This reactivity sequence is consistent with the charge distribution shown.[158]



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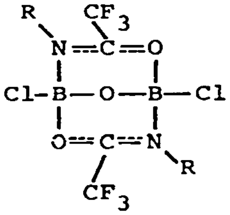
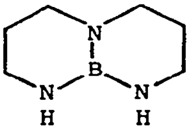


(49)

1,5-Dichloro-2,6,9-trioxa-4,8-diaza-1,5-dibora-bicyclo[3.3.1]-nonadiene compounds, (49, R=2,4,6-$Me_3C_6H_2$ or 2,6-$Me_2C_6H_3$) react with silver cyanide or cyanate to replace both chlorine atoms by pseudohalide groups. The products were characterised by infrared spectra, mass spectrometry, ^1H, ^{11}B and ^{19}F n.m.r.[159]

The electronic spectrum of 1,8,10,9-triazaboradecalin (50), has been recorded. The observed bands compared well with those predicted by a modified INDO calculation (the latter also agreeing quite well with the experimental photoelectron spectrum of this compound).[160]



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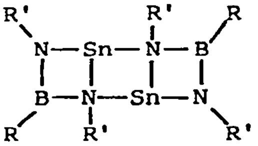
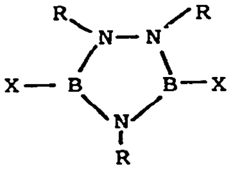


(51)

$SnCl_2$ reacts with Me_3Si-N(Li)-BMe_2 to form a dimeric diazastannaboretidine, (51, R=Me, R'=$SiMe_3$). The tricyclic tub-structure was revealed by an X-ray structure determination - it is built up from three condensed four-membered rings.[161]



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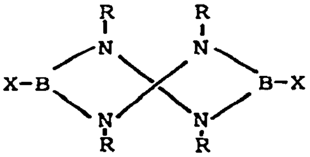
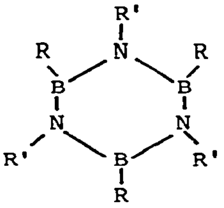


(53)

RBX_2, where R=Me, X=Me, Ph,NMe_2,OMe,SMe,H,Cl or Br, reacts with monoalkylhydrazines to form B_2N_3 heterocyclic compounds with six π-electrons and a planar structure, (52), confirmed by n.m.r. evidence. The related six-membered ring systems, X-B(NR-NR)$_2$B-X, on the other hand, contain eight π-electrons, and exist in the twisted conformations (53). One-electron oxidation (by $AlCl_3$ in CH_2Cl_2) of the isomeric 5- and 6-membered heterocycles $R_2N-N(BR-NR-)_2$ and $RB(NRNR)_2BR$ gives rise to a dark blue radical cation $RB(NRNR)_2BR^+$ with a (presumably planar) seven π-electron system.[162]



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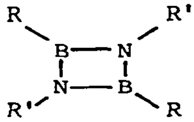
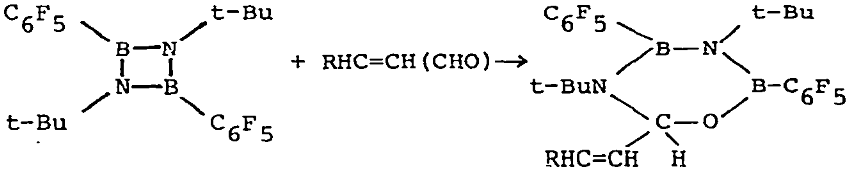


(55)

Gas-phase thermolysis of the aminoboranes $RB(Cl)-N(SiMe_3)R'$ gives the borazines (54, R=Cl, R'=Me or $SiMe_3$; R=Ph, R'=Me, t-Bu or 4-MeC_6H_4), the diazaboretidines (55, R=mesityl, R' = $SiMe_3$ or R=C_6F_5, R'=$SiMe_3$) or the boron imide R-B=N-R' (R=C_6F_5, R'=t-Bu). The last compound rapidly dimerises to a diazaboretidine at room temperature. Several other new cyclic derivatives were obtained from the four-membered ring compounds as shown in, for example, equation (21).[163]

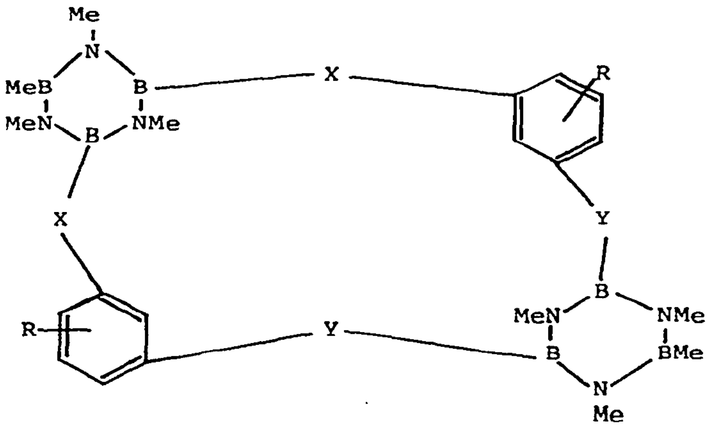


... (21)

The crystal structure of hexaphenylborazine, $(PhBNPh)_3$, has been determined. It is orthorhombic, space group $Pna2_1$. The phenyl rings are twisted out of the B_3N_3 plane by 60-70° to give a "propeller" conformation, just like hexaphenylbenzene.[164]

Gas-phase ion-molecule reactions and proton affinity of borazine were investigated by *ab initio* calculations and ion cyclotron techniques. The experimental proton affinity (from measurements on competitive proton transfer equilibria) was 196.4±0.2 kcal mol^{-1}. Ab initio calculations gave a proton affinity of 203.4 kcal mol^{-1}, with the most favoured structure of the borazinium ion being one in which very little structural change occurred compared to the parent borazine.[165]

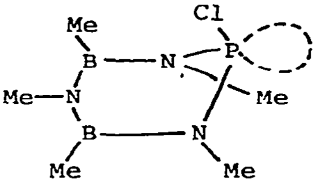
Self-consistent field and configuration interaction m.o. calculations have been performed on borazine, using a double-zeta basis set, augmented by six diffuse π-functions. Energies of low-lying singlet and triplet states of A_1', A_2' and E' symmetry were calculated, corresponding to $\pi\to\pi^*$ excited valence and Rydberg states. The results were compared with the experimental excitation energies, previous ab initio studies of borazine and recent ab initio studies on benzene. These comparisons revealed that the calculated excitation energies were 0.8 - 2.0 eV too high (the largest errors corresponding to ionic valence structures) and confirmed the remarkable similarity between the electronic structures of benzene and borazine.[166]



(56)

Macrocyclic oligomeric molecules (56) where X=Y=O, R=H, 5-Me or 2-Me; X=O, Y=NH, X=Y=NH, X=Y=S, X=S, Y=NH, X=Y=CH_2 - all with R=H only, are less stable than those formed from borazine units only. Several non-cyclic oligomers were also reported.[167]

N.m.r. parameters (^{1}H, ^{11}B, ^{13}C and ^{31}P) have been reported for ClPNMeBMeNMeBMeNMe and ClPNMeBMeNMeNMe. The geminal ^{31}P-^{13}C coupling constants were consistent with non-planarity of the rings, i.e. the former can be written as (57).[168]



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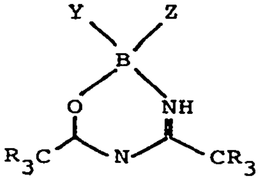
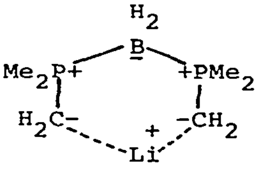


(58)

2,2,2-Trihalogeno-N-(trimethylsilyl)acetamides react with BCl_3, BBr_3 or RBX_2 to form (58), where R=F, Y=Z=Cl or Br; R=F,Y=Cl, Z=nBu or Ph; R=F, Y=Br,Z=Me; R=Y=Z=Br.[169]



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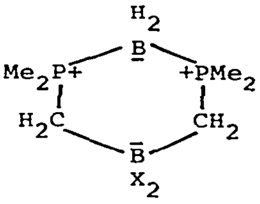

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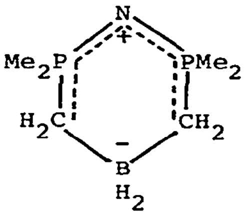
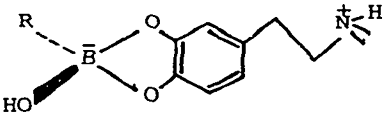


(61)

The Li^+ salt (59) reacts with boron compounds to yield the new heterocycles (60, X=H or Me). The crystal structure of the analogous compound (61) showed that it had a chair conformation and equal P-N bond lengths. The latter shows that there is indeed charge delocalisation in the "cationic" part of the ring.[170]

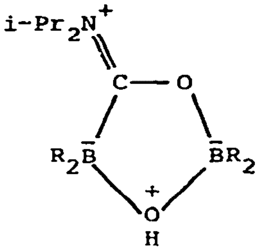


(62)

The boronic acids $RB(OH)_2$, where R=Ph or p-MeC_6H_4, form chelate complexes with the catecholamines dopamine, epinephrine and L-norepinephrine, e.g. (62). Their formation constants were determined by the "pH-depression" technique.[171]

Diphenylbromoborane and di-isopropylcarbamoyl-lithium react at low temperatures to give $Ph_2BCON(i\text{-}Pr)_2$ in solution. On warming to ambient temperature and passing through silica, the new compound 5-(di-isopropyliminio)-2,2,4,4-tetraphenyl-2,4-diborata-1-oxa-3-

oxonia cyclopentane, (63, R=Ph), is formed.[172]



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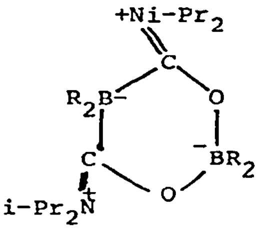
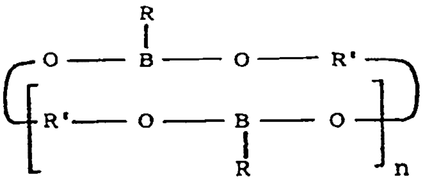


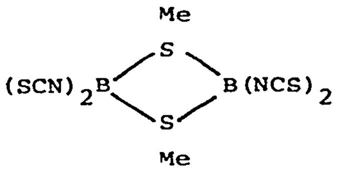
(64)

Reactions of di-n-hexylbromoborane with di-isopropylcarbomoyllithium give rise to (63) and (64), with R=n-hexyl. The latter is the first reported example of a new class of organoboranes, and it is remarkably resistant to oxidation, as it is unaffected by 50% H_2O_2 and base.[173]



(65)

Metathesis reactions of boron-containing heterocycles with -O-B(R)-O- groups with trivalent boron give oligomeric and/or polymeric ring structures, (65), with R=Ph, $R' = -(CH_2)_4-$, $-CH_2CH{:}CHCH_2-$ or $-CH_2CHBrCHBr\ CH_2-$. The equilibrium between rings of different sizes was disturbed by the crystallisation process.[174]



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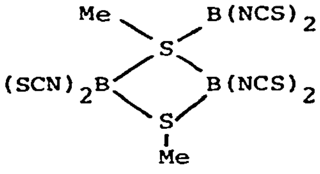

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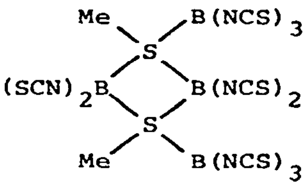
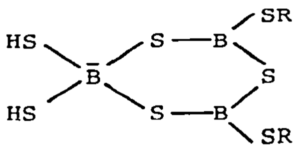
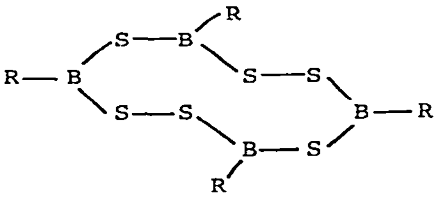


