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Chapter 3

ELEMENTS OF GROUP 3

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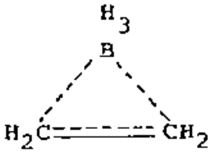
3.1 BORON

3.1.1 Boranes

Ab initio LCAO-MO-SCF Hartree-Fock-Roothaan calculations were carried out on B^{3+}, B^+, BH, BH_2^-, BH_2^+, BH_3 and BH_4^-. Proton and hydride affinities were calculated, together with energies of reaction between various pairs of these species.[1]

Detailed electron density calculations have been carried out for BH (together with H_2O and H_2S). The effects of basis set variations, and the inclusion of electron correlation, were determined.[2]

Ab initio m.o. calculations on the reaction of BH_3 with ethylene suggest that the reaction is exothermic, via an intermediate π-complex (1), and with no overall activation barrier. The mechanism in the gas-phase consists of two facile stages: (i) formation of the π-complex, and (ii) rearrangement to the ethyl borane product.[3]



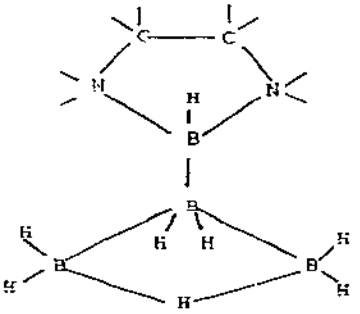
(1)

Irradiation of B_2H_6 with the 973 $cm.^{-1}$ line of a CW CO_2 laser produced $B_{10}H_{14}$, B_5H_9, B_5H_{11}, $(BH)_n$ and H_2. The number of photons needed to produce one molecule of $B_{10}H_{14}$, $(B_5H_9+B_5H_{11})$, H_2, and to transform one molecule of B_2H_6 were: 22000, 287, 156 and 156 respectively. No evidence was found for a chain process, no light emission occurred during the reaction, and no $B_{20}H_{16}$ was formed.[4,5]

Vibrational assignments were proposed for *cis*- and *trans*-1,2-dimethyldiborane. Previous data were shown to be due to a *cis*-/*trans*- mixture.[6]

The low-temperature ^{19}F n.m.r. spectra of $B_4H_8PF_2NMe_2$ reveal the presence of two geometrical isomers. One form has slow rotation about the P-B bond at low temperatures, to give resolvable resonances due to the non-equivalent fluorines in that isomer (believed to be the one in which the PF_2NMe_2 group is *endo*- with respect to the ring).[7]

Variable-temperature ^{11}B and ^1H n.m.r. spectra have been reported for the fluxional *hypho*-borane $(Me_2NCH_2CH_2NMe_2)B_4H_8$. The low-temperature, limiting structure has two equivalent and two unique boron atoms. All of the observations are accounted for by the structure (2). The mechanism of the fluxional behaviour was not settled however.[8]



(2)

The ^{11}B n.m.r. spectra of B_4H_{10} and B_5H_9 were analysed to find the factors responsible for line-broadening. It was found that scalar relaxation and partially-collapsed spin-spin multiplets, as well as unresolved B-B spin-spin coupling are all significant.[9]

Extended-Hückel m.o. calculations have been performed on $(BH)_n$ systems, where n = 1 to 9. The energies of alternative structures were calculated for 6-, 7- and 8-vertex structures with differing overall charges. Thus, for $B_6H_6^{n-}$, (n = 0,2,4 or 6), the most stable structures are predicted to be bicapped tetrahedral (C_{4v}), octahedral (O_h), pentagonal pyramidal (C_{5v}) and trigonal prismatic (D_{3h}) respectively. All stable forms have their bonding orbitals filled, and therefore their structures are anticipated by the 'capping' principle.[10]

The effects on the electronic structures of $B_5H_5^{2-}$ or $B_6H_6^{2-}$ of adding one or two extra terminal or bridging protons have been calculated. Trigonal bipyramidal and square pyramidal $B_5H_6^-$ and B_5H_7 were the five-vertex species considered. The six-vertex systems examined were octahedral, trigonal prismatic and capped square pyramidal $B_6H_7^-$ and B_6H_8. If the polyhedron consists of triangular faces only, then there is little preference for bridging ligands. If square faces are present there is a marked preference for bridging ligands at the edge of such faces.[11]

Measurements of thermochemical data have been made for the B_5H_8 radical, using mass-spectrometric observations on a series of proton transfer reactions, see equation (1), where R is a stable

$$B_5H_9^+ + R \longrightarrow RH^+ + B_5H_8 \tag{1}$$

molecule of known proton affinity. The value of the (B_5H_8)-H dissociation energy was found to be 98.4 ± 2 $kcal.mol^{-1}$, i.e. close to the value of the energy of dissociation of a proton from HBF_2, but less than the value from borazine.[12]

1-$C\ell$-and 2-$C\ell$-B_5H_8 isomerise under the influence of diethyl ether as catalyst. The reaction is first-order in borane and in ether. The rate constants for equation (2) are $k'_{12} = 2.72 \times 10^{-6}$

$$1\text{-}C\ell B_5H_8 + Et_2O \underset{k'_{21}}{\overset{k'_{12}}{\rightleftharpoons}} 2\text{-}C\ell B_5H_8 + Et_2O \tag{2}$$

$M^{-1}s^{-1}$ and $k'_{21} = 0.48 \times 10^{-6}M^{-1}s^{-1}$ (at 24.5°C, with 0.174M 1-$C\ell$-B_5H_8, 3.65M Et_2O). The activation energy for the forward reaction is 14.6 $kcal.mol^{-1}$. The isomerisation probably proceeds via a boron cage rearrangement involving an $Et_2O.C\ell B_5H_8$ complex, and not via B-$C\ell$ bond breaking.[13]

An improved route, equation (3), has been devised for the conversion of KBH_4 to $B_{10}H_{12}(SEt_2)_2$. This avoids the hazardous pyrolysis

$$\begin{tikzcd}
KBH_4 \arrow[r, "resin", "Et_4N^+"'] & Et_4NBH_4 \arrow[r, "pyrolysis"] & (Et_4N)_2B_{10}H_{10} \arrow[d, "resin"', "NH_4^+"] \\
 & B_{10}H_{12}(SEt_2)_2 & (NH_4)_2B_{10}H_{10} \arrow[l, "Et_2S"', "+HC\ell"]
\end{tikzcd} \tag{3}$$

of B_2H_6, and involves two ion-exchange stages.[14]

$B_{10}H_{14}$ can be synthesised conveniently from $NaBH_4$. The first step isthe preparation of $B_{11}H_{14}^-$ from $NaBH_4$ and $BF_3.OEt_2$ in diglyme, under N_2. Subsequent oxidation, by $Na_2Cr_2O_7$, of the resulting aqueous solution yields $B_{10}H_{14}$ as the major product.[15]

Reaction of X_2 (X = Br or I) with $Me_2SnB_{10}H_{12}$ gives Me_2SnX_2 and $B_{10}H_{12}X_2$. The crystal structure of 5,10-$B_{10}H_{12}Br_2$ was determined, showing that the B-Br distance is 1.941Å, and that the B_{10} cage is only very slightly distorted compared to that in $B_{10}H_{14}$. When $Me_2SnB_{10}H_{12}$ reacts with a deficiency of Br_2, traces of Me_2SnBrB_{10}

$H_{12}Br$ were detected. Thus Br_2 cleavage occurs via stepwise cleavage of B-Sn-B three-centre bonds in an oxidative cleavage mechanism.[16]

MNDO m.o. calculations had been reported for some boranes previously; the series has now been extended to include all boron hydrides up to $B_{10}H_{16}$ and all boron hydride dianions to $B_{12}H_{12}^{2-}$. The results confirm the tendency of MNDO calculations to underestimate the strengths of three-centre bonds, but they agree sufficiently well with experiments to suggest that the method may be useful in boron hydride chemistry.[17]

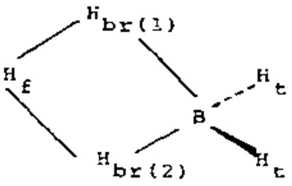
3.1.2 Borane Anions and Metallo-derivatives

Gas-phase ^{11}B and ^{1}H n.m.r. spectra of $Be(BH_4)_2$ show that only one, monomeric, species is present, with a linear B-Be-B framework. The hydrogens of each BH_4 unit undergo rapid intragroup internal exchange. $Be(B_3H_8)_2$, $cpBe(B_3H_8)$ and $(MeBeB_3H_8)_2$ were also prepared and characterised. These show a range of fluxional character, as shown by variable-temperature n.m.r. studies. The reactions of $Be(BH_4)_2$ and $Be(B_3H_8)_2$ were summarised.[18]

The i.r. and Raman spectra of $Zr(BH_4)_4$ and $Zr(BD_4)_4$ could be assigned equally well using effective T or T_d symmetry. A normal coordinate analysis was carried out; the resulting valence force field incorporated a significant Zr-B stretching force constant.[19] However, a second reported normal coordinate analysis of $Zr(BH_4)_4$ (using previously published vibrational data and assuming T_d symmetry) did not require a significant Zr-B stretching force constant. The valence force field given (including a $B-H_t$ stretch-force constant of 3.50 mdyn. $Å^{-1}$, $B-H_{br}$ of 2.74 mdyn. $Å^{-1}$ and $Zr-H_{br}$ of 0.5 mdyn. $Å^{-1}$) only gave moderate agreement with experimental wavenumbers.[20]

He(I) and He(II) photoelectron spectra were reported for $M(BH_4)_4$, where M = Zr, Hf or U, and the He(I) spectrum of $A\ell(BH_4)_3$. They could be interpreted using a simple m.o. model with a basis set of localised bond orbitals. The latter suggested that doubly- and triply-bridging $M(BH_4)$ units should give significantly different photoelectron spectra. This was borne out by comparing the spectra of $M(BH_4)_4$ with that of $A\ell(BH_4)_3$.[21]

The vibrational spectrum of $(MeC_5H_4)_2Hf(BH_4)_2$ shows that the perturbation of the BH_4^- ion is less than in most transition metal tetrahydroborate complexes. N.m.r. spectra show that the exchange of bridge and terminal H atoms of the BH_4^- groups is rapid down to $-155^{\circ}C$ on the n.m.r. time scale (thus $\Delta G^{\ddagger}$ is less than about 4.9 kcal. mol^{-1}). The crystal structure shows that the coordination of BH_4^- is unsymmetrical, (3). Thus $Hf-H_{br(1)} = 2.069Å$, $Hf-H_{br(2)} = 2.120Å$, with $H_{br(1)}-B = 1.255Å$, $H_{br(2)}-B = 1.208Å$.[22]



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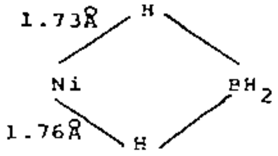


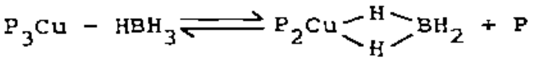
(4)

From reactions of $NaBH_4$ with Co(II) salts in the presence of PPh_3, it has been possible to isolate two Co(I) complexes, $Co(BH_4)(PPh_3)_n$ (where n = 2 or 3).[23] Similar reactions with Ni(II) salts give Ni(I) complexes; thus $NiCl_2.6H_2O$,PPh_3 and $NaBH_4$ give $[Ni(BH_4)(PPh_3)_3]_2$, while $NiX_2(PPh_3)_2$ (where X = Cl,Br or I) and $NaBH_4$ give $Ni(BH_4)(PPh_3)_{1.5}$.[24]

The crystal structure of $Ni(H)(BH_4)(PCy_3)_2$ shows that the tetrahydroborate is bonded in a bidentate fashion, (4);note that the bonding is almost symmetrical, unlike the Co analogue which is much more distorted. The difference is related to the different electron configurations, the Ni(II) (d^8) prefers trigonal bipyramidal, the Co(II) (d^7) square pyramidal, coordination.[25]

A new diamagnetic Cu(I)-BH_4 complex has been prepared: $[(MeO)_3P]_2$ $CuBH_4$. This is soluble enough to enable low-temperature n.m.r. spectra to be obtained. and these show a slowing-down of the fluxional process.[26]