(68)

$B(SMe)_3$ reacts with $B(NCS)_3$ to give, at room temperature, $B(SMe)_3$ with low concentrations of $B(NCS)(SMe)_2$ and $B(NCS)_2(SMe)$, together with association compounds. Structures involving S→B bonds were proposed for $\{B(NCS)_2(SMe)\}_2$, (66), $\{B(NCS)_2(SMe)\}_2$—$\{B(NCS)_3\}$, (67) and $\{B(NCS)_2(SMe)\}_2\{B(NCS)_3\}_2$, (68). These react with trimethylamine to form $Me_3N.B(NCS)_3$ and $Me_3N.B(NCS)_2(SMe)$. The acidity strengths decrease in the sequence: $B(NCS)_3 > B(NCS)_2(SMe) > B(NCS)(SMe)_2 > B(SMe)_3$.[175]



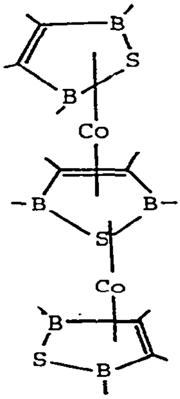
(69)



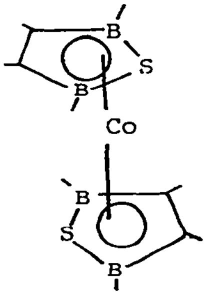
(70)

In liquid H_2S at 195K, $B(SEt)_3$ reacts with NR_4SH (R=Me or Et) to give the thioborates $(NR_4)_{2-x}[B_3S_3(SH)_{4-y}(SR)_y]^{y+1-x}$, where x=0 or 1, y=0,1 or 2, e.g. (69) when x=1, y=2.[176]

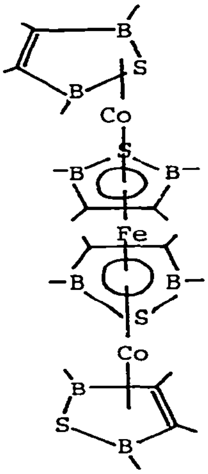
Substituent exchange reactions of trithiadiborolanes have been studied by a ^{10}B isotope technique. There is simultaneous exchange of the substituent and the boron atom to which the substituent is attached. The proposed mechanism involves a conformationally flexible ten-membered ring e.g. (70).[177]



(71)



(72)



(73)

A new four-decker sandwich complex, bis(η-thiadiborolenecobalt-μ,η-thiadiborolene)iron has been prepared by the reaction of $C_5H_5^-$ with (71), which gave the anion (72). The latter reacts with $FeCl_2$ to give the four-decker sandwich, which was shown by X-ray diffraction to have the structure (73).[178]

3.1.11 Boron Carbides and Metal Borides

Synthetic $B_{13}C_2$ was investigated by X-ray diffraction. The structure contains B_{12} icosahedra and C-B-C units, i.e. the ideal formula is $(B_{12})CBC$. The icosahedra form a cubic close-packed array.[179] The structure of rhombohedral $B_{13}C_2$ gave a similar formulation, while measurements of electron density in the CBC unit provided experimental confirmation of the suggested transfer of one electron from CBC to B_{12}, giving a ten-electron closed-shell configuration for the former.[180]

Several new ternary borides have been prepared, and their structures characterised. $SrRh_2B_2$ and $SrIr_2B_2$ belong to the space group Fddd, and are isostructural with $CaRh_2B_2$ and $CaIr_2B_2$. $BaRh_2B_2$ and $BaIr_2B_2$ belong to the space group I4/mmm, and are isostructural with $ThCr_2Si_2$. Finally, $Ba_7Ir_{12}B_{12}$, which belongs to the space group $R\bar{3}m$, has a new structure, but one which contains elements of that of $SrIr_2B_2$.[181]

A separate report gives details of further new ternary borides: MOs_4B_4 (where M=La,Ce,Pr,Nd or Sm) and MIr_4B_4 (where M=Y,La,Ce, Pr,Nd,Sm,Gd, or Tb). All crystallise with the $NdCo_4B_4$-type of structure.[182] Another new compound with the same structure is $LaRu_4B_4$, which forms tetragonal crystals, belonging to the space group $P4_2/n$. It was prepared from the elements by arc-melting under an argon atmosphere. The structure contains pairs of boron atoms (B-B=1.83(2)Å) separated by chains of La atoms and infinite chains of edge-sharing Ru_4 tetrahedra.[183]

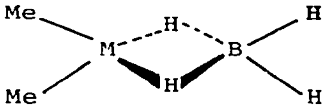
The new phases $(Nb,Ru)_{23}B_6$ and $(Ta,Ru)_{23}B_6$ have been reported, and classified as τ-borides. Their homogeneity ranges were established from lattice parameter measurements. The phases $Ta_{1-2}Co_{22-21}B_6$ were also investigated.[184]

3.2. ALUMINIUM

3.2.1 Aluminium Hydrides

A pattern recognition search method was used to seek basic regularities in the stabilities of complex hydrides $AA'H_4$ (A = alkali metal; A' = Al,Ga,In or Tl). Stabilities of eight so far unknown hydrides (A = Na,K,Rb,Cs; A' = In or Tl) were predicted to be low. Some similar calculations for $AA'H_3X$ (X = organic or inorganic ligand such as Me, F etc.) also gave a correct classification of stability patterns.[185]

Treatment of $M(CO)_6$, where M = Cr,Mo or W, with excess AlH_3 in tetrahydrofuran at 22°C gave a mixture of hydrocarbons, but predominantly C_2H_4 (95% of the mixture). At a ratio $Cr(CO)_6$: AlH_3 of 1:6, 17 ± 3% of the carbonyl ligands were converted to C_2H_4. The suggested mechanism involved the formation of metal carbene complexes ($M = CH_2$) as intermediates.[186]



(74)

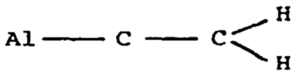
The molecular geometries of $M(BH_4)Me_2$, where M = Al or Ga, have been determined by electron diffraction. Both are monomeric, with C_{2v} symmetry and bidentate BH_4 groups, (74). The M-C distances are 1.929(4)Å (Al), 1.944(4)Å (Ga), while $M\text{-}H_{br}$ are 1.770(32)Å (Al), 1.791 (30)Å (Ga).[187]

A number of homogeneous catalysts for the hydrogenation of unsaturated hydrocarbons have been described. They are based on Co(II) compounds and several aluminium hydrides: $AlH_3.NMe_3$; $AlHCl_2.OEt_2$; AlH_2NMe_2; $HAl(NMe_2)_2$ and $(HAlNR)_n$, where n = 4, R = t-Bu; n = 6, R = i-Pr; n = 8, R = nPr.[188]

Interactions in the $Cp_2TiCl_2/LiAlH_4$ and $CpTiCl_3/LiAlH_4$ systems have been studied by calorimetry and e.p.r. Evidence was found for a number of mixed hydride species: $Cp_2TiH_2AlCl_2.Cp_2TiCl$; $[Cp_2TiH_2Al(H)Cl]_2$, $(Cp_2TiH_2)_2Al_2H_3Cl$ etc.[189]

3.2.2 Compounds containing Al-C or Al-Si Bonds

^{13}C n.m.r. spectra have been reported for triallylaluminium compounds, together with some dimeric and trimeric alkoxy- or amido-bridged organoaluminium compounds. In the alkoxy-derivatives, the data are consistent with the presence of O→Al p_π-d_π dative bonding.[190]



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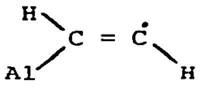


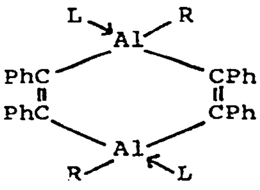
(76)

Calculated optimum geometries for the Al-C_2H_2 system suggest that the vinylidene form, (75), should be the most stable, rather than any system such as (76). These calculations were not consistent with experimental data on Al atom/C_2H_2 reactions at liquid helium temperatures suggesting that the less stable form is trapped at such low temperatures.[191]

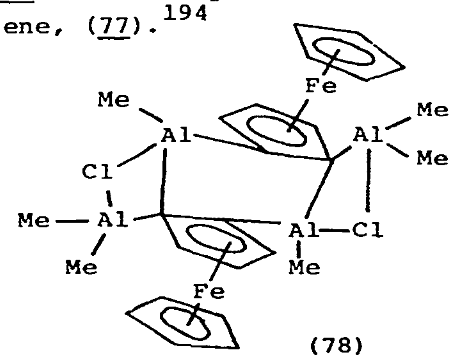
Evidence has been obtained for the presence of $Me_3N.AlEt_3$ as an intermediate in the thermolysis of tetramethylammonium μ-chlorobis (triethylaluminate), in addition to the previously reported $[Me_4N][ClAlEt_3]$ and Al_2Et_6.[192]

A crystal structure determination of $(\eta\text{-}C_5H_5)_2Yb(\mu\text{-}Me)_2AlMe_2$ shows that both the ytterbium and aluminium atoms have approximately tetrahedral environments. The $YbMe_2Al$ unit is very similar to the $AlMe_2Al$ fragment in Al_2Me_6. The following bond lengths and angles were found: Yb-C_{br}, 2.59(3)Å; Al-C_{br},2.18(5)Å; Al-C_b, 2.00(1)Å; ∠Yb-C-Al, 79.9(1.6)°; ∠C-Al-C, 113.3(8)°.[193]

Photochemical reaction of trans-1,2-(diethylaluminium)stilbene gave a 1,4-dialuminacyclohexadiene, (77).[194]



(77)



(78)

A single crystal X-ray structure determination on $(\eta^5\text{-}C_5H_5)Fe\text{-}[\eta^5\text{-}C_5H_4Al_2(CH_3)_4Cl]$ has been performed. The two Me_2Al units are bridged together by the chlorine atom and one carbon atom of a cyclopentadienyl group, (78). No significant Al-Fe bonding interaction was found (Al-Fe distance of 3.100(3)Å).[195]

Ph_3E (where E = Al, Ga or In) complexes of $CpFe(CO)_2^-$, $CpW(CO)_3^-$ $Co(CO)_4^-$ or $Mn(CO)_5^-$ have been prepared by simply mixing the components in methylene chloride or (for $CpFe(CO)_2^-$ only) tetrahydrofuran. The following crystalline complexes were isolated: $Et_4N^+Ph_3EFe(CO)_2Cp^-$ (E = Al,Ga or In); n-$Bu_4N^+Ph_3EW(CO)_3Cp^-$ (E = Al or In); $(Ph_3P)_2N^+Ph_3InCo(CO)_4^-$ and n-$Pr_4N^+Ph_3InMn(CO)_5^-$. A crystal structure determination for $Et_4N^+Ph_3AlFe(CO)_2Cp^-$ showed the presence of an Al-Fe bond (2.510(2)Å). ν(CO) data for all the complexes were consistent with E-M bonding in all cases except for $Ph_3AlW(CO)_3Cp$, where the unit WC≡OAl unit is present. Methylene chloride solutions of $Ph_3GaW(CO)_3Cp^-$ show that here there are two isomers present, one with a Ga-W bond, the other a WC≡OGa link.[196]

Trimethylsilyl chloride reacts with aluminium and lithium in ether (in the presence of Hg) to form lithium tetrakis(trimethylsilyl)aluminate, coordinated by solvent, equation (22). The unsolvated form was obtained by the repeated sublimation of the

$$5Li + Al + 4Me_3SiCl \rightarrow LiAl[SiMe_3]_4.n\ solv. + 4LiCl \quad \ldots (22)$$
$$(n.solv = 3Et_2O \text{ or } 4THF).$$

ether adduct. Infrared and Raman spectra ($\nu_s AlSi_4$ 312cm^{-1}; $\nu_{as}AlSi_4$ 406/402 cm^{-1}) and n.m.r. data (^1H, ^{13}C, ^{27}Al) were reported.[197]

The molecular structure of the 1-ethyl-3-methyl-1-aluminaindane dimer has been deduced from a single-crystal X-ray diffraction study. Discrete dimeric molecules were present, with crystallographic symmetry $\bar{1}$ (C_i). Each aluminium atom bonds to ethyl carbon (1.964(2)Å), alkyl (1.974(2)Å) and aryl (2.168(1)Å) C atoms of one monomer and, surprisingly, to the aryl C (2.104(1)Å) of the inversion-related monomer. The Al-Al distance was 2.6639(7)Å - see Figure 2.[198]

Organozirconium(IV) complexes (produced by the hydro-zirconation of olefins or acetylenes by $Cp_2Zr(H)Cl$) are precursors of organoaluminium compounds. Stoichiometric transmetalation leads to a stereospecific transfer of the η^1-organic ligand from Zr to Al.[199]

3.2.3 Compounds containing Al-N Bonds

^{27}Al n.m.r. spectra were used to study the species present in acetonitrile solutions of $AlCl_3$ or $Al(ClO_4)_3$. Previous work was reassigned in the light of the new results. Solutions of $AlCl_3$ give a sharp $AlCl_4^-$ resonance, a feature due to $Al(MeCN)_6^{3+}$, and two

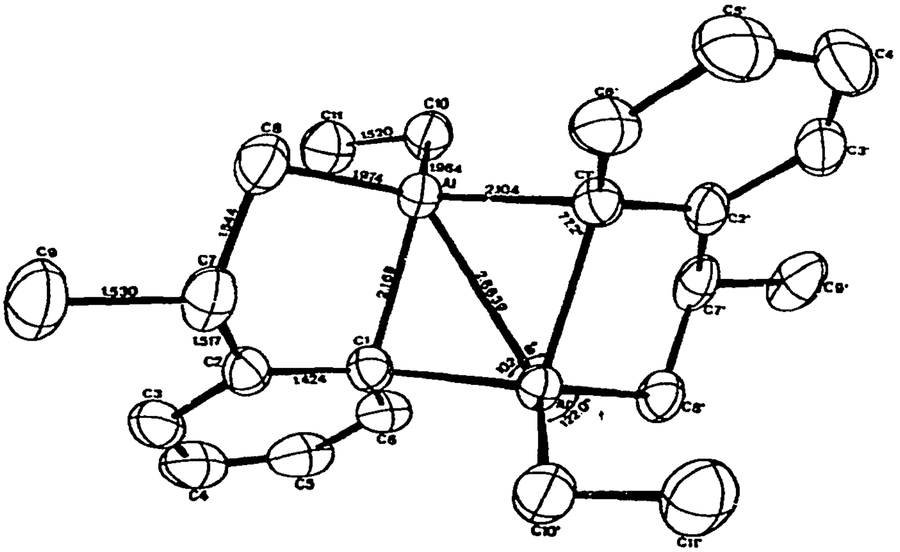
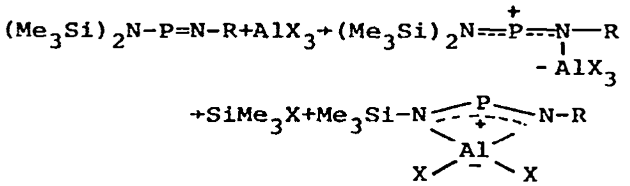


Figure 2. Molecular structure of the 1-ethyl-3-methyl-1-alumina-indane dimer (reproduced by permission from Z.Naturforsch., 34b (1979) 1293).

minor features thought to be Al(MeCN)$_5$Cl^{2+} and Al(MeCN)$_4$Cl$_2$$^+$. The Al(ClO$_4$)$_3$ solutions gave some evidence for complexing of Al^{3+} by the perchlorate ions.[200]

N-silylated aminoiminophosphines react with aluminium trihalides to four acyclic zwitterions, which decompose at room temperature by eliminating a silyl halide, to form 1,3,2 ^{2},4-diazaphosphonia-aluminata-cyclobutanes, (23), where R=SiMe$_3$, X=Cl,Br or I; R=CMe$_3$, X=Cl. Infrared and n.m.r. (^{1}H, ^{31}P) data were reported and partly assigned.[201]



... (23)

The compounds [Me$_2$AlN$_3$]$_2$ and [Me$_2$GaN$_3$]$_2$ have been prepared by new routes, (24) and (25), which are useful for preparing ^{15}N-labelled derivatives. ^{15}N n.m.r. spectra were recorded, which showed a temperature-dependent exchange of the azido-groups on the

$$Me_3M + HN_3 \xrightarrow{C_6H_6} "Me_2MN_3" + CH_4 \qquad \ldots (24)$$

$$Me_3Ga + ClN_3 \xrightarrow{C_6H_6} "Me_2GaN_3" + CH_3Cl \qquad \ldots (25)$$

n.m.r. time-scale. The vibrational spectrum of the gallium compound was recorded and partly assigned.[202]

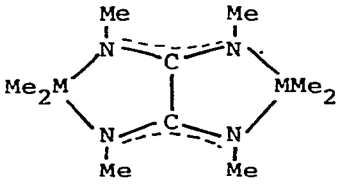
Kinetic studies on the hydrogen elimination reaction between dimethylaluminium hydride and N-methylaniline show that reactions (26) and (27) occur. Note that the formation of the adduct is

$$HMe_2Al + HNMe{-}C_6H_5 \rightleftharpoons HMe_2AlN(C_6H_5)MeH \qquad \ldots (26)$$

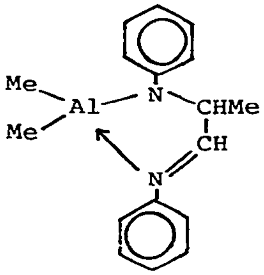
$$HMe_2Al + HNMe{-}C_6H_5 \longrightarrow H_2 + Me_2AlN(Me)C_6H_5 \qquad \ldots (27)$$

a dimer: $[Me_2AlN(Me)C_6H_5]_2$, as a <u>cis</u>/<u>trans</u> mixture (4:1).[203]

N,N',N",N'"-Tetramethyloxamidine, $(HNMe)_2C_2(=NMe)_2$, reacts with MMe_3, where M=Al,Ga or In, in a 1:2 molar ratio, and the products are monomeric bis(dimethylmetal)oxamidines, $(Me_2M)_2C_2(NMe)_4$. Vibrational spectra (infrared and Raman) and X-ray diffraction show that they all consist of two fused five-membered rings, with an essentially planar structure, (79).[204]

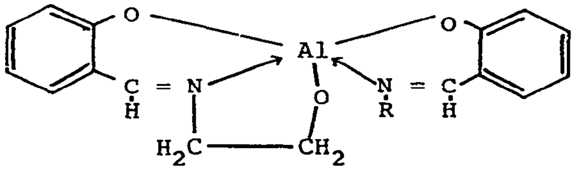


(79)



(80)

RN:CHCH:NR (where R=2,6-$Me_2C_6H_3$ or 2,4,6-Me_3CoH_2) react with Al_2Me_6 giving $Me_3Al.RN{:}CHCH{:}NR$. If R=4-ClC_6H_4, 4-MeC_6H_4 or 4-$MeOC_6H_4$, on the other hand, insertion occurs, to form, for example, (80).[205]



(81)

1:1:1 molar reactions of $Al(Oi\text{-}Pr)_3$ with monofunctional bidentate (HSB) and bifunctional tridentate Schiff bases ($H_2S'B'$) give complexes of the type $(S'B')Al(SB)$. These appear to be monomeric, with five-coordinate aluminium, as in (81).[206]

Crystals of $(Me_2AlNHMe)_2(MeAlNMe)_6$ are orthorhombic, and belong to the space group Abam. The molecule forms a cage-structure, with apparent C_{2h} symmetry. Each aluminium and nitrogen atom is four-coordinate, with the methyl groups pointing outwards. The gallium analogue has an exactly similar structure.[207]

The crystal structure of $[HAlNCH(CH_3)C_6H_5]_6 \cdot C_6H_{14}$ shows that the molecule is built up from a prismatic hexagonal network $(AlN)_6$. The average Al-N distances are 1.893(6)Å and 1.981(7)Å in the six-membered rings and in the transverse ring bonds respectively.[208]

3.2.4 Compounds containing Al-O or Al-S Bonds

The preparation and electronic spectra of $M[Al(OR)_4]_2$, where M=Co,Ni or Cu; R=Me,Et,n-Pr or n-Bu, have been described. The spectral data show that green $Ni[Al(OR)_4]_2$ contains octahedral $Ni(OR)_6$ units formed by sharing of faces with two $Al(OR)_4$ tetrahedra. The Co^{2+} and Cu^{2+} are in distorted octahedral arrangements. The alkoxide ligands appear to be close to H_2O in the spectrochemical and nephelauxetic series.[209]

$AlEt_3$ undergoes an addition reaction with iron(III) stearate to form adducts involving C=O-Al interaction: $AlEt_3{:}Fe(C_{17}H_{35}CO)_3 \leqslant 2$. The dimeric structure of the iron(III) stearate is maintained.[210]

Aluminium isopropoxide reacts with 2-furoic or 2-thenoic acid (in the presence of benzene) giving $Al(Oi\text{-}Pr)_2X$, $Al(Oi\text{-}Pr)X_2$ and AlX_3, where X=2-furoate or 2-thenoate anion. The $Al(Oi\text{-}Pr)X_2$ species are probably dimeric, with bidentate carboxylato ligands.[211]

The molecular structure of tris(1,1,1,5,5,5-hexafluoroacetylacetonato)aluminium(III) was determined by gas-phase electron diffraction. The data were consistent with a D_3 model, the oxygen atoms forming a slightly distorted octahedron about Al (mean $\angle OAlO=87.2^{\circ}$). The Al-O bond distance (1.893(14)Å) is very close to that found for $Al(acac)_3$ by X-ray diffraction.[212]

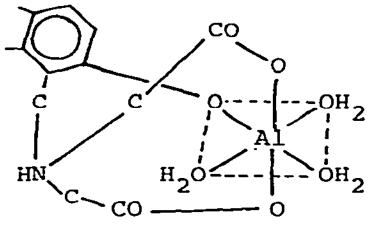
Complex formation between $Al(Oi\text{-}Pr)_3$ and $AlCl_3$ in either polar or non-polar solvents leads to only one stable product: $\beta\text{-}AlCl(Oi\text{-}Pr)_2$, a crystalline material. Metastable $\alpha\text{-}AlCl(Oi\text{-}Pr)_2$ and $AlCl_{1.67}(Oi\text{-}Pr)_{1.33}$ were also detected.[213]

The crystal structure of $\mathrm{Al(Oi\text{-}Pr)_3}$ confirms the centrosymmetric non-cyclic tetramer model previously proposed. The physico-chemical properties of the solid, liquid and solutions of $\mathrm{Al(Oi\text{-}Pr)_3}$ can be rationalised in terms of Scheme 1.[214]

$$\begin{tikzcd}
\begin{array}{c}[\mathrm{Al(Oi\text{-}Pr)_3}]_3\\ \text{liquid}\end{array} \arrow[r, shift left] \arrow[d] & \begin{array}{c}[\mathrm{Al(Oi\text{-}Pr)_3}]_4\\ \text{solid}\end{array} \arrow[l, shift left] \arrow[d] \\
\begin{array}{c}[\mathrm{Al(Oi\text{-}Pr)_3}]_3\\ \text{in solution}\end{array} \arrow[r, shift left] & \begin{array}{c}[\mathrm{Al(Oi\text{-}Pr)_3}]_4\\ \text{in solution}\end{array} \arrow[l, shift left]
\end{tikzcd}$$

Scheme 1

Equilibria and kinetics of complex formation have been reported for Al(III) with Semi-Xylenol Orange and Semi-Methylthymol Blue indicators. In each case three complexes are formed: AlHL, $\mathrm{AlL^-}$, $\mathrm{Al(OH)L^{2-}}$ e.g. for L=SXO, (82).[215]