The crystal structure of $Cu(PPh_2Me)_3BH_4$ has been determined, and this showed that the BH_4^- is attached to the Cu via a single hydrogen bridge, with $Cu-H_{br} = 1.47Å$, $H_{br}-B = 1.19Å$. The solid-phase i.r. data are consistent with this, but in benzene solution there was evidence for the presence of bidentate BH_4, presumably



$$P_3Cu - HBH_3 \rightleftharpoons P_2Cu\overset{H}{\underset{H}{\lessgtr}}BH_2 + P \qquad (4)$$

due to the equilibrium, equation (4), being set up ($P = PPh_2Me$).[27]

$Y(BH_4)_3(THF)_3$ contains one bidentate BH_4 and two tridentate BH_4 groups. In the $Y\overset{H}{\underset{H}{-H-}}B{-}H$ unit the ligand is tilted slightly from C_{3v} symmetry, with unequal Y-H bond lengths.[28]

$Er(BH_4)_3.2THF$ is formed from $NaBH_4$ and $ErC\ell_3$ in THF. It is not possible to remove the solvate without decomposition.[29] A preliminary report has appeared of the i.r. spectrum of $U(BH_4)_4$.[30]

The adducts $U(BH_4)_4.L$ (where $L = Me_2O$ or Et_2O) were studied by X-ray diffraction. Each complex contains infinite linear chains of alternating U and B atoms, joined by double hydrogen-bridge bonds. The remaining BH_4 units were joined to U by triple hydrogen-bridge bonds.[31]

THF forms an adduct with $U(BH_4)_4$, formulated as $U(BH_4)_4.2(OC_4H_8)$. It crystallises in the space group Pnc2 or Pncm, and the complex is monomeric, with a U-B distance (2.56(4)Å) typical of triple hydrogen-bridge bonding. It is the only known solid complex of uranium borohydrides to be monomeric.[32]

The dimeric complex $[U(BH_4)_4(O\text{-}\underline{n}\text{-}Pr_2)]_2$ contains two different U atoms - one bonded to two ether molecules and 4 BH_4 groups (via eleven H atoms). The other U atom has 14 hydrogen neighbours from 5 BH_4 groups - one of which forms a bridge to the first U atom. This structure should be compared with the linear, symmetrical polymers formed by the Me_2O and Et_2O complexes.[33]

Tris(indenyl)thorium tetrahydroborate, $(\eta^5\text{-}C_9H_7)_3ThBH_4$ has been prepared from the chloro-analogue and $NaBH_4$. Its i.r. spectrum is consistent with tridentate BH_4 coordination.[34]

The actinide borohydrides $An(BH_4)_4$, where An = Pa, Np or Pu, have been reported for the first time. They are prepared, as are the U and Th analogues, by the reaction in equation (5). X-ray powder

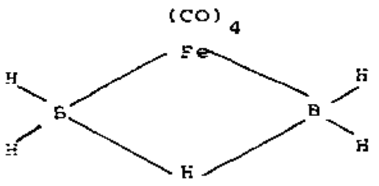
$$AnF_4 + 2A\ell(BH_4)_3 \longrightarrow An(BH_4)_4 + 2A\ell F_2(BH_4) \qquad (5)$$

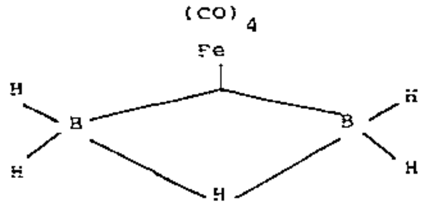
diffraction patterns show that the Pu and Np compounds are isomorphous, with a tetragonal crystal structure. I.r. spectra show that all of the BH_4 units are equivalent (in a tetrahedral array) and tridentate, thus the metals are formally 12 coordinate.[35]

The first example of a substituted diborane(6) with a transition metal at a bridge site has been reported. It is $K[\mu\text{-}Fe(CO)_4B_2H_5]$, prepared as in equation (6). There is insufficient experimental

$$K_2Fe(CO)_4 + 3THF.BH_3 \longrightarrow K[\mu\text{-}Fe(CO)_4B_2H_5] + KBH_4 + 3THF \qquad (6)$$

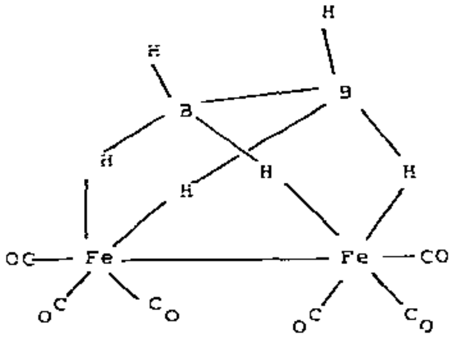
evidence to differentiate between the two possible modes of bonding, (5) and (6).[36]

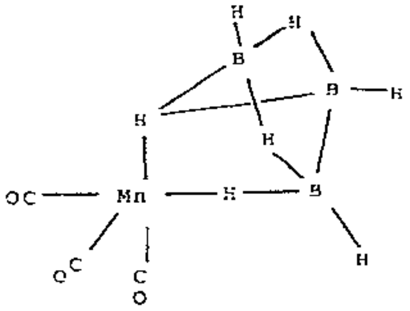




(5) (6)

The reaction of $Fe(CO)_5$ and B_5H_9 gives as one product $B_2H_6Fe_2(CO)_6$ (yield 1–10%). I.r., n.m.r. and mass spectra are consistent with the formulation (7). This framework is *nido*- according to electron-counting rules – a derivative of the unstable B_4H_8. It could alternatively be viewed as $B_2H_6^{2-}$ acting as an eight-electron donor to $Fe_2(CO)_6^{2+}$, in agreement with the eighteen-electron rule.[37]





(7) (8)

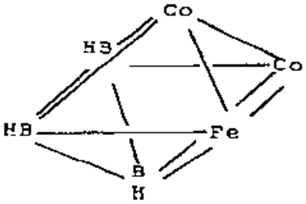
$B_3H_8^-$ and B_5H_{11} were studied by m.o. methods to see whether they are likely to show fluxional behaviour. Methods used were PRDDO (for both) and *ab initio*, extended basis 4-31G, (for $B_3H_8^-$ only). Results for $B_3H_8^-$ suggest that the barrier to hydrogen exchange is *ca.* 1 kcal. mol^{-1}, consistent with fluxional behaviour. For B_5H_{11} the preferred geometry appears to be of C_s symmetry, with no fluxionality. Nevertheless, a low-lying vibration of the unique H atom on the apex was indicated.[38]

$(OC)_3Mn(B_3H_8)$ contains a tridentate $B_3H_8^-$ ligand attached to Mn via three Mn-H-B bridges, one bridge to each B atom, (8). The molecule has approximately C_s symmetry, and each B atom has a single terminal H atom. This is the first reported example of a tridentate $B_3H_8^-$ ligand.[39]

Preparative and spectroscopic results for a number of other $B_3H_8^-$ complexes have also been reported. The ligand is generally bidentate, as in $(OC)_4MnB_3H_8$, $(OC)_4ReB_3H_8$, $cpFe(CO)B_3H_8$, $cpMo(CO)_2B_3H_8$, $(OC)_3Fe(H)B_3H_8$ etc. Only in $(OC)_3MnB_3H_8$ is the ligand tridentate. Detailed ^{11}B and ^1H n.m.r. results were analysed, revealing the existence of interesting selective hydrogen-exchange processes.[40]

He(I) and Ne(I) photoelectron spectra for B_4H_8–, B_5H_9–, $B_5H_3(CO)_2^-$, $C_2B_3H_5$– and $C_2B_3H_7$–$Fe(CO)_3$ were assigned by analogy with the parent boranes and carbaboranes. Comparison of $(B_4H_8)Fe(CO)_3$, B_5H_9, and $(C_4H_4)Fe(CO)_3$ reveals that the electronic structure of the borane is largely retained in the ferra-derivative.[41]

Reactions of 2-$(\eta^5$-$C_5H_5)CoB_4H_8$, which is a formal analogue of B_5H_9, have been described and discussed. Most of the reactions of the complex are closely related to those of B_5H_9, but with $Fe(CO)_5$ it gives a low yield of a new compound, $1,2,3$-$(\eta^5$-$C_5H_5)Co_2(CO)_4Fe$–B_3H_3. The structure of this is thought to contain an octahedral Co_2FeB_3 cage, with all of the B atoms on the same triangular face, (9).[42]

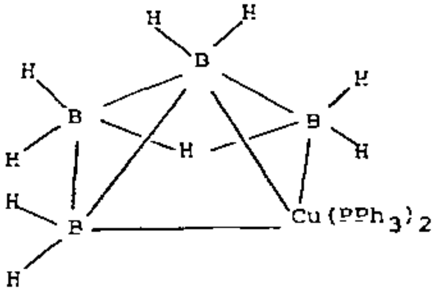


(9)

Tetrametallic Ni-B clusters have been reported: $(\eta^5$-$C_5H_5)_4Ni_4B_4H_4$ and $(\eta^5$-$C_5H_5)_4Ni_4B_5H_5$. Structures were proposed on the basis of spectroscopic evidence. The compounds are new representatives of "hybrid" cages linking the borane and metal-cluster families.[43]

M.o. calculations on $(B_4H_8)Fe(CO)_3$, using S.C.F.-Xα-S.W. methods, gave good agreement with experimental u.v. photoelectron spectra. A first-principle, one-electron treatment is therefore able to provide accurate results for this type of compound. Previous work, using a Hartree-Fock model, had suggested that this was not so.[44]

$(Ph_3P)_2CuB_4H_9$ is the first metallo-derivative containing the B_4H_9 unit to be reported. It has a unique structure in that the copper atom is at the vertex of a cluster skeleton, and there is no evidence for Cu-H-B bridge bonding, (10).[45]



(10)

New tetra-organophosphonium and tetraphenylarsonium salts of $B_5H_8^-$ and $B_6H_9^-$ show that increasing the cation size does stabilise the system significantly.[46]

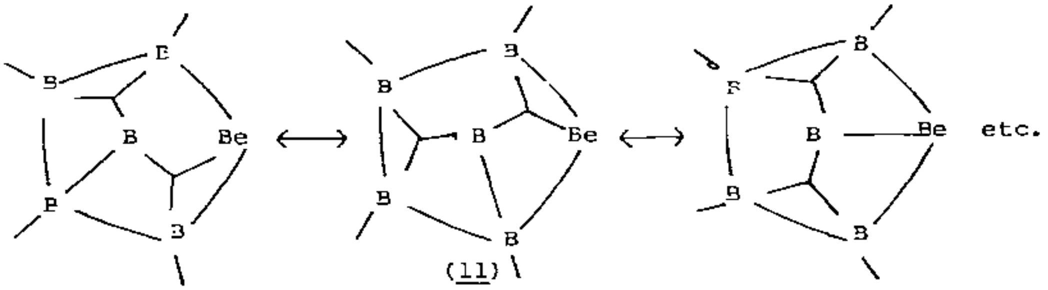
$B_5H_8^-$ reacts with $[Fe(CO)_2(\eta-C_5H_5)I]$ to form $[Fe(2-B_5H_8)(\eta-C_5H_5)-(CO)_2I]$. KH deprotonates this to give the anionic complex $[Fe(2-B_5H_7)(\eta-C_5H_5)(CO)_2]^-$. The latter can react with a further 1 mole of $[Fe(CO)_2(\eta-C_5H_5)I]$, forming $[\{Fe(\eta-C_5H_5)(CO)_2\}_2(2,4-B_5H_7)]$ The structures of the complexes are consistent with the idea that the *nido*-pentaborane anions act as 2-3-η ligands in the 16-electron compounds, and as 2-σ ligands in the 18-electron compounds.[47]

Potassium *nido*-octahydropentaborate, KB_5H_8, reacts with *cis*-bis (phosphine) complexes of Pd(II) or Pt(II) to give *cis*-$[M(B_5H_8)-(PR_3)_2X]$, where M = Pd or Pt; X = Cℓ, Br, I or Me; $PR_3 = PPh_3$, PMe_2Ph, PMe_3 or ½$(Ph_2PCH_2CH_2PPh_2)$. The Pt complexes are more stable than those of Pd. Analogous reactions produce $AsPh_3$ derivatives, *cis*-$[\{Pt(B_5H_8)X(PMe_2Ph)(\mu-SMe)\}_2]$ and the less stable *trans*-$[Pt(B_5H_8)X(PMe_2Ph)_2]$, where X = I or Me. The B_5H_8 is always η^2-bonded.[48]

16-electron Cu(I) complexes, $[Cu(\mu-1-BrB_5H_7)(PPh_3)_2]$ and $[Cu(\mu-B_5H_8)dppe]$, where dppe = $Ph_2PCH_2CH_2PPh_2$, have been prepared. They are very similar to $[Cu(\mu-B_5H_8)(PPh_3)_2]$. The silver analogue, $[Ag(\mu-B_5H_8)(PPh_3)_2]$, decomposes in solution even in the absence of light, although ^{11}B n.m.r. spectra show that it is not fluxional. The species "$Au(B_5H_8)(PPh_3)$" is possibly formed at −78°C, but it could not be isolated.[49]

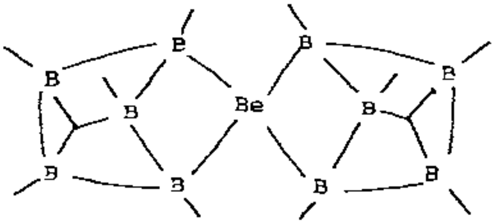
Trans-IrCℓ(CO)(PMe$_3$)$_2$ reacts with 1- or 2-halopentaboranes with insertion into a basal B-H bond at the site predicted to be the most susceptible to nucleophilic substitution by S.C.F. calculations. The relative order of reactivity is: $2\text{-BrB}_5\text{H}_8 \sim 2\text{-C}\ell\text{B}_5\text{H}_8 > 1\text{-BrB}_5\text{H}_8 > 1\text{-C}\ell\text{B}_5\text{H}_8 \sim \text{B}_5\text{H}_9 \gg 1\text{-MeB}_5\text{H}_8$.[50]

Several beryllaboranes have been prepared in which the Be atom occupies a basal position in a pentagonal-pyramidal borane cage, $\text{B}_5\text{H}_{10}\text{BeX}$ (where X = BH_4, B_5H_{10}, Cℓ, Br, Me or C_5H_5). The beryllium atom has unusual flexibility in coordination, and the bonding in several compounds cannot be interpreted using conventional bond concepts. The styx bonding description classifies these $\text{B}_5\text{H}_{10}\text{BeX}$ species as 5210 forms, with several resonance forms, probably not all of equal weight, (11).[51]



(11)

The crystal structure of $\text{B}_5\text{H}_{10}\text{BeBH}_4$ has been elucidated. The molecule consists of a pentagonal-pyramidal cage with Be in a basal position. The BH_4 is attached to the beryllium by two bridging hydrogens. For 2,2'-commo-bis[2-berylla-nido-hexaborane-(11)], $\text{B}_5\text{H}_{10}\text{BeB}_5\text{H}_{10}$, there are two pentagonal-pyramidal cages linked by a common Be atom. The topological structure is shown in (12).[52]



(12)

Various 10- or 12-vertex, *closo*- or *nido*-metalloboranes are formed by *nido*-cage closure or polyhedral expansion of *closo*-borane anions, with metallocenes being used as sources of the metal vertex. Thus $(\eta^5\text{-}C_5H_5)_2Ni$ reacts with *nido*-$B_{11}H_{13}^{2-}$, $B_{10}H_{13}^-$ or $B_9H_{12}^-$ in the presence of a catalytic amount of Na/Hg to produce, respectively, *closo*-$[(\eta^5\text{-}C_5H_5Ni)B_{11}H_{11}]^-$, *nido*-$[(\eta^5\text{-}C_5H_5Ni)B_{10}H_{12}]^-$ and the isomeric *closo*-[1- and -$[2\text{-}(\eta^5\text{-}C_5H_5Ni)B_9H_9]^-$. The polyhedral expansion of borane anions involves the first recorded oxidative addition of a B-B bond unit of a borane to a metal complex.[53]

M.O. calculations have been performed on $B_{11}H_{11}^{2-}$ using the partial retention of diatomic differential overlap (PRDDO) method. C_{5v} isomers were found to be of considerably higher energy than those of C_{2v} symmetry. A mechanism of rearrangement connecting C_s and C_{2v} geometries was believed to have a very low energy barrier (1-3 kcal. mol^{-1}), estimated by the linear synchronous transit approach. There were found to be very small energy differences between C_1, C_s and C_{2v} structures, and it was not possible to choose between these geometries for the ground state.[54]

Extended Hückel m.o. calculations on $[Cu(B_{11}H_{11})_2]^{n-}$ indicate that the electronic configuration of the metal, and the nature of any substituents on the borane cage influence the extent of any "slip" distortion. These theoretical conclusions support observed X-ray structural studies.[55]

A new one-step synthesis of $B_{11}H_{14}^-$ has been proposed, see equation (7). Alternatively, the $B_3H_8^-$ may be prepared *in situ* from

$$17B_3H_8^- + 16BF_3.OEt_2 \longrightarrow 5B_{11}H_{14}^- + 33H_2 + 16OEt_2 \qquad (7)$$

$BF_3.OEt_2$ and $NaBH_4$, giving the overall stoichiometry shown in (8).[56]

$$17BH_4^- + 20BF_3.OEt_2 \longrightarrow 2B_{11}H_{14}^- + 15BF_4^- + 20OEt_2 + 20H_2 \qquad (8)$$

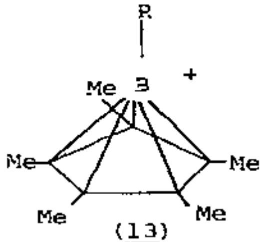
Synthetic routes to $B_{12}H_{11}SH^{2-}$ have been investigated. The most favourable route involves nucleophilic attack of N-methylbenzothiazole-2-thione on $B_{12}H_{12}^{2-}$, followed by base hydrolysis. Other methods give a variety of by-products. Several new compounds could be obtained from oxidative reactions of $B_{12}H_{11}SH^{2-}$, *viz* $B_{12}H_{11}SSR^{2-}$ and $B_{12}H_{11}SOSB_{12}H_{11}^{4-}$.[57]

Theoretical calculations have been carried out on hypothetical large *closo*-borane anions, using the PRDDO technique. They suggested that (a) some structures can have full polyhedral symmetry only if they are neutral, that is 2n framework electrons for n vertices; (b) there is no difference, on average, in the stabilities of even and odd numbered polyhedra; and (c)22 vertices probably represents the upper limit for truly stable structures.[58]

Further details of these calculations show that $B_{17}H_{17}^{2-}$ (D_{5h}) and $B_{14}H_{14}^{2-}$ (D_{6d}) are surpassed in stability only by $B_{12}H_{12}^{2-}$ (I_h). There is therefore a good chance that they may be synthesised. Each structure could also have *nido*- and *arachno*-analogues, so that there is an immense number of structural possibilities.[59]

3.1.3 Carba- and other Non-metal Heteroboranes

$(Me_5C_5)BC\ell_2$ reacts with $(Me_5C_5)Li$ to form $(Me_5C_5)_2BC\ell$ and $LiC\ell$. The former reacts with further $BC\ell_3$ to give (13), as the $BC\ell$ salt, where $R = C_5Me_5$.[60]

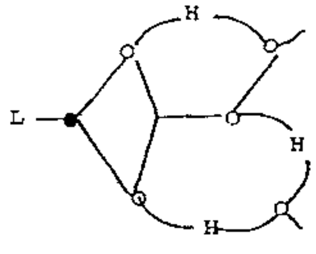


(13)

He(I) and Ne(I) photoelectron spectra have been reported for $1,6\text{-}C_2B_4H_6$, $1,5\text{-}C_2B_3H_5$, $2,4\text{-}C_2B_5H_7$, B_5H_9 and $2\text{-}CB_5H_9$, together with He(I) spectra for B_6H_{10}, $2,3\text{-}C_2B_4H_8$, B_5H_{11} and B_6H_{12}. An empirical model was devised to rationalise the observed spectra, in which the cage orbitals are separated into σ- and π-symmetry classes with respect to cage substituent bonds. The model suggests a method of analysing data on more complex cage structures.[61]

Microwave studies on CB_5H_7 suggest that the structure is distorted octahedral, with C_s symmetry. N.m.r. data suggest that a solitary bridge hydrogen is present, which tautomerises rapidly, equating boronatoms 2 to 5 on the n.m.r. time scale. PRDDO m.o. calculations suggest that this hydrogen is best described as participating in a slightly delocalised equatorial-equatorial bridge bond, interacting only weakly with B(6). It will undergo tautomerism at room temperature by passing through an equatorial-apical B-H-B bridge.[62]

Alkaline methanolysis of $6\text{-}NMe_2\text{-}6\text{-}CB_9H_{11}$ produces a 75% yield of hypho-3,4-μ-(trimethylaminecarba)hexaborane(11), $Me_3N.CB_5H_{11}$ (14) where ● is CH, o is BH, σ is BH_2 and L = NMe_3. Thus the 3,4-H-bridge of B_5H_{11} has been replaced by a $CHNMe_3$ bridge.[63]



(14)

A discussion has been given of the appropriate descriptions for a number of heteroboranes containing hetero-atoms which could contribute different numbers of electrons to the cage structure, e.g. S in $6,8\text{-}S_2B_7H_9$ etc. It appears that the majority of nine-atom arachno- and nido-frameworks differ only in electron count, and not in both electron count and framework structure.[64]

Aqueous $K[B_9C_2^{7,8}H_{12}]$ reacts with aqueous $FeC\ell_3$ to produce 33% of $B_8C_2^{5,6}H_{12}$, with small amounts of $B_8C_2^{5,6}H_{11}(OH)$, 1.6%, $B_8C_2^{5,6}C\ell H_{11}$, 0.9%, and $B_7C_2^{4,5}H_{11}$, 4.2%. Decreasing the reactant concentrations leads to an increase in the percentage yield of the last, giving a simple route to an otherwise inaccessible carbaborane.[65]

$B_{10}H_{12}CNMe_3$ reacts successively with trimethylamine and then $RPC\ell_2$, R = Me, Et or Ph, to form nido-$Me_3NCB_{10}H_{10}PR$. When R = Ph, an X-ray structure determination showed that the PPh group bridges two boron atoms at the open face of the $B_{10}H_{10}CNMe_3$ icosahedral fragment, i.e. B(9) and B(10).[66]

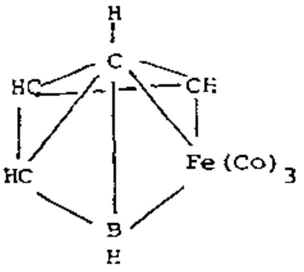
Dicarbadodecarborate(14) dianions react with ArMgX or ArLi to form B-aryldianions. Oxidation of these by $CuC\ell_2$ produces 3-, 4-, 8- and 9-aryl-o-carbaboranes. The 4-o- and 9-o-carbaboranyl groups were established as electron-releasing substituents.[67]

A report has been given of the formation of 1,2-dicarbadodecaborane(12) attached to polystyrene, and its conversion to a polymer-bound Rh complex, written as $P\text{-}CH_2C_2B_9H_{10}Rh(H)(PPh_3)_2$, where P represents the rigid polystyrene framework, which is a potentially useful hydrogenation catalyst.[68]

3.1.4 Metallo-heteroboranes

Closo-metalloheteroboranes apparently having fewer than (n+1) skeletal electron pairs to hold together n skeletal atoms may contain incompletely-filled metal d-orbitals or hyperpolyhedral M-M bonding.[69]

The reaction of $(C_4H_4)Fe(CO)_3$ with pentaborane(9) yields a new ferra carbababorane, $(BC_4H_5)Fe(CO)_3$, in small quantities. The possible structure, based on n.m.r. results, is (15).[70]



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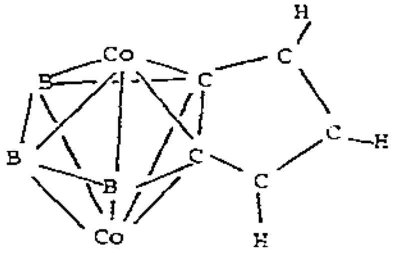