(82)

Equilibrium- and rate-constants have been determined for the reaction of Al(III) with 5-nitrosalicylic acid.[216]

The rate of extraction of Al(III) from aqueous HCl or $\mathrm{HNO_3}$ solutions by di(2-ethylhexyl)phosphoric acid (HX) has been investigated under equilibrium conditions. The rate of the forward reaction is $k_f[\mathrm{Al}]_{aq}[(\mathrm{HX})_2]_{org}[\mathrm{H}^+]^{-1}_{aq}$. The extraction process is governed by dissociation of a water molecule from $\mathrm{Al(H_2O)_6^{3+}}$.[217]

The mineral phuralumite, $\mathrm{Al_2[(OH)_2(PO_4)_2(UO_2)_3](OH)_4 \cdot 10H_2O}$, forms monoclinic crystals, belonging to the space group $P2_1/a$. The structure contains $[\mathrm{(OH)_2(PO_4)_2(UO_2)_3}]_n^{2n-}$ layers, mainly connected by $\mathrm{Al_4O_4}$ groups, composed of two octahedra and two trigonal bipyramids sharing edges.[218] Crystals of $\mathrm{AlCuCl(SO_4)_2 14H_2O}$ are triclinic, space group $P\bar{1}$. Isolated $\mathrm{Al(H_2O)_6^{3+}}$ ions are present.[219]

D.t.a. results and infrared spectra show that in the $Al_2(SO_4)_3$-K_2SO_4 system there is peritectic fusion of $K_3Al(SO_4)_3$ at 680°C, and of $KAl(SO_4)_2$ at 780°C.[220]

The only well-defined product from the reaction of $LiAlCl_4$ with $LiClO_4$ in $HClO_4$ is $Li_2Al(ClO_4)_5$. There was no evidence for $LiAl(ClO_4)_4$ or $Li_3Al(ClO_4)_6$.[221] Reaction of $AlCl_3$ and $HClO_4$ in the presence of $MClO_4$ (M=Cs,Rb or NH_4) yields $M[Al(ClO_4)_4].HClO_4$ and $Cs_2[Al(ClO_4)_5].HClO_4$. All lose the $HClO_4$ molecule reversibly in vacuo at 50-70°C.[222] The same authors reported solubility measurements on $M[Al(ClO_4)_4].HClO_4$ (M=NH_4, Rb or Cs), $Rb_2[Al(ClO_4)_5]$ and $Cs_2[Al(ClO_4)_5].HClO_4$ in $HClO_4$. The tetrakis(perchlorato)-aluminates are all only slightly soluble, the pentakis-complexes more so. Thus, at equilibrium, the $Rb_2[Al(ClO_4)_5]$ solution contains the equivalent of 11g of $Al(ClO_4)_3$ per 1000g of $HClO_4$.[223]

An attempt has been made to characterise the stereochemical requirements of $Al(OH)_5^{2-}$ by molecular orbital calculations using the CNDO/2 formalism. Total energy surfaces calculated as the bond angles vary within the constraints of C_{2v} symmetry clearly show the "reaction coordinate" for the Berry pseudo-rotation. For fixed Al-O and O-H bond distances of 1.84Å and 1.00Å respectively, the activation energy for the trigonal bipyramidal/square pyramidal interconversion was calculated to be 7.1 kJ mol^{-1}. For dimeric $Al_2(OH)_8^{2-}$ (two trigonal bipyramidal units sharing a common edge of variable length) the energy minimum was found at a shared-edge length of 2.246Å; 13% shorter than in the undistorted polyhedron. This agrees well with experimental results on the mineral andalusite, Al_2SiO_5.[224]

^{27}Al n.m.r. was used to follow the hydrolytic polycondensation of Al(III) aquo-ions. There was found to be a marked dependence of the mechanism of the reaction on the original concentration of the Al(III) in the solution. At low Al(III) concentrations, sol particles are formed from units containing 13 aluminium atoms.[225]

Condensed aluminium oxo-cations, e.g. $[Al_2(OH)_2(H_2O)_8]^{4+}$ and $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{2+}$ react more slowly than $Al(H_2O)_6^{3+}$ with ferroin, to form a complex. A higher degree of condensation gave slower complex formation because only the $Al(H_2O)_6^{3+}$ can form the complex, and so the rate depends upon the rate of degradation of the polymeric cations.[226]

Aluminium oxo-cations in dilute ammonium salt solutions with various OH/Al ratios can be assigned into three groups: $Al_{monomeric}$, $Al_{oligomeric}$, $Al_{polymeric}$. If $[Al] \sim 10^{-4}M$, the relative percentage of $Al_{monomeric}$ decreased from 100 to almost 0 on increasing the OH/Al ratio from 0 to 3. In the OH/Al range between 0.5 and 2.5, ageing leads to an initial decrease in $Al_{monomeric}$, reaching a constant value after two weeks.[227]

Approximately 2M basic $AlCl_3$ solutions with OH/Al ratios between 1.1 and 2.3 have been studied by separating the aluminium cations by gel-permeation chromatography, together with measurements of reaction rates with ferroin. The results were very similar to those reported in the two previous references.[228]

Amorphous hydrated Al(III) gel consists of two phases. During ageing one phase crystallises as $Al(OH)_3$ (bayerite), the other as pseudoböhmite ($Al_2O_3.xH_2O$, $2.0>x>1.0$).[229]

A number of metastable phases (preceding the formation of thermodynamically stable phases) have been identified in crystallisation from the Al_2O_3-Li_2O-H_2O system in the temperature range 25-150°C.[230]

Phase relationships have been elucidated in the Al_2O_3-Li_2O-MgO system at 1200°C for Li_2O 22.7 mass %. The equilibrium can be represented by four phase triangles.[231]

25°, 75°, 100°, 150°C isotherms of the Al_2O_3-Li_2O-H_2O system have been constructed. The following equilibrium solid phases were identified: hydrargillite ($Al(OH)_3$), 25-100°C; böhmite (AlO(OH)), 150°C; $LiOH.H_2O$ (25-100°C); LiOH(150°C) and hydrated aluminates; $Li_2O.2.0$-$2.3\ Al_2O_3.nH_2O$ (n=9-11; 25-150°C) and $Li_2O.Al_2O_3.0.5H_2O$ (100-150°C).[232] High-temperature X-ray diffraction and d.t.a. suggest a phase transformation in $K_2O.Al_2O_3$ at 540°C.[233]

Single-crystal X-ray diffraction of $BaAl_2O_4$ showed that it belongs to the space group C_6^6-$P6_3$. It is not isotypic with $BaGa_2O_4$, and contains linked groups of six AlO_4 tetrahedra, all with the same geometry (in the Ga compound there are several different types of GaO_4 tetrahedra).[234]

The phase diagram of the Al_2O_3-SrO system has been studied: the phases $SrAl_4O_7$ (m.p. 1780°C), $SrAl_2O_4$(1960°C), $Sr_3Al_2O_6$(1720°C) were identified. There was evidence for the (incongruently melting) phases $Sr_4Al_2O_7$ and $SrAl_{12}O_{19}$.[235]

The crystal structure of a dickite:N-methyl formamide intercalate $[Al_2Si_2O_5(OH)_4.HCONHMe]$, has been determined. The stacking of the octahedral, AlO_6, part of the clay layers upon the SiO_4 tetrahedra is different from that found for dickite itself and for its intercalate with formamide.[236]

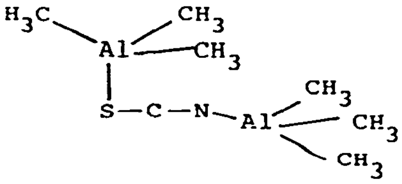
The crystal structure of the phase $Al_2O_3.2P_2O_5.9H_2O$ reveals that two different structural units are present: isolated PO_4 tetrahedra and larger aggregates consisting of two AlO_6 octahedra connected by three PO_4 tetrahedra with common vertices. The hydrogen atom positions could not be determined. Bond distances and the molecular symmetry, however, suggest that the structural formula is $[Al_2(H_{1+x}PO_4)_3(H_2O)_6][H_{3-3x}PO_4]$, where $0 \leq x \leq 1$.[237]

The infrared spectra of anodic aluminium oxides obtained in solutions of e.g. $H_2C_2O_4$, H_3PO_4, Na_2CO_3 etc. show that they are of very variable composition. The main phases present were γ-Al_2O_3, γ-AlOOH and γ-$Al(OH)_3$.[238]

Two new aluminium hydroxychromates, $Al_{13}(OH)_{11}(CrO_4)_4.xH_2O$, where x=41 or 51, have been isolated from the Al_2O_3-CrO_3-H_2O system at 20°C or 50°C. There was no evidence for the $Al_2(CrO_4)_3.5H_2O$ previously reported.[239]

$BaTe_{1.5}Al_{0.5}O_4$ crystallises with hexagonal symmetry, space group C^6_6-$P6_3$.[240] Sr_2EuAlO_4 forms tetragonal crystals, space group I4/-mcm. AlO_4 tetrahedra are present, arranged about the (001) plane. They have an Al-O distance of 1.753(2)Å, but they are angularly distorted.[241]

Raman spectra of molten $Sm_{0.8}La_{0.2}AlO_3$ up to 1470K show the presence of a first-order phase transition at 580K. It is probably due to a rhombohedral to cubic phase transition.[242]



(<u>83</u>)

The crystal structure of $K[Al_2(CH_3)_6(SCN)]$ has been determined. The crystals are monoclinic, space group C2/m, and an S,N-bridging thiocyanate is present, with a linear S-C-N unit. The Al-N bond length is normal, 1.951(5)Å, but Al-S is long, 2.489(2)Å, consistent with a rather weak interaction (<u>83</u>).[243]

$AlInS_3$ is tetragonal (space group $P6_1$); the indium is five-coordinate by sulphurs (In-S distances in the range 2.447-2.683Å). The aluminium is tetrahedrally four-coordinate (Al-S, 2.228-2.310Å), giving a structure which is closely related to that of In_2S_3.[244]

3.2.5 Aluminium Halides

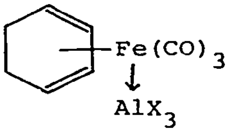
The effects on the stability of M_2X_6 (M=Al or Ga; X=halogen) of replacing X by OH have been examined by mass spectrometry. There is little change in stability for M=Al, but the stabilities of the gallium dimers are increased by such replacement.[245]

The complex fluoride $(NH_4)_2Al_4HF_3(PO_4)_4.5H_2O$ can be isolated from the $Al(OH)_3$-NH_4F-H_3PO_4 system at 190°C.[246]

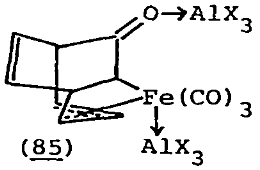
Vitreous fluoride materials have been obtained from various systems containing AlF_3, alkali, alkaline-earth and lanthanide fluorides. X-ray diffraction and Raman spectra suggest that the structures are built up from AlF_6^{3-} octahedra, linked together by a small number of AlF_4^- tetrahedra.[247]

Phase relationships in MF_3-CH_3COOH-H_2O (where M=Al or Ga) systems reveal the formation of compounds $MF_3.CH_3COOH.3H_2O$ in both cases.[248] Single crystals of $CsAlF_4$ have been grown from a mixture of CsF and AlF_3. They are hexagonal, belonging to the space group $P62m(D^3_{3h})$, and isostructural with $CsCrF_4$. $AgAlF_4$, on the other hand, forms orthorhombic crystals, isostructural with α-$RbFeF_4$.[249] Unit cell dimensions were determined for Ag_3MF_6 (where M=Al,Ga,In or Tl). For M=Al or Ga the crystals are tetragonal, isostructural with Rb_3TlF_6, while for M=In or Tl they are monoclinic, and isostructural with Na_3AlF_6. $AgGaF_4$ forms tetragonal crystals, isostructural with $KFeF_4$.[250]