(16)

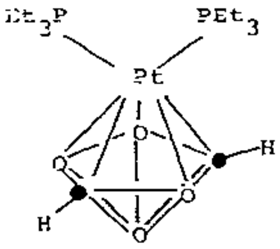
The crystal structure of $\mu(2,3)$-1,3-C_3H_4-1,7,2,3-$(\eta^5-C_5H_5)_2Co_2C_2B_3H_3$ shows that it is a new type of "triple-decker" sandwich complex. The central unit is a seven-vertex $Co_2C_2B_3$ pentagonal bipyramid, (16). The central ligand is formally $C_5B_3H_7^{4-}$, isoelectronic with the pentalene mono-anion, $C_8H_7^-$. It can be regarded as a metalloborane skeleton into which a cyclopentadienyl group has been inserted.[71]

The complexes 5-$[(\eta^5-C_5H_5)Co(\eta^5-C_5H_4)]$-$[2,3-Me_2C_2B_4H_3]$Co-$[2,3-Me_2C_2B_3H_5]$ and σ-$(CH_2)_4O$-$[2,3-Me_2C_2B_4H_3]Co[2,3-Me_2C_2B_3H_5]$ have been prepared by the action of $(\eta^5-C_5H_5)Co(CO)_2$ in THF on $[2,3-Me_2C_2B_3H_5]CoH[2,3-Me_2C_2B_4H_4]$ under u.v. irradiation. A single crystal X-ray diffraction study of the former shows that it is a zwitterion comprising an $[Me_2C_2B_4H_3]Co^{III}[Me_2C_2B_3H_3]^-$ unit with a $cpCo^{III}(C_5H_4)^+$ group, with the latter attached to the *closo*-portion of the metallocarbaborane at B(5). The metallocarbaborane fragment consists of a Co^{3+} ion face-bonded to a pyramidal C_2B_4 and a cyclic C_2B_3 ligand.[72]

Treatment of dicarbon cobaltaboranes *closo*-1,2,3-$(\eta^5-C_5H_5)$-$CoC_2B_4H_6$, *nido*-1,2,3-$(\eta^5-C_5H_5)CoC_2B_3H_7$ and their C,C'-dimethyl derivatives with a 10% solution of KOH in ethanol, open to the atmosphere, led to oxidative fusion of the dicarbon species. This gave tetracarbon 12-vertex cage systems with $Co_2C_4B_6$ and CoC_4B_7 frameworks respectively e.g. $(\eta^5-C_5H_5)CoC_4B_7H_{11}$ and three isomers of $(\eta^5-C_5H_5)_2Co_2C_4B_6H_{10}$, the first parent tetracarbon metallocarbaboranes. The crystal structure of one of the latter showed the presence of an open 12-vertex cage system, with cobalt atoms at five- and six-coordinate vertices, and all four carbon atoms at the open face.[73]

Metallocarbaboranes can be prepared using metal atoms or organometallic reagents without prior synthesis of the carbaborane system. Thus, cyclopentadiene, B_5H_9 and 2-butyne react with Co atoms to give $cpCo(C_2Me_2B_4H_4)$, the "triple-decker sandwich" $cpCo(C_2Me_2B_3H_3)$-Cocp, and $cpCo_2(C_2Me_2B_5H_5)$. Yields are low, but further experiments have suggested possible improvements.[74]

$Pt(PEt_3)_2$ reacts with *nido*-2,3-$C_2B_4H_8$ or *nido*-2,3-Me_2-2,3-$C_2B_4H_6$ to give [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2Pt(H)$}-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$], and its 2,3-dimethyl derivative. Pyrolysis of these gave *closo*-platinacarbaboranes with adjacent , non-adjacent carbon atoms respectively, e.g. (*17*) where O is BH, ● C.[75]



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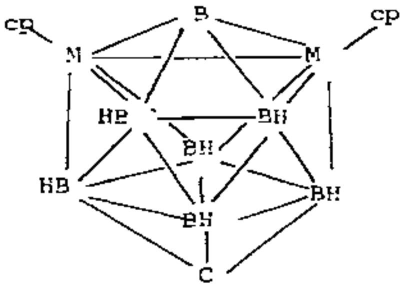


(*18*)

The crystal and molecular structures of 2,3-$(\eta-C_5H_5)_2$-(2,3)-NiCo-10-CB_7H_8 have been determined. The structure has the bicapped square antiprismatic geometry expected for a *closo* ten-vertex polyhedron. The two metal atoms are indistinguishable, and occupy adjacent sites in the same equatorial belt; the carbon atom is not adjacent to the two metal atoms, (*18*).[76]

The molecular structure of 1,8-$(\eta-C_5H_5)_2$-1-Fe-8-Co-2,3-$C_2B_7H_9$, shows that although the complex is one electron short of the 2n+2 electrons required for *closo*-polyhedral bonding, the molecule has the *closo*-11-vertex, octadecahedral geometry. The iron atom is at a six coordinate vertex, the two carbon atoms at four-coordinate vertices, and the Co atom at a five-coordinate position, adjacent to carbon, not iron.[77]

Transition metal complexes of arsaboranes have been reported. Thus, $CoC\ell_2$ or $NiC\ell_2$ react with $B_{10}H_{12}As^-$ to form $M(B_{10}H_{10}As)_2^{n-}$ (where M = Co, n = 3; M = Ni, n = 2). Related complexes are also formed which contain $B_9H_9As_2^-$ as ligand. It is found that the number of transition metal complexes formed by arsaboranes is very much less than for other heteroborane systems.[78]

Polyhedral expansion of $3,1,2\text{-}C_5H_5FeC_2B_9H_{11}$ leads to the formation of three new electron-deficient biferracarbaboranes: $(cpFe)_2\text{-}C_2B_9H_{11}$, $(cpFe)_2C_2B_8H_9(OH)$ and $(cpFeC_2B_9H_{11}FeC_2B_9H_{11})^-$. All contained formally Fe(III) atoms, and were diamagnetic. They are the first recorded complexes in which there is long-range electron-spin coupling through a carbaborane polyhedron.[79]

SCCC m.o. calculations on cp_2Fe and $cpFe(C_2B_9H_{11})^-$ show that in the former the cyclopentadienyl π-orbitals are mainly involved in bonding, whereas the dicarbollide ligand bonding gives the σ-orbitals an important role. Thus the view that the frontier orbitals of the dicarbollide ligand are directly comparable to the cyclopentadienyl π-orbitals is in need of qualification. In $cpFe(C_2B_9H_{11})^-$ the cyclopentadienyl ligand donates 0.164 of an electronic charge to Fe(II), the dicarbollide ligand 1.037 of an electronic charge.[80]

Oxidative addition of 7,9- or $7,8\text{-}C_2B_9H_{12}^-$ to $(PPh_3)_2Ru(H)C\ell$ gives respectively $2,2\text{-}(PPh_3)_2\text{-}2,2\text{-}H_2\text{-}2,1,7\text{-}RuC_2B_9H_{11}$ and $3,3\text{-}(PPh_3)_2\text{-}3,3\text{-}H_2\text{-}3,1,2\text{-}RuC_2B_9H_{11}$. Heating the 2,1,7-isomer _in vacuo_ led to reversible elimination of one molecule of H_2, giving a five-coordinate, d^6, formal Ru(II) complex.[81]

The crystal structure of $[(PPh_3)_2RhC_2B_9H_{11}]_2$ shows that each Rh atom is symmetrically bound to the pentagonal face of a $C_2B_9H_{11}$ ligand, and that it interacts with the other ligand by a Rh-H-B bridge.[82]

The crystal structures of $3\text{-}[C_2H_4(NMe_2)_2]\text{-}3,1,2\text{-}PdC_2B_9H_{11}$ and of $3,3\text{-}(PMe_3)_2\text{-}3,1,2\text{-}PdC_2B_9H_{11}$ show a considerable structural influence of the ligands _trans_ to the $C_2B_9H_{11}$ cage. The amino-compound adopts a "slipped" configuration, while replacement by $(PMe_3)_2$ leads to more symmetrical metal-cage bonding.[83]

$AuBr_2(S_2CNEt_2)$ reacts with $T\ell(B_9C_2^{1,2}T\ell^3H_{11})$ to produce, in addition to the known ion $[3,3^1\text{-}Au(B_9C_2^{1,2}H_{11})_2]^-$, the novel carba-auraborane $B_9C_2^{1,2}[Au(S_2CNEt_2)]^3H_{11}$. Single-crystal X-ray diffraction shows that the molecular structure is definitely distorted.

The gold atom is chiefly bonded to the three boron atoms of the C_2B_3 open face ($Au-B_{ave} = 2.22Å$; $Au-C_{ave} = 2.78Å$). This face is distinctly non-planar, illustrating the severe distortion within the B_9C_2 framework.[84]

The crystal structure of $12-(EtO)-1,2,3,7,8-(\eta^5-C_5H_5)Co(CH_3)_4-C_4B_7H_6$ shows that the molecule has a novel structure - a severely distorted icosahedron whose two halves have been partially separated. This leads to a very large opening on one side. Replacement of an apex BH of $Me_4C_4B_8H_8$ by $(\eta^5-C_5H_5)Co$, and severing the central cage C-C bond, would generate this structure. This compound is the fifth example of a twelve-vertex, 28-electron cage system, and these five give four different cage geometries. This fact is related to the limitations of the skeletal electron-counting theory for cluster compounds.[85]

The crystal structure of $1,14,2,5,9,12-(\eta^5-C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$ shows that the $Fe_2C_4B_8$ unit forms a <u>closo</u>-cage (fourteen-vertex) with idealised D_{2d} symmetry (a bicapped hexagonal antiprism). The iron atoms are at high-coordinate vertices, at opposite ends of the molecule. The four cage carbon atoms are arranged in staggered fashion in the 2 equatorial rings so as to maximise C-C separations.[86]

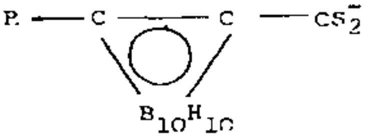
Carbaboranes with B-Tℓ bonds are prepared by the reaction of $T\ell(O_2CCF_3)_3$ with carbaboranyl derivatives mercurated at B(9), equation (9). The mercury compound is therefore a possible convenient starting material for the formation of other B-M bonded species.[87]

$$(C_2H_2B_{10}H_9)_2Hg + (CF_3CO_2)_3T\ell \longrightarrow 9-(CF_3CO_2)_2T\ell-B_{10}H_9C_2H_2 + Hg(O_2CCF_3) \quad (9)$$

This was borne out by further reactions with $SnC\ell_2$, $MC\ell_3$ (M = As or Sb) and S, giving B-Sn, B-M or B-S carbaboranes.[88]

Raman spectra of bis(dicarba-<u>closo</u>-dodecarboran(12)yl)mercury and its TℓCℓ analogue show νHg-C or νTℓ-C bands in the region 130-180 cm^{-1}. The low values suggest that the vibrations involve motion of the whole carbaborane fragements.[89]

Ni, Pd and Pt complexes of 1,2-carbaboranyldithiocarboxylates, (19) i.e. S_2C-carb-R, have been reported: $LM(S_2C\text{-carb-}R)_2$ and $L_2M(S_2S\text{-carb-}R)_2$, where L = tertiary phosphine; M = Ni,Pd or Pt. The bisphosphine adducts were preferred by platinum. The nickel compounds were all five-coordinate - so that the monophosphine



(19)

compounds all contain two bidentate ligands, while in the bisphosphines there is one uni- and one bidentate ligand. The Pd and Pt bisphosphine complexes are all four-coordinate - so both the ligands are unidentate.[90]

The five-coordinate nickel complexes of 1,2-bis(diphenylphosphino)-o-carbaborane, (dpc), Ni(dpc)X_3^-, where X = Cℓ,Br or I, have been prepared. Their electronic spectra are consistent with their having square pyramidal geometry.[91]

3.1.5 Compounds containing B-C Bonds

Ammonia-cyanoborane, $NH_3.BH_2(CN)$, has been prepared by the amine displacement reaction (10). This is the first definite report of

$$PhNH_2.BH_2(CN) + NH_3 \longrightarrow NH_3.BH_2(CN) + PhNH_2 \qquad (10)$$

this species. A crystal structure determination confirms this formulation, with a B-N bond distance of 1.58Å.[92]