Infrared spectra show that AlX_3 (where X=Cl or Br) form Lewis acid adducts at the iron atom in polyolefin tricarbonyliron complexes, (<u>84</u>). When X=Cl, the CO stretching wavenumbers were at 2121 and 2069 cm^{-1}, compared with 2042 and 1962 cm^{-1} in the original complex. If the organic fragment contains a ketonic grouping a 2:1 adduct is formed, e.g. (<u>85</u>), $\nu(C\equiv O)$ is shifted to higher, $\nu(C=O)$ to lower wavenumbers in comparison with the parent complex.[251]



(<u>84</u>)



(<u>85</u>)

Electrical conductivity data on $AlCl_3$ solutions in MeCN cannot differentiate between 1:1 and 1:2 electrolyte behaviour. Quantitative Raman and ^{27}Al n.m.r. studies show that about 70% of the aluminium is present as $AlCl_4^-$ in the MeCN solution. An X-ray study of a single crystal of "$AlCl_3.2MeCN$" showed that it is in fact $[AlCl(MeCN)_5]^{2+}.2AlCl_4^-MeCN$. The spectroscopic data for the solutions can be interpreted on the basis of these ions being present there also.[252]

$C(CH_3)_3^+$ is formed by the reaction of $AlCl_3$ or $GaCl_3$ with t-butyl chloride in anhydrous HCl as solvent.[253] Potentiometric studies were used to follow complex formation by Mg(II) in $KCl/AlCl_3$ melts.[254]

$MAlCl_4$ (where M^+ is a large cation, e.g. NO^+, NH_4^+, Rb^+, Cs^+) crystallise with the $BaSO_4$ (barytes) structure (space group Pnma). $KAlCl_4$ (space group $P2_1$) and $NaAlCl_4$ ($P2_12_12_1$) possess structures which are deformed versions of this. $LiAlCl_4$ ($P2_1/c$), on the other hand, is built up from $LiCl_6$ octahedra in layers, linked by $AlCl_4$ tetrahedra.[255] Crystal structure data on $MAlCl_4$ (M = Li, Na, K, Cs or NH_4) were then used to compute total lattice energies. $\Delta H_f^o[AlCl_4^-(g)]$ was estimated to be -1188 kJ mol^{-1}.[256]

Raman spectra of $SnCl_2/MAlCl_4$ (M=Li, Na or Cs) were studied throughout the composition ranges. No specific $SnCl_2$-$MAlCl_4$ interaction could be detected in any case.[257]

Phase diagrams were determined for MCl-$AlCl_3$-SO_3, where M = Li, Na, K or NH_4. The following solid compounds were identified: $MAlCl_4.nSO_3$ (M=Li or Na, n=1.5 or 3; M=K, n=1.5 or 5; M=NH_4, n=5).[258]

The salt system $AlCl_3$-n-butylpyridinium chloride is molten at 40°C over a wide concentration range. Electrochemical and spectroscopic studies of aromatic hydrocarbons in this system showed that they underwent a one-electron oxidation to a cation-radical. These participate in an acid-base type of equilibrium with $Al_2Cl_7^-$ to give complexes whose spectra are similar to those of the carbonium ions of the parent hydrocarbons.[259]

The acid-base properties of the molten mixture of $AlCl_3$ and 1-butylpyridinium chloride itself (at molar ratios from 2.2:1.0 to 0.6:1.0) were examined by potentiometry. The equilibrium

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \qquad \dots (28)$$

constant for (28) was estimated to be $<3.8 \times 10^{-3}$ at 30°C.[260]

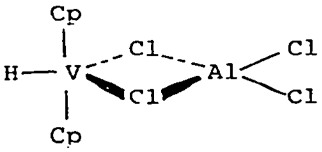
Potentiometric, and also vapour pressure, measurements were carried out on the KCl-$AlCl_3$ system in the temperature range 275-350°C. The combined results could best be explained in terms of three equilibria, (28), (29) and (30). pK values for (28)

$$3Al_2Cl_7^- \rightleftharpoons 2Al_3Cl_{10}^- + Cl^- \qquad \ldots (29)$$

$$2Al_3Cl_{10}^- \rightleftharpoons 3Al_2Cl_6 + 2Cl^- \qquad \ldots (30)$$

were: 8.15, 7.80, 7.47 and 7.15 at 275, 300, 325 and 350°C respectively. Comparable values for (29) were: 7.6, 7.3, 7.1, 7.1, and for (30) 15.4, ? , 14.0, 12.1.[261]

Infrared and mass spectra have been measured for $Al_3Cl_5(OR)_4$ and β-$AlCl(OR)_2$, where R=isopropoxide.[262]



(<u>86</u>)

Dicyclopentadienylvanadium dichloride in methylene chloride reacts with Et_2AlCl in n-heptane to give a paramagnetic product. Analysis of e.s.r. data suggests that the species is (<u>86</u>).[263]

Mass spectra of the vapours above Al_2Cl_6/Fe_2Cl_6 mixtures show that the main mixed species present are $AlFeCl_5$, $AlFeCl_4$ and $AlFeCl_6$.[264]

Chemical transport experiments have been carried out with $CoCl_2$, $NiCl_2$ or $CuCl_2$, using Al_2Cl_6 as the complexing and transport agent. Diffusion coefficients were calculated.[265]

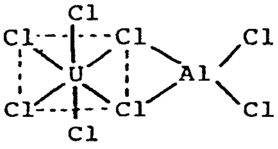
Raman spectroscopic evidence has been produced for complex formation between $ZrCl_4$ and $AlCl_3$ in both liquid and vapour phases. The spectra were consistent with the zirconium being octahedrally six-coordinate, with two bidentate $AlCl_4$ ligands. Above 300°C the complex dissociates back to $ZrCl_4$ and Al_2Cl_6. The $ZrBr_4$-Al_2Br_6 system behaves similarly.[266]

Thermodynamic considerations suggest that the chief vapour species formed above the $SmCl_3$-$AlCl_3$ system is $SmAl_3Cl_{12}$.[267]

Resonance Raman spectra of $UCl_5/AlCl_3$ vapours show that the $UCl_5.AlCl_3$ adduct formed has the structure (87). Increasing the power of the laser excitation induced the reaction (31), which was

$$2UAlCl_8 \longrightarrow U_2Cl_{10} + 2AlCl_3 \qquad \dots (31)$$

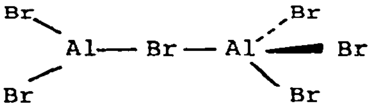
monitored by following the intensities of the U-Cl and Al-Cl stretches of the products.[268]



(87)

The t-butyl cation has been produced by dissolving t-BuBr in concentrated solutions of $AlBr_3$ in CH_3Br, CH_2Br_2 or $CHBr_3$. It was characterised by ^1H n.m.r. The reaction only occurs in concentrated solutions, but a saturated solution of $AlBr_3$ in CH_3Br gave an 80% yield of $^+C(CH_3)_3$.[269] ^1H n.m.r. evidence was also presented for the formation of the cations Me_2Br^+, Me_2I^+ in CH_3Br or CH_3I solutions saturated with $AlBr_3$.[270]

$AlBr_3$ reacts with alkali bromides (Li, Na or K) in acetonitrile to give solvates $MAlBr_4.4MeCN$ (M=Li,Na or K). Only for M=Li was this isolable as a solid (the others gave MBr and $AlBr_3.2MeCN$ on evaporation.[271]



(88)

Raman measurements on mixtures of Al_2Br_6 with aromatic compounds (e.g. toluene or o-xylene) can be interpreted by assuming the presence of a singly-bridged structure, assumed to be (88). A vibrational assignment was proposed for this, and a normal coordinate analysis carried out, which was compared with that for normal, doubly-bridged Al_2Br_6.[272]

Flow techniques were able to give measurements of the equilibrium (32), giving values for ΔH^o of 43.5kJ mol^{-1}, ΔS^o of 48.5J/^{o} at 686K. There was no evidence for the presence of significant

$$CoI_2(s) + Al_2I_6(g) \rightleftharpoons CoAl_2I_8(g) \qquad \ldots (32)$$

amounts of $CoAlI_5$.[273]

3.2.6 Intermetallic Compounds containing Aluminium

The intermetallic compounds NaAlM (M=Si or Ge) could be prepared from stoichiometric mixtures of the elements. They crystallise in an anti-PbFCl-type of lattice.[274]

The compounds $M_3Al_2Sn_2$ (where M=Sr or Ba) form orthorhombic crystals (space group Immm/D^{25}_{2h}). These contain an ordered variant of the Ta_3B_4 structure type.[275]

$Na_3(AlSi)Te_4$ was made from a stoichiometric mixture of the elements; its crystals were monoclinic (space group C2/m-C^3_{2h}). The structure is closely related to that of α-$NaFeO_2$. Half of the octahedral holes are occupied by Na^+, and the other half by a random mixture of Na^+ and Al-Si units.[276] $CaAl_6Te_{10}$ and $CaGa_6Te_{10}$ are also made from stoichiometric mixtures of the elements (by heating in a corundum vessel under an atmosphere of argon). The aluminium compound forms cubic crystals, space group $P4_132$, but those of the gallium compound are monoclinic, space group C2.[277]

Crystallographic cell volume data have been presented for $LaNi_{5-x}M_x$ (where M=Al,Ga or In; n=0 to 5). Thermodynamic quantities were calculated and compared with those previously obtained for $LaNi_{4.6}M_{0.4}$ (M=Al,Ga or In).[278]

3.3 GALLIUM

3.3.1 Compounds containing Ga-C Bonds

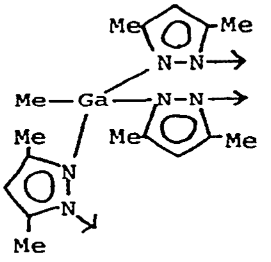
Several symmetrically 2-, 3- or 4-substituted triaryl gallium and triarylindium compounds have been prepared by transmetalation of the equivalent mercury compound by Ga or In metal. Electron-impact mass spectra of these species provide evidence for the presence of significant amounts of dimers in the gas-phase.[279]

MMe_3 or MMe_2Hal (M=Ga or In) interact with $Me_3M'Hal_2$ to produce $[Me_4M'][Me_{4-x}MHal_x]$, where M'=Sb or As; Hal=Br or I, x=1 to 3. The vibrational spectra of all the compounds were reported, and a number of assignments were proposed.[280]

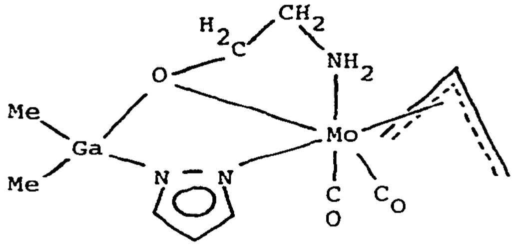
3.3.2 Compounds containing Ga-N Bonds

Extractions of Ga(III) or In(III) from aqueous media containing NCS-ions can be carried out by using trilaurylamine (TLA). The extracted species are probably: $Ga(NCS)_3$(HTLA-SCN), $Ga(NCS)_3$-$(HTLA\text{-}SCN)_2$ or $In(NCS)_3(HTLA\text{-}SCN)_3$. The extraction behaviour of the gallium is explicable in terms of cationic species $Ga(NCS)_n^{(3-n)+}$, where $0<n<3$, in the aqueous phase, but for indium it is also necessary to postulate the presence of $In(NCS)_n^{(n-3)-}$, $(n>3)$.[281]

A tridentate chelating ligand, methyltris(3,5-dimethylpyrazol-1-yl)gallate, (89,=L) has been prepared and characterised. The less sterically-demanding $MeGa(N_2C_5H_7)_2OH^-$ was also described. The complexes $LM(CO)_2(NO)$, (M=Mo or W), and $LM(CO)_2L'$ (M=Mo,W; L'=2-methylallyl) were characterised.[282]



(89)



(90)