A general synthesis of amine-cyanoboranes has also been proposed, (11), where the amine is Me_3N, Me_2NH, $MeNH_2$, py, $PhNH_2$ or pMeC_6H_4

$$NaBH_3CN + amine.HC\ell \xrightarrow[65^\circ C]{THF} (amine)BH_2CN + H_2 + NaC\ell \qquad (11)$$

NH_2. νCN values were as expected for B-CN, not B-NC bonding.[93]

Addition of an equivalent of X_2 (X = Cℓ, Br or I) to Na[H_3BCN] in 1,2-dimethoxyethane leads to formation of cyclic cyanoborane oligomers. In the presence of excess Lewis base, the oligomer forms cyanoborane adducts $L.BH_2CN$. If L = py, chlorination of $L.BH_2CN$ in moist C_6H_6 produces $L.BC\ell_2CN$.[94]

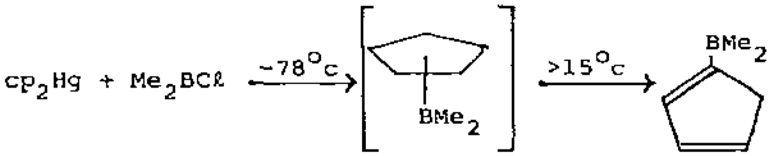
A complete assignment of all vibrational fundamentals of CH_3BF_2 has been proposed, using i.r. and Raman spectra of the normal compound, together with ^{11}B- and ^{10}B-enriched CH_3BF_2 and CD_3BF_2.[95]

$SiMe_4$ and BY_3 (Y = Br or I) react in 1:1 molar ratio at 120-150°C

(Br), 80-90°c (I), to give Me_3SiY and $MeBY_2$. In a 2:1 ratio, the products are Me_3SiY (2 moles) and Me_2BY. Except for $MeBI_2$ these are convenient routes for the preparation of these compounds.[96]

A microwave examination of the $Me_3N.BMe_3$ structure led to the following bond lengths being obtained: d(BN) 1.698Å; d(NC) 1.470Å; d(BC) 1.69Å. The NBC and BNC angles were 108.0°, 111.6° respectively.[97]

Cyclopentadienyldimethylborane is formed by the reaction (12). N.m.r. results reveal fluxional behaviour, described as |1,5|-sigmatropic migration of BMe_2. The pentamethyl analogue is stable as the form (20) to room temperature.



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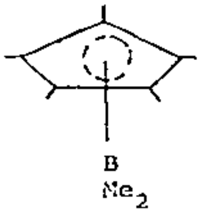

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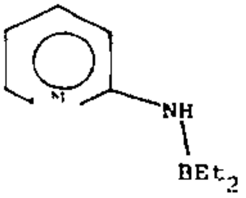

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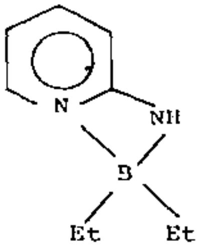

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The microwave, i.r. and Raman spectra of $Et^{10}BF_2$ and $Et^{11}BF_2$ have been reported. The BF_2 internal torsional mode is at 44cm^{-1}, corresponding to a two-fold barrier of 1.17 kcal.mol^{-1}. The B-C bond distance was calculated to be 1.572Å.[99]

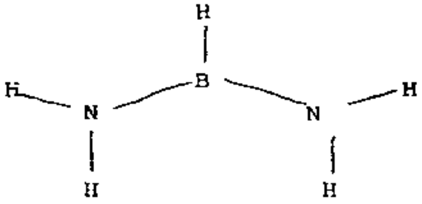
Triethylborane and 2-aminopyridine react in a molar ratio of 2:1, in the absence of a solvent to give a good yield of pure (2-pyridylamino)diethylborane. ^{13}C n.m.r. data suggest that there is an equilibrium between two different forms - one containing three-coordinate boron, (21), the other four-coordinate boron, (22).[100]

3.1.6 Aminoboranes and other Compounds containing B-N Bonds

Diaminoborane is formed by the reaction (13), where NH_3 is passed through molten borane ammine at 125°c, with the products

$$NH_3 + NH_3.BH_3 \longrightarrow BH(NH_2)_2 + 2H_2 \qquad (13)$$

being trapped out at -196°c, and $BH(NH_2)_2$ separated from NH_3 at -104°c. It is stable in the vapour-phase for several days. Four NH stretching bands and the BH stretch are seen in the infrared, with $\nu_{as}BN$ at 1605 or 1393 cm^{-1}. The ^{11}B n.m.r. spectrum was consistent with the structure (23). Structural parameters were obtained by analysing the rotational spectra.[101]



(23)

Methyllithium reacts with Me_2B-NH-X, where X = NMe_2 or $SiMe_3$, to form $[Me_3BNHX]^-Li^+$. These lose CH_4 to give the N-lithio derivatives, Me_2B-NLi-X. The B-N bond order in the latter is greater than one (from n.m.r. data), and it seems from mass spectrometry that when X = $SiMe_3$ the compound is hexameric, but when X = NMe_2 it is polymeric.[102]

The mean amplitudes of vibration were calculated for $Me_3N.BX_3$, where X = Cℓ or F, from force field calculations.[103]

Microwave spectra have been obtained for several isotopic variants of $Me_3N.BFH_2$, ($^{11}B/^{14}N$; $^{11}B/^{15}N$; $^{10}B/^{14}N$; $^{10}B/^{15}N$). Assuming the geometry of the Me_3N fragment, a value of 1.63 ± 0.01Å was obtained for the B-N distance, which is close to the values for the BH_3 and BF_3 analogues.[104]

Reaction of dimethylamine-N-d-borane with $Cℓ_2$ is accompanied by H/D exchange at the nitrogen. It is probable that the exchange process occurred via the loss of DCℓ from a molecule activated as a result of halogenation.[105]

1:1 Adduct formation was established in the following systems: L/BBr_nMe_{3-n}, where L = py, 4-Mepy, Me_3N or Me_3P, n = 1 or 2, except for py and 4-Mepy, which only form 2:1 adducts with $BBrMe_2$.[106]

The reactions of trimethylamine-fluoroboranes with phosphine or amine bases have been studied. It was found that for PMe_3 reactions incorporation of fluorine in the borane group increases the hardness of the latter. A similar trend was found for PPh_3 reactions. The results suggest that $MeNH_2$ and Me_2NH are both hard bases since both give larger equilibrium constants with BF_3 than with BH_3, although the differences were small.[107]

Monoalkylboranes, BH_2R, react with N,N,N',N'-tetramethylethylenediamine (TMED), to form adducts $TMED.BH_2R$ and $TMED.(BH_2R)_2$. BF_3 reacts with these, liberating the borane - and so these adducts are very convenient for the storage of BH_2R.[108]

Spectroscopic data, especially the observation of only one resonance in the ^{19}F n.m.r. spectra, on $(CF_3)_2C{:}NB(NMe_2)_2$ and other $(CF_3)_2C{:}NBR_2$ systems are consistent with linearity of the C:NB unit.[109]

A new, four-coordinate pseudo-halide compound of boron has been reported, in which only B-N bonds are present, equation (14). Infrared, ^1H n.m.r. and ^{19}F n.m.r. data were compatible with the

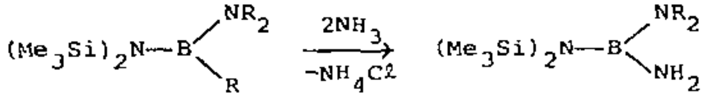
$$Ph_4P^+NSOF_2^- + B(NSOF_2)_3 \longrightarrow Ph_4P^+[B(NSOF_2)_4]^- \qquad (14)$$

formulation shown.[110]

3,3'-Diaminodipropylamine reacts with $Et_2B(NMe_2)$ to produce the new compounds $Et_2BN[(CH_2)_3NHBEt_2]_2$ and $HN[(CH_2)_3NHBEt_2]_2$.[111]

Lithiated silylamides, $\underline{t}$-$BuMe_2SiN(R)Li$, where R = H, Me or $SiMe_3$, react with chloroboranes to form t-butyldimethylsilyl-substituted aminoboranes, e.g. $[t\text{-}BuMe_2SiN(H)]_3B$. These decompose at or above room temperature to form borazines. When R is $SiMe_3$ the decomposition is most difficult, presumably because the bulk of the $SiMe_3$ group gives steric protection against nucleophilic attack.[112]

Some new amino(bis(trimethylsilyl)amino)boranes have also been prepared, equation (15), where R = Me, Et or i-Pr. The products

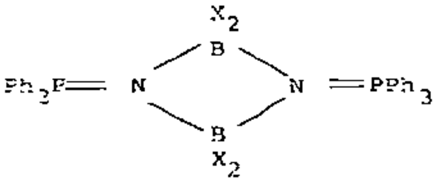


$$(Me_3Si)_2N{-}B\begin{matrix}\diagup NR_2\\ \diagdown R\end{matrix} \xrightarrow[-NH_4Cl]{2NH_3} (Me_3Si)_2N{-}B\begin{matrix}\diagup NR_2\\ \diagdown NH_2\end{matrix} \qquad (15)$$

show considerable thermal stability - which can be explained by the high barriers to rotation about the $B{-}NR_2$ bond.[113]

Bis(di-isopropylamino)alkylaminoboranes, $RR'NB[N(i\text{-}Pr)_2]_2$, possess helically chiral configurations, which are stereochemically rigid at low temperatures. Enantiomerisation occurs by correlated B-N rotations, through transition states in which substituents at two of the nitrogen atoms are in the BN_3 plane while those on the third nitrogen are perpendicular to that plane. When $R \neq R'$ there are in principle three different barriers for three possible non-degenerate routes for enantiomerisation. If R = H, R' = alkyl, $\Delta G^{\ddagger}$ for these are 13-15, 8-9 and < 5 $kcal.mol^{-1}$. The barriers were derived from a combination of steric and B-N π-bonding effects.[114]

N-Trimethylsilyl-triphenylphosphinimine reacts with R_2BX, where R = Ph, *n*-Bu, F, Cl or Br; X = F, Cl or Br, to give triphenylphosphiniminodi-halogeno- or -organylboranes: $Ph_3P = N-BR_2$. In solution the diorganyl derivatives are monomeric, while the dihalogeno species are associated, probably dimeric, (24). All are monomeric



(24)

in the gas-phase.[115]

3.1.7 Compounds containing B-P Bonds

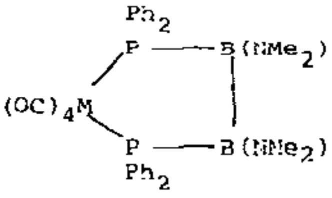
Detailed vibrational assignments and analysis have been given for silylphosphine-borane, $SiH_3PH_2BH_3$ and its BD_3 analogue. The B-P stretching force constant was calculated to the 2.10 mdyn. Å^{-1}, typical of phosphine-borane adducts.[116]

$B_2H_4.2PMe_3$ has been prepared, equation (16). This is the most

$$B_5H_9 + 3PMe_3 \xrightarrow[24h - 25^{o}C]{toluene} B_2H_4.2PMe_3 + Me_3P.BH_3 + \text{viscous oil} \qquad (16)$$

convenient synthesis yet for a $B_2H_4.2L$ compound. ^{11}B, ^{1}H, ^{31}P and ^{13}C n.m.r. data were reported.[117]

A series of borylphosphine complexes of group 6 metal carbonyls have been prepared: $(OC)_5M.PR_2B(NR'_2)_2$, *cis*-$(OC)_4M.(PR_2)_2B(NR'_2)$, and (25), where M = Cr, Mo or W; R = Ph, R = Me or Et. No evidence was found for significant M-B interaction.[118]



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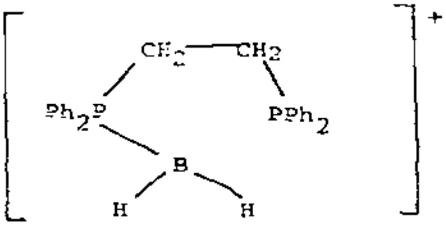


(26)

A number of new boron cations $LYBH_2^+$ and $YY'BH_2^+$ have been prepared, where L = amine; Y,Y' = phosphines, together with cyclic (26). ^1H and ^{11}B n.m.r., and i.r. data were reported.[119]

Trimeric $[(CF_3)_2PBH_2]_3$ reacts with excess NMe_3 leading to ring cleavage, and forming $Me_3N.BH_2P(CF_3)_2$ and $(Me_3N)_2BH_2^+(CF_3)_2PBH_2-P(CF_3)_2^-$. PMe_3 reacts similarly, but faster, and if it is present in smaller amounts, some $(CF_3)_2PBH_2P(CF_3)_2BH_2P(CF_3)_2^-$-containing products are formed. Also, even longer-chain compounds may be present.[120]

Comparison between the very stable cyclic phosphinoborines, $(BH_2PR_2)_n$, and an acyclic analogue is now possible with the synthesis of 1,4-dichloro-1,1,3,3-tetraphenyl-*catena*-borophosphane from $Me_4N^+B_3H_8^-$ and Ph_2PCl, equation (17). N.m.r. and X-ray data confirm the expected butane-like structure, with distorted tetra-

$$Me_4NB_3H_8 + Ph_2PCl \longrightarrow \{B_2H_4.PPh_2Cl\}^+BH_4^- \xrightarrow{Ph_2PCl} ClBH_2.PPh_2.BH_2.PPh_2Cl \qquad (17)$$

hedral angles about B and P.[121]

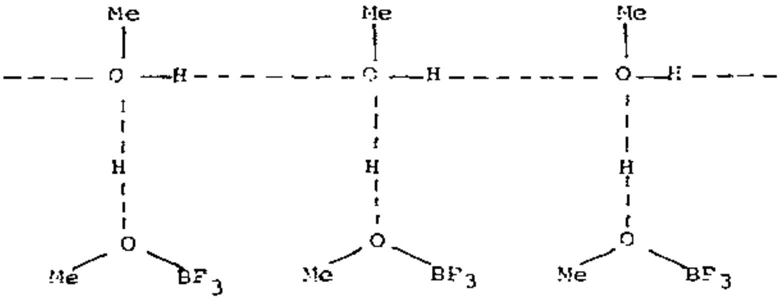
BH_3 adducts with $P(NMe_2)_{3-n}(t\text{-}BuO)_n$, n = 1-3, with 1:1 stoichiometry have been prepared and characterised by n.m.r. spectra. There was no obvious correlation between the magnitude of the $^1J_{BP}$ and complex stability.[122]

3.1.8 Compounds containing B-O Bonds

An electron-diffraction study of the gaseous MBO_2 molecules, M = Cs, Rb or Tl, has been reported. All have linear O-B-O groups but bent M-O-B units. The M-O distances were found to be 2.57Å (Rb), 2.62Å(Cs), 2.42Å(Tℓ).[123]

TℓBO_2 crystals belong to the space group $P4_1$. The structure contains a new unit: $B_2O_4^{2-}$, comprising a BO_3 triangle and a BO_4 tetrahedron. These units are linked to form an infinite chain anion, $[B_2O_4]_n^{2n-}$.[124]

I.r. and Raman studies on the 1:2 adduct $BF_3.2MeOH$ suggest that



(27)

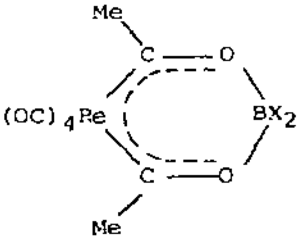
the structure can best be represented by (27).[125]

The solvent deuterium isotope effect on hydrolysis of boric acid has been studied. E.m.f. data suggest that in both H_2O and D_2O (= X_2O) the species $B(OX)_4^-$, $B_3(OX)_{10}^-$ and $B_4(OX)_{14}^{2-}$ are formed.[126]

An ^{11}B n.m.r. study of the methanolysis of sodium dimethylamide-bis(borane) reveals the sequence shown in (18). The $MeOH.BH_3$ adduct will rapidly decompose to form $HB(OMe)_2$ and $B(OMe)_3$.[127]

$$2MeOH + \mu\text{-}Me_2NB_2H_5 \longrightarrow MeOH.BH_3 + Me_2NBH_2.HOMe.$$
$$Me_2NBH_2.HOMe \longrightarrow Me_2NH.BH_2(OMe) \qquad (18)$$

Some novel metalloacetylacetone complexes of the boron trihalides, (28), where X = F, Cℓ, Br or I, have been prepared by the reaction of BX_3 with the parent metalloacetylacetone. ν(C⋯O) was found



(28)

between 1450 and 1475 cm^{-1}. The positions of the ^1H resonances suggest that there is considerable electron-withdrawal by the BX_2 group by comparison with the original ligand.[128]

The compound $K[B(SO_3Cl)_4]$ forms triclinic crystals, space group P1. The $B(SO_3Cl)_4^-$ anions are present as a racemic mixture. Crystal forces lead to positional inversion of some Cl and O atoms. The SO_3Cl^- ligands are unidentate, with an average $B-O_{br}$ distance of 1.465Å.[129]

Perhydrolysis (using an H_2O_2/H_2O mixture, 85:15 by weight) of $B(OR)_3$ in the presence of LiOR' or RbOn-Bu (where R = Me, i-Pr, t-Bu, n-C_8H_{17}; R' = Me, Et, n-Bu, t-Bu) gives a variety of peroxoborates, such as $LiBO_{3.7}.H_2O$, $RbBO_4.0.5H_2O$ etc. All contain active oxygen as B-O-O groups.[130]

Single crystals of LiB_3O_5 have been prepared for the first time. They are orthorhombic, and belong to the space group $Pna2_1$. B_3O_5 units are present, similar in geometry to those found in $CsBr_3O_5$, but the two compounds are not isotypic.[131]

$Na_2O.2B_2O_3.H_2O$ forms orthorhombic crystals, belonging to the space group Pbca. The structure contains B-O chains, with the repeating unit $[B_4O_6(OH)_2]^{2-}$. Connection between the B-O chains is provided by sodium polyhedra and by hydrogen-bonding.[132]

"Ester hydrolysis" or evaporation of solutions of base and boric acid under reduced pressure, with the very strong bases $BzN\overset{+}{R_3}OH^-$, Bz = benzoyl, R = Me or Et, give corresponding salts of $[B_5O_6(OH)_4]^-$. The more bulky, but less basic, n-Bu_3N produces [n-Bu_3NH][B_7O_6(OH)$_{10}$]. The less bulky but more basic R_3N, (R = Et or n-Pr), again give pentaborate salts. Benzylamine and tri-n-octylamine cannot form cations for polyborates.[133]

$NaB_5O_6(OH)_4$ forms monoclinic crystals, belonging to the space group $P2_1/c$. The isolated polyanion $B_5O_6(OH)_4^-$ is present, built up from a tetrahedron and three triangles, giving a double hexagonal ring.[134]

3.1.9 Boron Halides

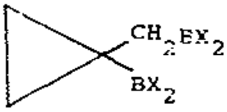
The species $ArBF_3$, N_2BF_3 and $OCBF_3$ are produced by supersonic expansion. In $ArBF_3$ the Ar-B bond length is 3.325(10)Å, and νAr-B is at 44(2)cm^{-1}. The corresponding figures for N_2BF_3 and $OCBF_3$ are 2.875(20)Å, ? ; 2.886(5)Å, 65(8)cm^{-1}. All three are weakly-bound charge-transfer complexes.[135]

BF_3 forms complexes formulated as $[BF_3(anion)]^-$ when anion =

$C\ell O_4^-$, NO_3^-, NO_2^-, CH_3OO^-, $HCOO^-$, N_3^-, CN^-, CNO^-, NCS^- or SPh^-. Anions of strong acids do not disproportionate to $[BF_2(anion)_2]^-$. Complexes of anions of weaker acids may disproportionate or complex a second molecule of BF_3.[136]

The new compound $Mg(BF_3OH)_2(THF)$ has been prepared from $BF_3.THF$ and a Grignard reagent RMgBr (where R is a very bulky group). The magnesium is octahedrally coordinated. B-F distances fall in the range 1.30 to 1.38Å, while the B-O distance is 1.42Å.[137]

B_2X_4 (where X = Cℓ or F) add to the C = C bond of methylene- or vinyl-cyclopropane to form (29), (30) respectively.[138]



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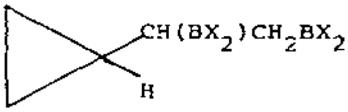


(30)

Anilinebis(difluoroborondimethylglyoximato)nickel(II) forms monoclinic crystals, space group $P2_1/c$. The nickel atom is surrounded by four nitrogen atoms of the planar macrocycle, plus a nitrogen atom of the aniline. The boron-fluorine distances are 1.364Å and 1.380Å.[139]

Passage of $S_2C\ell_2$ over crystalline boron at 800-1000°c produces the new unstable species $C\ell B{=}S$. Its identity was confirmed by photoelectron and microwave spectroscopic results. A possible

$$C\ell SSC\ell \xrightarrow{\Delta} 2C\ell S\cdot \xrightarrow{B} C\ell SB \longrightarrow C\ell B = S \qquad (19)$$

scheme for the formation of this species is given in (19).[140]

$MC\ell_3X^-$, where M = B or Aℓ, X = N_3 or NCO, are prepared from $MC\ell_3$ and X^- in liquid SO_2 as solvent. Excess halide must be avoided. Infrared spectra show that the NCO^- ligand is N-bonded.[141]

Nitrosyl chloride and $BC\ell_3$ react directly to form $NO^+BC\ell_4^-$. A Raman spectrum of the solid confirmed the ionic formulation. On melting, two layers are formed, one a mixture $NOC\ell+BC\ell_3$, the other a compound $(NO.nNOC\ell)^+BC\ell_4^-$.[142]

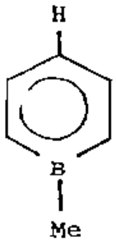
The reactions of $B_{10}C\ell_{10}/B_{11}C\ell_{11}$ mixtures with H_2, $C\ell_2$, Br_2 or I_2 have been examined. At 135°c, $C\ell_2$ reacts to produce $B_9C\ell_9$ in high yield, giving the best preparative route for this compound so far recorded.[143]

Nine equivalents of $SO_2C\ell_2$ react with a solution of $[Bu_4N]_2[B_9H_9]$ at $-78^{\circ}C$, and on warming to room temperature a good yield of $[Bu_4N]_2[B_9C\ell_9]$ is obtained. If a large excess of $SO_2C\ell_2$ (20 equivalents) is used, some $B_9C\ell_9$ is also formed, which can easily be separated from the ionic compound.[144]

The preparation of BBr_3 from KBF_4 and $A\ell Br_3$ has been improved, giving yields greater than 80%. The process is therefore now suitable forthe conversion of $K^{10}BF_4$ into $^{10}BBr_3$.[145]

3.1.10 Boron-containing Heterocycles

Ion-cyclotron resonance techniques were used to determine the gas-phase Brønsted and Lewis acidities, and the Brønsted basicity of 1-methyl-1,4-dihydroborabenzene, $MeBC_5H_6$. The ring proton is highly acidic, because of the formation of the six π-electron aromatic anion $MeBC_5H_5^-$, (31).[146]



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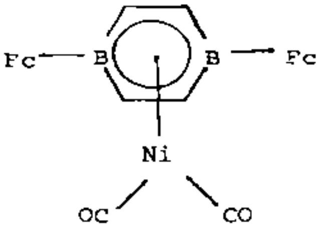
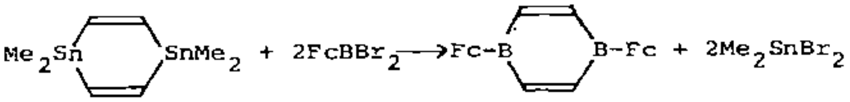


(32)

A new synthesis, equation (20) (where Fc = $cpFe(C_5H_4)$), has been

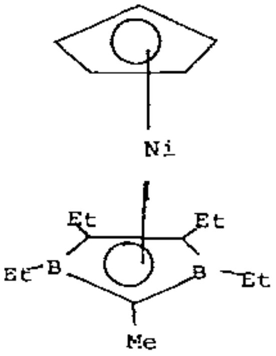


(20)

reported for 1,4-dibora-2,5-cyclohexadiene. This in turn reacts with $Ni(CO)_4$ to give the nickel complex (32).[147]