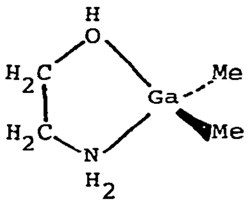
The coordinating properties of the tridentate chelating ligand $[Me_2Ga(OCH_2CH_2NH_2)(N_2C_3H_3)]^-$, and analogues with methyl groups on the amino-nitrogen and the 3- and 5-positions of the pyrazolyl ring, have been studied. All the complexes formed were monomeric, with octahedral geometry, and fac-coordination by the chelates, e.g. (90).[283]

Crystals of (η^3-2-methylallyl)[dimethyl(ethanolamino)(3,5-dimethyl-1-pyrazolyl)gallato(N(2), N(3),O)]dicarbonyl molybdenum, $LMo(CO)_2X$, where $L=Me_2Ga(N_2C_5H_7)(OCH_2CH_2NH_2)$; $X=\eta^3-C_4H_7$, are triclinic, space group $P\bar{1}$. Discrete molecular units are present, each linked to four others by N-H---O bonds.[284] The complex bis[methyltris(1-pyrazolyl)gallato]nickel(II), on the other hand, forms rhombohedral crystals, space group $R\bar{3}$. Well-separated molecules of $[MeGa(N_2C_3H_3)]_2Ni$ are present, with approximately D_{3d} symmetry.[285]

$(H_2NCH_2CH_2O)GaMe_2$ can be prepared by reaction (33). The crystal

$$H_2NCH_2CH_2OH + GaMe_3 \xrightarrow[\text{reflux}]{C_6H_6} (H_2NCH_2CH_2O)GaMe_2 + CH_4 \qquad \ldots(33)$$

structure of the product is tetragonal, belonging to the space group $P4_3$. Monomeric molecules, (91), are present, with four-coordinate gallium, and the following bond distances: Ga-O 1.917Å, Ga-N 2.06Å, Ga-C 1.962, 1.974Å.[286]



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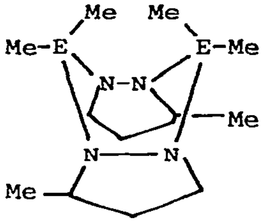

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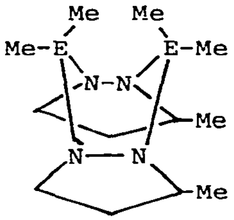

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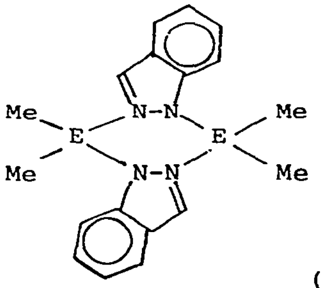


(94)

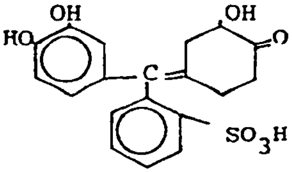
BMe_3 or $GaMe_3$ react with 3-methylpyrazole to form isomeric pairs of dimeric products, $[Me_2E(Mepz)]_2$, E=B or Ga; Mepz=3-methylpyrazole), (92) and (93). From $InMe_3$, the resultant product is a single species, possibly (92), (E=In), or a form containing a planar $[In(N\text{-}N)_2In]$ metallocycle. Me_3E (where E=Ga or In) react with indazole to yield a single isomer $[Me_2E(ind)]_2$, believed to be (94). This has either a planar central ring or a rapidly interconverting boat or chair conformation.[287]

Complexes have been reported between $GaCl_3$ and α-pyridineanthraquinone(L) or pyrazineanthraquinone(L'): $GaCl_3.L$, $1.5GaCl_3.L'.1.5H_2O$, $GaCl_3.L.HCl$, and also $InCl_3.L.2HCl$. Infrared spectra suggest that the ligands are coordinated via a nitrogen of the pyridine ring and a carbonyl oxygen, to give 6-membered chelate rings (for L). For L', this is believed to be tridentate, i.e. as for L, with an additional bond between the metal and the second nitrogen atom.[288]

3.3.3 Compounds containing Ga-O, Ga-S or Ga-Te Bonds

Reaction between $GaMe_3$ and SiO_2 surfaces produces $OGaMe_2$ groups at the surface. Treatment with HCl converts these to $OGaCl_2$, which catalyse the reaction of SiH_4 with HCl (giving SiH_3Cl and H_2).[289]

Kinetics and equilibria involving Ga(III) and pyrocatechol violet, (95), (H_4L), have been studied. They produce two complexes identified as $Ga(H_2L)^+$ and Ga_2L^{2+}. The rate of reaction of Ga^{3+} with H_3L^- is much slower than for $GaOH^{2+} + H_3L^-$, showing the enhanced reactivity of the hydrolysed cation.[290]



(95)

Infrared spectra and X-ray diffraction studies show that the basic carbonate $Ga_2O_3.2CO_2.2NH_3.3H_2O$ is ammonium dihydroxocarbonatogallate, $NH_4\ Ga(OH)_2CO_3$. The CO_3 group is coordinated to the gallium in a bidentate fashion.[291]

The new compound $BeGa_2O_4$ is prepared from the high temperature (approx. 2000°C) reaction between BeO and Ga_2O_3. Single crystal X-ray diffraction shows that it belongs to a hitherto unknown structure type. It is hexagonal, space group $P6_3/m$ (C_{6h}^2). The Be^{2+} and Ga^{3+} are statistically distributed and surrounded by O^{2-} tetrahedra.[292]

Slow cooling of $SrO:Ga_2O_3$ mixtures (ratio 0.29:0.71) in a platinum vessel forms single crystals of $SrGa_{12}O_{19}$ (space group $P6_3/mmc$).[293] Phase diagrams have been reported for Ga_2O_3-Na_2O-SiO_2-H_2O at 200°C, and H_2O concentrations of 95, 85, 80 and 70 mass %.[294]

A dimeric 5-tungstogallate(III): $[C(NH_2)_3^+]_6[(GaO_6)_2W_{10}O_{24}].12H_2O$ was inadvertently prepared as a result of attempting to prepare salts of the 6-tungstogallate(III) heteropolyanion.[295]

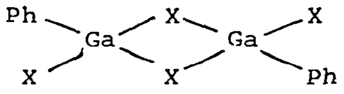
$EuGa_2S_4$ is orthorhombic, and belongs to the space group Fddd. It is prepared from a stoichiometric mixture of EuS and Ga_2S_3. The gallium is four-coordinate (three Ga-S at 2.30Å, and one at 2.24Å), and the europium eight-coordinate (square antiprism).[296]

The new compound Ga_2S_2Te is formed from stoichiometric mixtures of Ga_2S_3 and Ga_2Te_3. Its crystals are tetragonal, belonging to the space group $I4_1md$. The gallium atoms are four-coordinate, to give GaS_3Te units (Ga-S 2.307-2.353Å, Ga-Te 2.556Å), which are linked to give chains parallel to the (001) plane.[297] GaTe forms monoclinic crystals (space group B2/m). The gallium atoms are again four-coordinate, but this time to 3Te atoms (two at 2.669Å, one at 2.638Å) and one Ga (at 2.431Å).[298]

3.3.4 Gallium Halides

Electronic absorption spectra were measured for MX_3, where M=Ga or In, X=Cl,Br or I, in solution in MeOH, MeCN or H_2O. One-electron transitions responsible for the lowest-energy groups of absorption bonds are all of the type $nt_2 \rightarrow 3a$, (n=1,2 or 3).[299]

Ph_nGaX_{3-n} (n=1 or 2 for X=Cl,Br or I) have been prepared. Their infrared, Raman, mass and $^{69,71}Ga$ n.m.r. spectra were reported. All the data were consistent with the presence of discrete halogen-bridged molecular dimers, e.g. (96), in the solid state. The adducts $[Ph_nGaCl_{3-n}.dioxan]$ were also prepared. These



(96)

gave Ga-Cl stretches characteristic of terminal Ga-Cl only.[300]

Complexes between "gallium dihalides" and 1,4-dioxan (diox) have been investigated: $Ga_2X_4.2(diox)$, for X=Cl, Br or I. When X=Cl, triclinic crystals are formed, which contain discrete molecules with a Ga-Ga bond (2.406(1)Å). Raman data suggest that when X=Br or I similar structures are present. Extensive interaction occurs between νGaGa and νGaX, so no single wavenumber can be assigned to each mode.[301]

Extraction of gallium from HCl solutions by tributylphosphate takes place by two mechanisms, depending on the HCl concentration. At lower HCl concentrations, the Ga:Cl ratio in the extract is equal to 1:4 (i.e. $HGaCl_4$); at higher HCl concentrations the proportion of Cl is higher i.e. $HGaCl_4$ is extracted together with some HCl.[302]

Phase diagrams have been reported for $GaCl_3-SnCl_2$,$-PbCl_2$ or $-SnCl_4$. $M(GaCl_4)_2$ compounds are formed with the first two (M=Sn or Pb), while $GaCl_3-SnCl_4$ system is eutectic.[303] Similar data were reported for $GaBr_3-MBr$ (M=Cu or Ag). For M=Cu, two compounds were identified: $CuGa_2Br_7$ (melting incongruently at 140°C) and $CuGaBr_4$ (melting congruently at 274°C). Analogous compounds were found for M=Ag also.[304] Phase diagrams were also given for the systems $GaBr_3-SnBr_2$ (two compounds found: $SnBr_2.6GaBr_3$, $SnBr_2.2GaBr_3$, in addition to a solid solution based on $SnBr_2$) and

$GaBr_3$-$PbBr_2$ (four compounds: $PbBr_2.4GaBr_3$, $PbBr_2.GaBr_3$, $3PbBr_2.2GaBr_3$, $3PbBr_2.GaBr_3$).[305] For $GaBr_3$-$CdBr_2$, three compounds were formed ($CdBr_2.3GaBr_3$, $CdBr_2.2GaBr_3$, $3CdBr_2.2GaBr_3$) and for $GaBr_3$-$ZnBr_2$, three solid solutions, which decomposed to $2GaBr_3.ZnBr_2$ and $GaBr_3.4ZnBr_2$.[306]

Phase diagrams were reported for MI_2-TlI (where M=Ga or In). Several mixed Tl/M/I phases were identified.[307] Phase relations were elucidated for "GaI_2" i.e. $Ga^IGa^{III}I_4$ with AlI_3 and with Ga^IAlI_4.[308]

3.4 INDIUM

3.4.1 General

Crystal structures have been determined for Li_3In_2, Li_5Tl_2 and Li_3Tl. Li_3In_2 forms trigonal rhombohedral crystals (space group $R\bar{3}m(D^5_{3d})$), isotypic with Li_3Al_2 or Li_3Ga_2. Li_5Tl_2 is isotypic with Li_5Sn_2 (space group $R\bar{3}m$), and Li_3Tl forms cubic crystals, space group $Fm3m(O^5_h)$.[309]

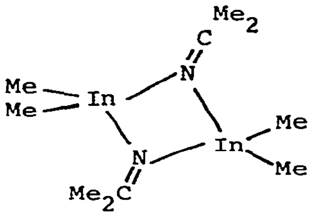
$Fe_2(CO)_8[InMn(CO)_5]_2$ forms tetragonal crystals (space group $I4_1/a$). A four-membered In_2Fe_2 ring is present (In-Fe distance 2.663(1)Å), but there was no evidence for In/In or Fe/Fe interactions in the ring.[310]

Another indium-containing carbonyl complex, $In_4Re_8(CO)_{32}$ also gives tetragonal crystals (space group $P\bar{4}2,c$). The core of the structure is the In_4Re_8 unit, held together by 16 In-Re bonds (the In-Re distances lie in the range 2.720-2.848Å) and 4 Re-Re bonds (2.997-3.034Å). Four Re atoms constitute an inner tetrahedron, with one In atom above each triangular face. This is then bound to one rhenium of an outer tetrahedron. The "inner" Re atoms are also attached to three CO groups, the "outer" to five carbon monoxide groups.[311]