1,3,4,5-Tetraethyl-2-methyl-1,3-diborolene reacts with dicyclopentadienylnickel or $[(C_5H_5)Ni(CO)]_2$ to form (33). The sandwich formulation was confirmed by X-ray diffraction.[148]

The new, air-stable π-complexes (34), where M,M' = Co or Ni, are the first known paramagnetic triple-decker sandwich complexes. They contain 31 (M = M' = Co), 32 (m = Co, M' = Ni) or 33 (M = M' = Ni) valence electrons.[149]



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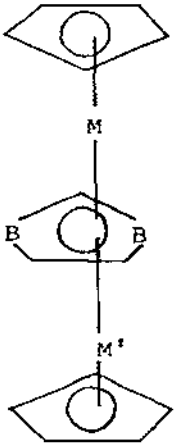
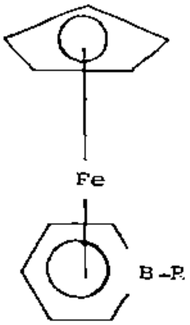


(34)

Thallium borinates, Tℓ(C_5H_5BR), where R = Me or Ph, can be made from alkali metal borinates and TℓCℓ in acetonitrile solution. Mass, ^1H, ^{11}B- and ^{13}C n.m.r. spectroscopic data were reported.[150]

Cyclic voltammetry of (borinato)cyclopentadienyl iron and of $(C_5H_5BR)_2M$, where M = Fe, Cr or V, shows that potentials of all the observed electron transitions are shifted to more positive values with respect to the isoelectronic metallocenes.[151]

The complexes (35), R = Me or Ph, can be prepared from the reaction of $[cpFe(CO)_2]_2$ with $Co(C_5H_5BR)_2$.[152]



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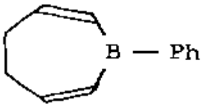

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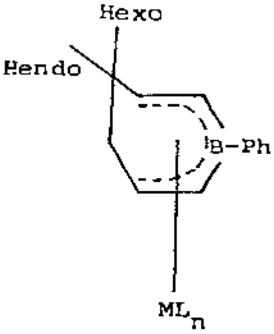
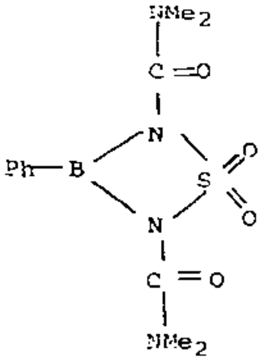


(37)

Bis(borinato)cobalt complexes, $Co(C_5H_5BR)_2$, where M = Me or Ph, are reduced by sodium amalgam to form the twenty-electron anions $Na^+[Co(C_5H_5BR)_2]^-$ in solution. They can be isolated as stable crystalline salts with the cation PPh_4^+.[153]

1-Phenyl-4,5-dihydroborepin, (36), reacts with substituted carbonyls of Cr, Mo, W or Mn to give the stable complexes (37), where ML_n = $M(CO)_4$, (M = Cr, Mo or W) or Mn(CO)Cp.[154]

A new BN_2S ring compound, (38), has been prepared by the reaction of $PhB(NiC\ell_2)_2$ with $SO_2(NCO)_2$. I.r. bonds due to ν(C=O) are seen at 1597 and 1620cm.$^{-1}$.[155]



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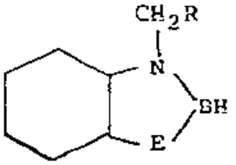

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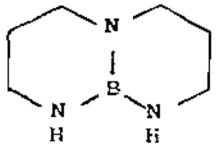


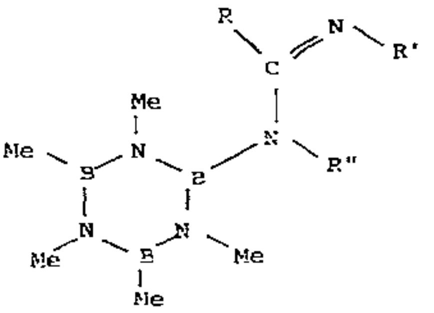
(40)

Diborane reacts with benzo-fused heteroaromatic compounds to produce (39), where R = H, E = O or S; R = Me, E = S or Se.[156]

BH_3, generated in situ from $Me_3N.BH_3$, reacts with 3,3'-diaminodipropylamine to form the BH_2B-bridge-associated |3,3'-bis(dihydroborylamino)dipropylamino|dihydroborane, 1-aminopropyl-1,3,2-diazaboracyclohexane or 1,8,10,9-triazaboradecalin, (40), depending upon the conditions.[157]

Vibrational spectroscopic assignments have been made for B-trimethylborazine, $(BMeNH)_3$. Although extensive mixing of modes occurs, it is clear that methylation of the boron or the nitrogen atoms has very little effect on the electronic nature of the ring.[158]

Trimethylsilylamidines react with 2-chloro-1,3,4,5,6-pentamethylborazine to form the amidinoborazines (41), where R = CF_3; R' = Ph or $3-CF_3-C_6H_4$; R" = $2-F-C_6H_4$ etc.[159] The same borazine will react with silyated carbonic acid amides and thioamides to give amido borazines, e.g. (42).[160]



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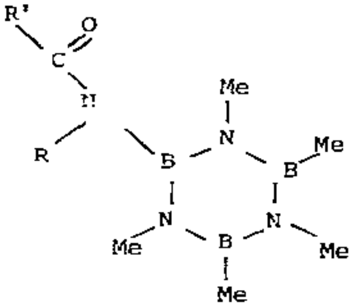
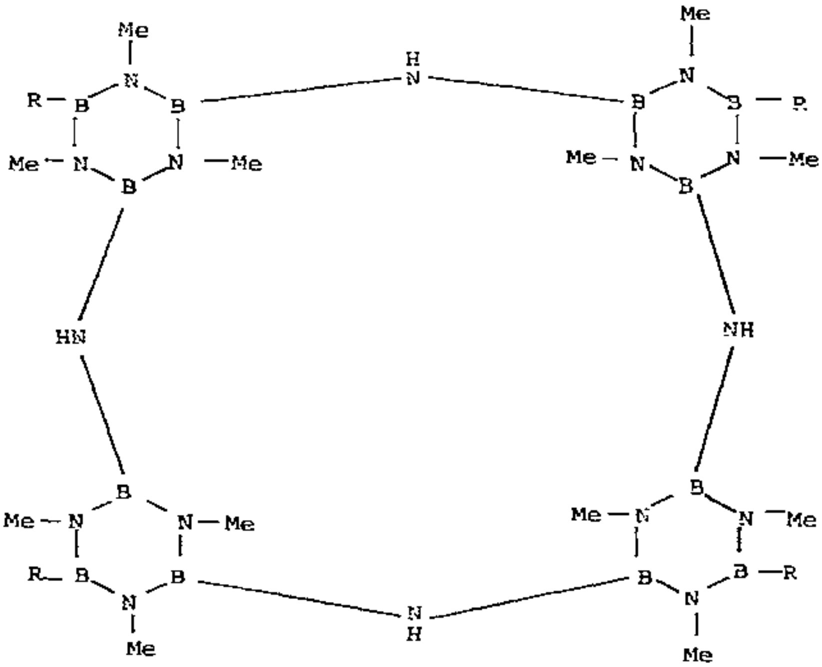


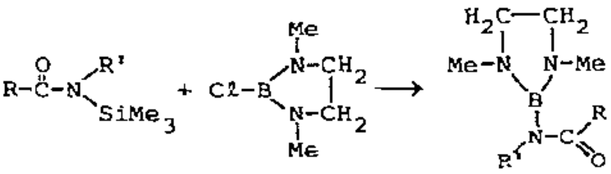
(42)

2-Alkyl-4,6-dichloro-1,3,5-trimethylborazines react with bis-(trimethylsilyl)amine to give, on pyrolysis *in vacuo*, macrocyclic polyborazines consisting of NH-bridged borazine rings e.g. (43).[161] Other such macrocycles result from the reaction of 2,4-dichloro-1,3,5,6-tetramethylborazine with N,N-dimethylformamide and dimethylamine.[162]



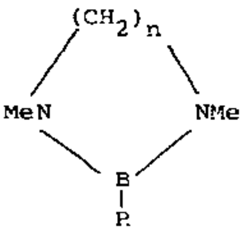
(43)

RC(=O)N(R')SiMe$_3$, where R,R' = Me or Ph, react with several boron compounds to give monomeric amido(amino)boranes, e.g. equation (21).[163]



(21)

^{1}H chemical shift differences, $\Delta\delta (= \delta(NC\underline{H}_2)-\delta(NC\underline{H}_3))$, of 1,3-dimethyl-1,3,2-diazaboracycloalkanes, (44), are dependent upon the ring size. ^{13}C n.m.r. measurements reveal the existence of conformational isomers of bis(methylamino)phenylborane and N-trimethyl-B-triphenylborazine at low temperatures, and confirm the pseudo-aromatic nature of the 1,3,2-diazaboroline ring system.[164]



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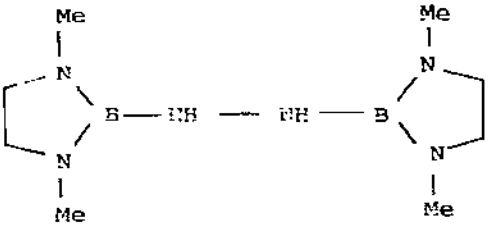
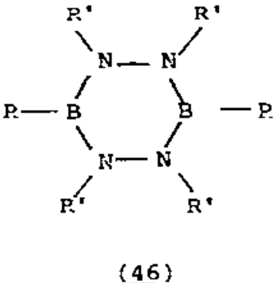


(45)

Several mixed amino-hydrazinoboranes have been prepared and characterised, from the reaction of 1,3-dimethyl-2-chloro-1,3,2-diazaboracycloalkanes with substituted hydrazines, and by condensation of the corresponding 2-methylthio-derivatives with hydrazine. A typical example is (45). N.m.r. and i.r. data were reported.[165]

There have been several reports of preparations of hexahydrotetrazadiborines, (46), where R,R' = Me, Et or Ph. For example, R'NHNHR' reacts with RB(SMe)$_2$ or certain boron-sulphur heterocyclic compounds to give these products.[166-168]

Benzo-1,2,3,6-diazadiborines react with M(CO)$_6$, (M = Cr, Mo or W), to give (47), where R = R' = H; R = H, R' = Me or R' = Me, R = H. ^{1}H, ^{11}B and ^{13}C n.m.r. results confirm the metal-ring π-bonding as shown.[169]



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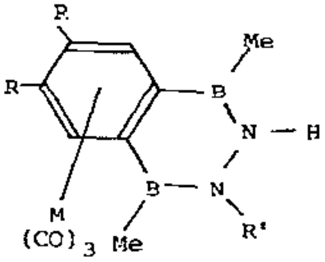
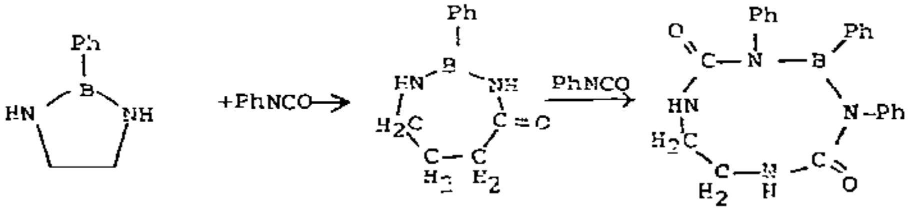


(47)

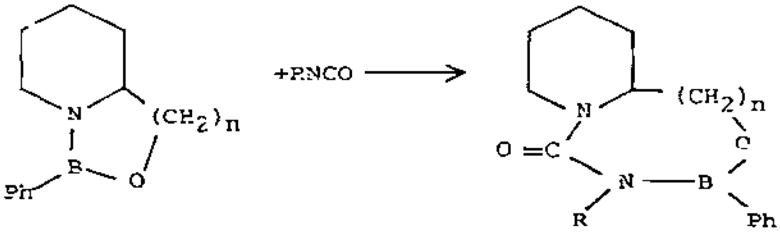
Aminoboration of double bond systems with 1,3,2-diazaboracycloalkanes leads to expansion of the heterocyclic ring system by