New In(III) porphyrins containing a metal-carbon bond can be made by reaction of chloroindium(III) porphyrin with alkyl- or aryl-lithium.[312]

Methods of preparation of InN have been reported, crystallographic parameters were measured and physical properties determined. InN is resistant to hydrolysis, but it is readily oxidised by air and attacked by acids and bases.[313]

$[Me_2C{=}N{-}InMe_2]_2$ was prepared from N-chloro-2-propanimine and $InMe_3$. Infrared, Raman and ^1H n.m.r. spectra were consistent with a centrosymmetric structure, (97), with a four-membered $(InN)_2$ ring. An X-ray structure determination confirmed this



(97)

structure. $\nu(InN)_2$ (A_g) was assigned to a very strong Raman band at $482cm^{-1}$, the B_u mode to an infrared band at $437cm^{-1}$.[314]

3.4.2 Compounds containing In-O- or In-S Bonds

The crystal and molecular structures of cubic $In(OH)_3$ have been studied by X-ray and neutron diffraction. The crystals belong to the space group $Im3(T_h^5)$. The indium is octahedrally coordinated by six oxygen atoms (2.162Å), while each oxygen is coordinated by two indium atoms. The hydrogen atoms are disordered, and infrared spectra of $In(OH)_3$ and $In(OD)_3$ revealed two different strengths of hydrogen bonding by these disordered hydrogen atoms.[315]

Photoelectron (x-ray excitation, XPS) and Auger spectra have been reported for the following indium compounds: In_2O_3, $In(OH)_3$, In_2S_3, InX_3 (X=F,Cl,Br or I), InF_6^{3-}, as well as indium metal. For the In-O and In-F compounds there is a straight-line correlation between the XPS and the Auger data. A different straight line is found for the In-Cl, In-Br, In-I and In-S compounds. The difference between the two groups is clearly related to the amount of ionic and covalent bonding in each.[316]

The crystal structures of $In(CH_3COO)_3$.2,2'-bipyridine and $In(CH_3COO)_3$.1,10-phenanthroline show that both form monoclinic crystals (space group $P2_1/c$). The acetate ligands are all bidentate in both cases, and so the In atoms have a coordination number of 8. The geometry is that of a distorted dodecahedron.[317]

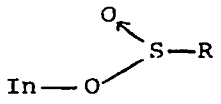
Tris(acetylacetonato)indium(III) also forms monoclinic crystals (space group $P2_1/n$). The In-O distances are in the range 2.108-2.146Å: the irregular geometry is consistent with covalent interaction. The chelate rings are planar within experimental error.[318]

Indium is extracted from solutions containing NO_3^- by thenoyltrifluoroacetone according to the equation (34).[319]

$$In(NO_3)_3 + 3HTTA \rightleftharpoons In(TTA)_3 + 3H^+ + 3NO_3^- \qquad \ldots (34)$$

In the presence of a large excess of $P_2O_7^{4-}$, indium(III) forms the complexes $InH(P_2O_7)_2^{4-}$ and $In(P_2O_7)_2^{5-}$. The formation constants were measured and found to be: $\log \beta_1=21.99 \pm 0.02$, $\log \beta_2=23.80 \pm 0.02$.[320]

Sulphinato-indium(III) porphyrins can be prepared by SO_2 insertion into an In-R bond. They are readily oxidised to the corresponding sulphonato-compounds. Both classes of compound can also be made by the photochemical oxidation of thioalkyl (or -aryl) indium(III) porphyrins. For the sulphinates it was not possible to differentiate between the possible bonding models (98) and (99). For the sulphonates, In-O, not In-S, bonding was indicated.[321]



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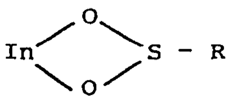


(99)

$HIn(SO_4)_2.4H_2O$ forms orthorhombic crystals, belonging to the space group Pnam. Layers (perpendicular to the c-axis) of In atoms joined to four others by sulphato-groups were present. The coordination polyhedron of the indium was completed by two water molecules, giving a distorted octahedron, $InO_4(OH_2)_2$. These units were linked by $H_5O_2^+$ ions.[322]

The thorveitite form of $In_2Si_2O_7$ converts to a monoclinic phase (of $Er_2Si_2O_7$ type) at 45 kbar and 1000°C.[323]

A single-crystal X-ray diffraction analysis of $CuAlInO_4$ showed that the crystals were monoclinic, space group Cm. The In^{3+} has octahedral six-coordination, while Al^{3+} and Cu^{2+} are five-coordinate (distorted trigonal bipyramidal). All the compounds $M(II)M(III)InO_4$ (M(II)=Mg,Mn,Co,Cu or Zn; M(III)=Al or Ga) have the same structure.[324]

Polarographic measurements on the In(III)-thiourea system were used to determine the stability constant of the monothiourea complex of In(III): $\beta=93 \pm 12$ (at I=0.5 and 25°C).[325]

Complex formation has been studied in aqueous solution (pH 5) for systems containing In(III), nitrilotriacetic acid and NCS^-.

The following species were identified, with logarithmic formation constants (log ; where these could be measured): $[In(NTA)(SCN)]^-$, $[In(NTA)(SCN)_2]^{2-}$, $[In(NTA)(SCN)_3]^{3-}$ (15.24), $[InH(NTA)(SCN)]$, $[InH(NTA)(SCN)_2]^-$, $[InH(NTA)(SCN)_3]^{2-}$ (19.05), $[In(NTA)_2]^{3-}$ (24.4Z), $[InH_2(NTA)_2(SCN)_3]^{4-}$ (29.47).[326]

Complex formation was also studied between $In(SCN)_3$ and iminodiacetic acid (H_2IMDA), hydroxyethyliminodiacetic acid (H_2HEIDA), glycine bis(methylphosphonic)acid (H_5GP) or nitrilotrimethylphosphonic acid (H_6NTP). The following mixed compounds (together with logarithms of their stability constants) were found: $[In(HIMDA)(SCN)_3]^-$(8.87), $[In(IMDA)(SCN)_3]^{2-}$ (13.21), $[In(HHEIDA)(SCN)_3]^-$ (9.33), $[In(HEIDA)(SCN)_3]^{2-}$ (13.87), $[In(H_3GP)(SCN)_3]^{2-}$ (9.11), $[In(H_2GP)(SCN)_3]^{3-}$ (11.02), $[In(GP)(OH)]^{3-}$ (19.42), $[In(H_2NTP)(SCN)_3]^{4-}$ (15.58) and $[In(NTP)(OH)]^{4-}$ (29.11).[327]

Metal-rich chalcogenides $M_3M_2'X_2$ (M=Ni,Co,Pd or Rh; M'=In or Tl; X=S or Se) with the shandite-type structure have been prepared (from mixtures of the elements or the binary compounds). $Co_3In_2S_2$ forms rhombohedral crystals, belonging to the space group $R\bar{3}m$.[328]

Spinel phases $A_xIn_xSn_{1-x}S_2$ (where A=Cu or Ag) have been detected in the pseudo-binary systems $AInS_2$-SnS_2. They possess wide homogeneity ranges: $0.07<x<0.50$ (A=Cu); $0.40<x<0.60$ (A=Ag).[329]

3.4.3 Indium Halides

Phase diagram studies on the systems $RCOOH$-InF_3-H_2O (where R= H or Me) have revealed the existence of the new compounds $InF_3.RCOOH.3H_2O$.[330]

Investigations on the extraction of In(III) from acidic aqueous solutions containing Cl^- by cadmium bis(diethyldithiocarbamate) showed that the reacting In(III) species was $InCl^{2+}$, and that the indium was extracted as indium tris(diethyldithiocarbamate).[331]

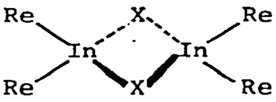
Phase diagrams were reported for $InCl$-MCl_2 and $InCl_2$-MCl_2 (M= Ca or Mg). The following compounds were reported for the InCl systems: $InCaCl_3$, $InCa_2Cl_5$, In_2MgCl_4, $InMgCl_3$. The $InCl_2$ systems were eutectic.[332]

$In(CH_2SiMe_3)_xCl_{3-x}$ (where x = 1,2 or 3) can be prepared from $InCl_3$ and Me_3SiCH_2MgCl (x=3), followed by reactions with further $InCl_3$ (x=1 or 2). $In(CH_2SiMe_3)_3$ in a three-coordinate pyramidal monomeric liquid at room temperature. $[In(CH_2SiMe_3)_2Cl]_2$ and "$In(CH_2SiMe_3)Cl_2$" are both crystalline solids at room temperature

- the mono-chloro compound being a chlorine-bridged dimer, the dichloro compound a higher polymer.[333]

The vibrational spectrum of monomeric $InCl_3$ in solid Kr at 20K has been reported, and a complete assignment given. The assignment is perfectly consistent with D_{3h} symmetry and is: $\nu_1(a_1')$ 349.5cm^{-1} (Raman); $\nu_2(a_2'')$ 102cm^{-1} (infrared); $\nu_3(e')$ 392cm^{-1} (infrared), 394cm^{-1} (Raman); $\nu_4(e')$ 98cm^{-1} (infrared), 98.5cm^{-1} (Raman). The $^{35}Cl/^{37}Cl$ isotopic fine structure was resolved for ν_1.[334]

The crystal structures of $[\{Re(CO)_5\}_2In(\mu\text{-}X)]_2$ (where X=Cl,Br or I) have been determined. The central molecular unit consists of a planar In_2X_2 ring with the following (average) In-X distances: 2.624(6)Å (Cl), 2.764(3)Å (Br), 2.986(2)Å (I). Two $Re(CO)_5$ groups are bonded to each indium to give distorted tetrahedral coordination, (100).[335]



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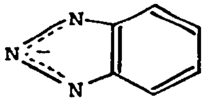
The conductances, densities and viscosities of mixed aqueous solutions of $InCl_3$ and NH_4Cl have been measured. The conductances are always less than the sum of those of the individual components, and sometimes less than that of $InCl_3$ alone. These results are consistent with complex formation in these solutions.[336]

Tetrachloro-indates and -thallates, $MM'Cl_4$ (M=K,Rd or NH_4; M'=In or Tl) are isotypic (tetragonal $CaWO_4$ type). They can all be prepared by crystallisation from highly-concentrated aqueous $M'Cl_3$ in the presence of small amounts of MCl. Single crystal results were reported for NH_4TlCl_4, and some assignments were given of infrared data for the tetrachlorothallates.[337]

3.5 THALLIUM

3.5.1 Thallium(I) Compounds

U.v., visible and infrared spectra of $TlCo(CO)_4$ suggest that the structure should be viewed as an ion pair. The infrared data are consistent with C_{3v} symmetry and a direct Tl-Co bond.[338]



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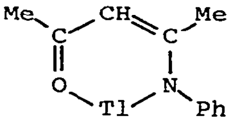
The crystal and molecular structures of (benzotriazolato)-thallium(I) show that sheets of Tl^+ ions are separated by benzotriazole anions, (101). The thallium is coordinated by three nitrogen atoms at 2.725–2.792Å, and a further three nitrogens at 3.271–3.326Å giving a distorted trigonal prismatic geometry. The Tl^+ ions are arranged in zig-zag chains. The anions form very close packed layers, similar to those predicted for the protective layer formed when benzobriazole is used as an inhibitor of metallic corrosion.[339]



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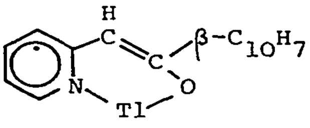

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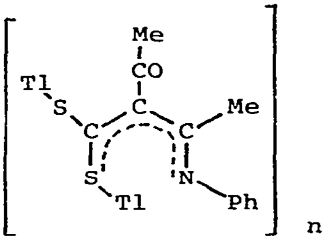

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The chelate compounds (102) and (103) have been prepared. CS_2 causes an electrophilic substitution to occur at the central carbon atoms of the chelate rings to form dithallium compounds of dithiocarbonic acids, e.g. (104).[340]

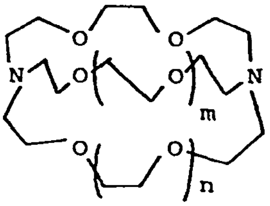
The luminescence behaviour of Tl^+ in aqueous solution can be explained by a mechanism based on thallium ion-water excimers.[341]

Raman spectra have been reported for pure molten $TlNO_3$ and for aqueous $TlNO_3$ solutions over a wide range of concentrations. In the more concentrated solutions evidence was found for a π-interaction, C_s "roll-on", contact ion-pair. A similar interaction occurs in $TlNO_3$ solutions in liquid ammonia.[342]

Infrared and Raman spectra were recorded for several crystalline modifications of $TlNO_3$: $\alpha(O_h^1)$, $\beta(C_{3v}^2)$ and $\gamma(D_{2h}^{16}$ or $C_{2v}^9)$. The β- and γ-modifications do not differ spectroscopically: all four normal modes were active in both the infrared and Raman spectra, and the E' mode was split. There must therefore be C_s site symmetry for NO_3^- in both. The α-form obeys the selection rules for O_h symmetry.[343]

Crystals of TlH_2PO_4 are monoclinic, probably of C2 symmetry. The thallium is seven-coordinated by oxygen atoms (mean Tl-O 2.966(17)Å), unlike that in $TlH_5(PO_4)_2$, which is six-coordinate (mean Tl-O 3.048(2)Å).[344] Tl_2HPO_4 also forms monoclinic crystals, space group Pc. There are several very short (2.5-2.6Å) Tl-O bonds in the structure.[345] $Tl_{0.33}(NH_4)_{0.67}H_2PO_4$ forms crystals belonging to the space group $I4_1md$ or $I\bar{4}2d$.[346]

The thallium(I) hydroxide antimonate, $Tl_2Sb_2O_6(OH).14H_2O$, can be prepared from $TlNO_3$ and potassium antimonate solutions. It forms cubic crystals of the pyrochlore type.[347]



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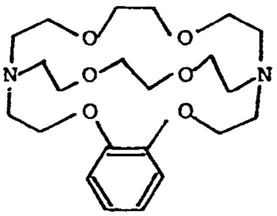

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^{205}Tl n.m.r. studies on thallium(I) complexes with (105, m=1, n=0 or m=n=1) and (106) show that the chemical shifts of the complexes are independent of the solvent. Thus the Tl^+ ions are completely shielded by these cryptand molecules.[348]

$Tl_3Na(SO_3)_2$ was shown by d.t.a., X-ray diffraction and Raman spectroscopic studies to exist in α-, β- -nd γ-modifications. The crystal structure of the γ-phase was reported: the crystals were orthorhombic, space group Pnam.[349]

The thallium(I) germanate $Tl_8Ge_5O_{14}$ crystals are monoclinic (space group C2/c). The structure is based on isolated $(Ge_5O_{14})^{8-}$ units: $5GeO_4$ tetrahedra linked by bridging oxygen atoms. Tl^+ ions lie between these units, in tunnels parallel to the b-axis.[350]

A new compound has been isolated from the Tl-Nb-O system: $TlNb_7O_{18}$ (idealised formula). Its crystals are tetragonal, space group P4/mbm. The actual formula is believed to be $Tl_{7.7}Nb_{54+x}O_{146-y}$. The thallium ions are irregularly coordinated by 6-8 oxygen atoms (Tl-O 2.78 - 3.47Å).[351]

The mixed oxides $Tl_{10}M_{29.2}O_{78}$ (where M=Nb or Ta) were prepared by cationic exchange in aqueous solution or the solid state (from H_3O^+ salts).[352]

Evidence has been found for non-stoichiometric phases $Tl_2S_{1+x}O_2$ (0<x<0.5). They decompose on heating to Tl_2SO_2 and Tl_2S (with loss of SO_2). Under oxygen, decomposition yields Tl_2SO_4.[353]

Tl_6TeO_6 has been prepared for the first time by the thermal decomposition of Tl_6TeO_{12}. Its crystals belong to the space group $R\bar{3}$ or R3, and the formula can be written as $Tl_6TeO_6E_6$ (E=lone pair). Like Tl_6TeO_{12} it is isostructural with Y_6UO_{12}.[354]

Tl_2WO_4 crystals are prepared by heating a mixture of Tl_2CO_3 and WO_3 at 973K for 3 hours; they are trigonal (space group $P\bar{3}m1$). The Tl–O bond distances fall into three groups (ca.2.70, ca.3.25, ca.3.29Å).[355]

A high-temperature X-ray diffraction study of Tl_2S revealed a phase transformation at 450°C, giving a new hexagonal phase.[356] Phase diagrams of the K_2S–Tl_2S and Rb_2S–Tl_2S systems were examined by D.T.A. and X-ray diffraction. The potassium system gave evidence for hexagonal red $K_4Tl_2S_3$ and monoclinic red K_7TlS_4. The rubidium system gave only one compound: hexagonal $Rb_4Tl_2S_3$.[357]

Tl_3SbS_4 has been isolated for the first time, from the Tl_2S/$TlSbS_2$ system; it was characterised by d.t.a. and X-ray diffraction.[358]

$TlFeS_2$ was synthesised from Tl_2S/FeS/S mixtures; the crystals were monoclinic, space group C2/m. The Tl^+ was coordinated by six sulphur atoms (3.09–3.49Å), with further interactions involving another Tl(3.66Å), two iron atoms (3.70Å) and three sulphurs (3.73–3.76Å).[359] The new ferromagnetic compounds $TlFe_{1+x}S_2$ ($0.25 \leqslant x \leqslant 0.85$) have been prepared and their structures studied. Monoclinic $Tl_3Fe_2S_4$ was also investigated: space group C_{2h}^5.[360]

$TlFeSe_2$ is monoclinic, space group C2/m(C_{2h}^3), isotypic with $TlFeS_2$. The thallium atoms interact with nine selenium atoms (3.235–3.945Å) and two iron atoms (ca. 2.35Å).[361]

The crystal structure of non-stoichiometric $Tl_xNbO_{2+x}F_{1-x}$ ($0.5 \leqslant x \leqslant 1$) is cubic, space group Fd3m, of the pyrochlore type. The Tl^+ ions were located, on two sets of positions. The properties of the Tl^+ motion are related to the high polarisability of Tl^+ and to the large number of sites available.[362]

$TlCdI_3$ is orthorhombic (space group Pnma), and adopts the NH_4CdCl_3 structure. There are double chains of edge-sharing CdI_6 octahedra with Tl^+ in between these. The Tl^+ ions are nine-coordinate, Tl–I distances range between 3.578 and 4.302Å.[363]

α-Tl_4CrI_6 exists as tetragonal crystals, space group P4/mnc. Isolated CrI_6 octahedra are present, with eight-coordinate Tl^+ ions (as bicapped trigonal prisms). The Tl–I distances lie in the range 3.441 to 3.947Å.[364]

Tetragonal Tl_4HgI_6 belongs to the space group P4/mnc and as in the previous case the Tl^+ ions are at the centre of bicapped trigonal prisms (eight coordinate).[365]

Crystals of $Tl_6Au_2I_{10}$ are black, with a golden lustre. They decompose in a closed system at 276°C. In vacuo they decompose above 65°C with liberation of one molecule of iodine. They belong to the space group $P\bar{6}2c$, and are built up from a Tl_6I_6 framework, with channels parallel to the c-axis which contain Au^+, I_3^- and I^- ions.[366]

3.5.2 Thallium(III) Compounds

Tris(polyfluorophenyl)thallium(III) compounds, R_3Tl (where R= C_6F_5, p-HC_6F_4, o-HC_6F_4) have been prepared from the corresponding

$$2R_2TlBr + (RSO_2)_2Ba \longrightarrow 2R_3Tl + BaBr_2 + SO_2 \quad \ldots (35)$$

bromobis(polyfluorophenyl)thallium(III) species and barium or thallium(I) polyfluorobenzene sulphinates in pyridine, e.g. (35).[367]

^1H and ^{13}C n.m.r. measurements on dialkyl thallium amides and on dimethylthallium diphenylphosphide show that in these compounds, with a $(TlX)_2$ four-membered ring structure, the size of the bridging groups affect the bonding strength within the ring. Exchange reactions between different dialkylthallium compounds proceed via dimer-monomer equilibria.[368]

Tris(triazenido)thallium(III) complexes have been prepared for the first time, equation (36), where HL=1,3-diphenyltriazene or 1-phenyl-3-(2'-pyridyl)triazene. ν_{as}(NNN) was seen near 1350cm^{-1}.

$$(C_6F_5)_3Tl(dioxan) + 3HL \rightarrow TlL_3 + 3C_6F_5H + dioxan \quad \ldots (36)$$

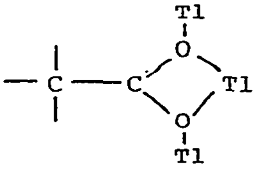
The compounds are monomeric in benzene: consistent with bidentate triazenido ligands and six-coordinate thallium.[369]

Thallium(III) trifluoromethanesulphonate has been prepared following equation (37). This compound can then be used to thallate a wide variety of polyfluoroarenes to give $R_FTl(O_3SCF_3)_2$, where R_F=p-$MeOC_6F_4$, p-MeC_6F_4, C_6F_5 etc.[370]

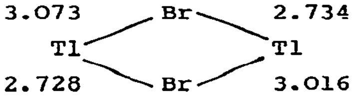
$$Tl(O_2CCF_3)_3 + 3CF_3SO_3H \quad ^{CF_3CO_2H} \quad Tl(O_3SCF_3)_3 + 3CF_3CO_2H \quad \ldots (37)$$

Cyclopropylbis(isobutyrato)thallium(III) has been synthesised and its crystal structure determined (orthorhombic, space group $Pna2_1$). Linear polymers were present in which the thallium is seven-coordinate. Two types of carboxylate group are present:

one weakly chelating, the other chelating and bridging, (107), with $\nu_{as}(CO_2)\nu_s(CO_2)$ at 1505-1540 and 1411-1428cm^{-1} respectively.[371]



(107)



(108)

Crystalline $RTl[SC(:S)NR'_2]_2$ and $RTl[SC(:S)OR']_2$ have been obtained and characterised by n.m.r. They were prepared by reactions of $RTlX_2$ (where X=Cl or $OCOCF_3$) with the sodium salts NaSC(:S)YR' (YR'=NMe_2, NEt_2, OMe; R=Ph or p-MeC_6H_4).[372]

$TlCl_3$ forms catalyst mixtures of Ziegler-Natta type with various organometallics e.g. C_2H_5MgBr; n-BuLi. These are analogous to those formed by $TiCl_4$.[373]

The crystal structure of $(p\text{-}C_6HF_4)_2Tl(III)Br$ shows that it is in fact an unsymmetrical bromine-bridged dimer, containing the bridge unit (108). The distances from thallium to bromine atoms of adjacent dimer units show that there is significant bonding interaction between these - hence it can be regarded as being a polymeric chain structure. The thallium is five-coordinated, with a distorted trigonal bipyramidal geometry. νTl-Br values are very similar in this compound and in $(C_6F_5)_2TlBr$: the latter may have a very similar structure.[374]

3.5.3. Other Thallium Compounds

$Tl_4Bi_2S_5$ is orthorhombic, space group Pnam. The thallium atoms are 4- or 5-coordinated, with Tl-S distances 2.80-3.28Å. The thallium lone pair is stereochemically significant.[375]

The SnSe-TlSe section of the Sn-Tl-Se ternary system has been studied showing the existence of $Tl_3Sn_2Se_5$ and Tl_3SnSe_4. Both undergo peritectic decomposition, at 490°C and 364°C respectively.[376]

$TlFe_3Te_3$ forms hexagonal crystals, space group $P6_3/m$ (C^6_{2h}). It is a new structure type, with Tl coordinating to 9Te atoms, six at 3.504(1)Å and three at 3.442(1)Å.[377]

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