(22)

insertion of two atoms of the double bond system, e.g. (22).[170]

Organic isocyanates react with heterocyclic aminoboranes, giving some novel heterocyclic organoboranes. A typical example is shown

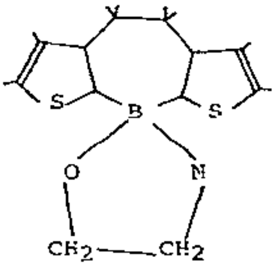


(23)

in equation (23) where n = 1 or 2, R = Ph or p-$MeC_6H_4SO_2$.[171]

$C_{12}H_{14}BNOS_2$, (48), gives monoclinic crystals, space group $P2_1/n$. The seven-membered ring is in a boat conformation, while the oxazaborolidine ring is in the "half-chair" conformation. The two rings are approximately perpendicular to one another.[172]

$K(t\text{-}Bu)P\text{-}P(t\text{-}Bu)K$ reacts with $(i\text{-}Pr)_2NBCl_2$ in n-hexane at -40°c to form the first three-membered P_2B heterocycle, (49). There was no evidence for dimerisation in the range -50°c to +140°c.[173]



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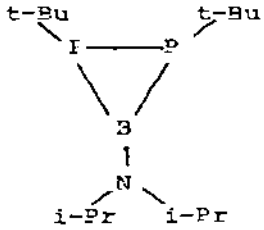
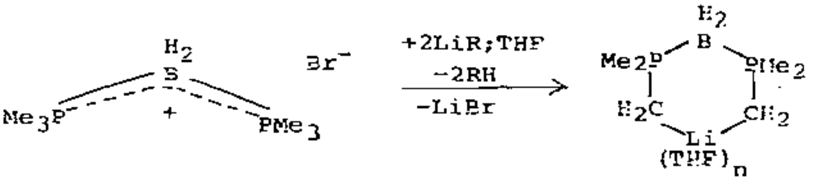


(49)

The boratobis(dimethylphosphinomethylide) anion can be prepared as in equation (24), where R = t-Bu or n-Bu. It reacts with MX_2, where M = Zn, Cd or Hg, X = halide, to form the chelate complexes (50). The aluminium compound (51) can be prepared from the original starting material by the action of $LiAlMe_4$.[174]



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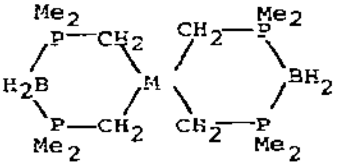

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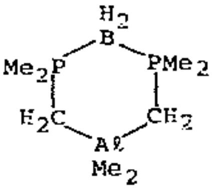
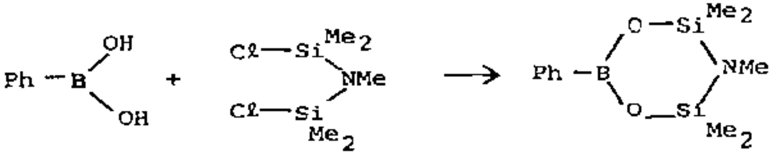


(51)

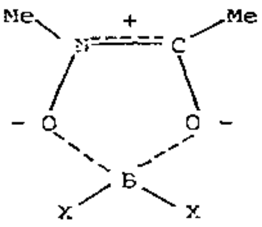
A group of new 6-membered, BNO_2Si_2, and 8-membered, BO_3Si_4, inorganic heterocycles have been reported for the first time. The



(25)

former are given by the coupling reaction (25). The latter result from the action of $PhB(OH)_2$ on $SiMe_2C\ell SiMe_2C\ell$, via an unisolable 5-membered ring intermediate, BO_2Si_2.[175]

The crystal structure of diphenylboron N-methylacethydroxamate (orthorhombic, space group Pnam) shows that a five membered BO_2CN ring is present. It can best be represented by (52).[176]



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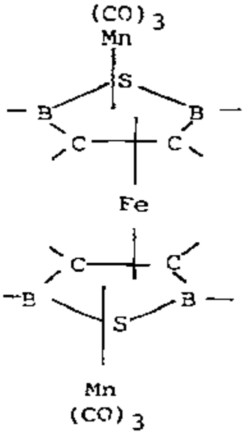
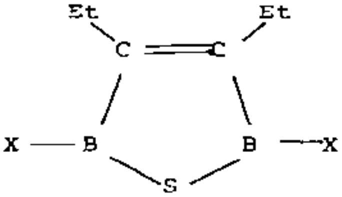


(53)

The first reported 'four-decker' sandwich complex contains two C_2B_2S rings, which act as six π-electron donors, (53).[177]

BI_3 reacts with 3-hexyne to give cis- and trans-3-diiodoboryl-4-iodo-3-hexene. This in turn reacts with $(IBS)_3$ to form (54), where X = I. Derivatives with X = Br, Cℓ, SMe, OEt or NMe_2 were also reported. ^1H, ^{11}B n.m.r. and i.r. data were given.[178]



(54)

3,4-Diethyl-2,5-dimethyl-Δ^3-1,2,5-thiadiborolene, (54, X = Me) L, reacts with $M(CO)_6$, where M = Cr or Mo, to form $LM(CO)_4$ and

$L_2M(CO)_2$. Spectra suggest that L is an η^5-ligand, and in the bis-complex they are thought to be cis-.[179]

3.1.11 Boron Nitride, Metal Borides

$S_2O_6F_2$ oxidises boron nitride to $(BN)_4^+(SO_3F)^-$: the first example of a first-stage boron nitride salt. Its formation is believed to involve the removal of electrons from the highest filled Brillouin zone of $(BN)_x$.[180]

CaM_2B_2, where M = Rh or Ir, are prepared by heating together appropriate mixtures of the powdered elements. Both give orthorhombic crystals, belonging to the space group Fddd. The structures contain isolated boron atoms, each surrounded by a tetrahedron of M atoms.[181]

The phase $ZrIr_3B_{\sim 4}$ forms hexagonal crystals, space group $\underline{P}6_3/m$. Two different types of boron atom are present: (i) isolated atoms, in distorted trigonal prisms, and (ii) linear chains (B-B distance 1.756Å) at the centres of Ir octahedra. The crystal structure is related to thatof Fe_2P.[182]

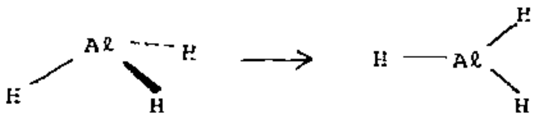
3.2 ALUMINIUM

3.2.1 Aluminium Hydrides

AℓH can be produced in an argon matrix at 14K by using a hollow-cathode sputtering source. νAℓ-H was seen at 1593 cm^{-1}, and νAℓ-D at 1158 cm^{-1}.[183]

AℓCℓ and HCℓ react in an argon matrix under mercury lamp irradiation to form $HA\ell C\ell_2$. The vibrational bands observed were consistent with a planar model: νAℓ-H, 1967.6cm^{-1}; νAℓ-D, 1430.1cm^{-1}; νAℓ-Cℓ 481.3cm^{-1} ($HA\ell^{35}C\ell_2$) 477.6cm^{-1} ($HA\ell^{35}C\ell^{37}C\ell$), 477.5$cm^{-1}$ ($DA\ell^{35}C\ell_2$), 473.6cm^{-1} ($DA\ell^{35}C\ell^{37}C\ell$).[184]

The reorganisation energy of $A\ell H_3$, (55), ΔE_r, has been calculated as 9.8 kcal. mol^{-1}. This enables the strength of the Aℓ-H-Aℓ bridge bond in $A\ell_2H_6$ to be calculated, i.e. 27.7 kcal. mol^{-1}.[185]



(55)

Vibrational assignments have been given for $A\ell(BH_4)_3.L$, where $L = NH_3$, NH_2Me, $NHMe_2$ or NMe_3. The results suggest that $A\ell(BH_4)_3.NHMe_2$ possesses a plane of symmetry, passing through the Aℓ, B, N and H atoms. The vibrations of the $A\ell(BH_4)_3$ fragments were only slightly affected by changes in L.[186]

$A\ell(BH_4)_3$ reacts with $(A\ell Et_2H)_3$ in appropriate molar ratios to form liquid hydridoaluminium tetrahydroborates, equations (26) and (27). The ethyl compound can be removed easily. The $A\ell(BH_4)_2H$ is

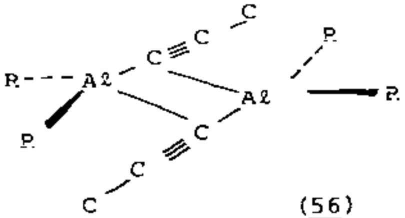
$$(A\ell Et_2H)_3 + 6A\ell(BH_4)_3 \longrightarrow 3A\ell(BH_4)_2H + 6A\ell(BH_4)_2Et \qquad (26)$$

$$2(A\ell Et_2H)_3 + 9A\ell(BH_4)_3 \longrightarrow 3A\ell(BH_4)H_2 + 12A\ell(BH_4)_2Et \qquad (27)$$

the more stable compound, but in vacuo both disproportionate. This produces $A\ell(BH_4)_3$ and a residue increasingly rich in Aℓ-H bonds. The latter solidifies when the concentration of $A\ell H_3$ units exceeds 78 mole%.[187]

3.2.2 Compounds containing Aℓ-C or Aℓ-Ge Bonds

Electron diffraction studies on di(μ-1-propynyl)bis(dimethylaluminium) suggest that the molecule has C_{2h}, not D_{2h}, symmetry, i.e. (56). There are two short and two long Aℓ-C bonds. It is thought that the π-electrons of the C≡C interact with the aluminium of the other monomeric unit.[188]



(56)

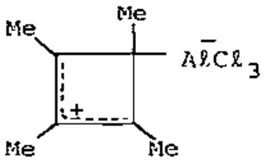
Trimethylaluminium reacts with the caesium salts of SO_4^{2-}, $S_2O_3^{2-}$ or $S_2O_6^{2-}$ to form $Cs_2SO_4.4A\ell Me_3$; $Cs_2S_2O_3.4A\ell Me_3$ and $Cs_2S_2O_6.4A\ell Me_3$. Some vibrational assignments were given.[189]

The crystal structure of $[(\eta\text{-}C_5H_5)_2YMe_2A\ell Me_2]$ shows the presence of a dimethyl bridge - the average bridging bond distances being 2.58(3)Å for Y-C and 2.10(2)Å for Aℓ-C. The Y-Aℓ separation is 3.056(6)Å.[190]

The mass spectra of $(Me_2A\ell OPh)_n$, where n = 2 or 3, have been recorded. Skeletal fragmentation was observed at low temperatures.

The high-temperature spectrum of the trimer was very complex; there was evidence for the presence of ions containing at least five aluminium atoms. This suggested that more associated species are formed during the trimer   dimer conversion process.[191]

N.m.r. studies on the σ-complex of $A\ell C\ell_3$ with a substituted cyclobutadiene, (57) show that the molecule is fluxional, with the main process being a 1,2-shift of the $A\ell C\ell_3$ group.[192]



(57)

$A\ell(i\text{-}Bu)_3$ reacts with potassium metal in hexane at 20°c to form a novel dialuminium compound, $K_2[i\text{-}Bu_3A\ell\text{-}A\ell i\text{-}Bu_3]$. The ^1H and ^{13}C n.m.r. spectra, together with its chemical properties, are consistent with the presence of an Aℓ-Aℓ σ-bond.[193]

Triphenylaluminium dissolves in $A\ell(BH_4)_3$ giving the dimeric solid "$Ph_2A\ell BH_4$". The monophenyl form could not be isolated. The alkyl derivatives show the reverse trend in stabilities.[194]

The first alkylgermyl aluminium compound has been prepared, equation (28). The THF adduct has considerable thermal stability;

$$3Hg(GeMe_3)_2 + 2A\ell \xrightarrow[\text{pentane}]{\text{THF}} 2A\ell(GeMe_3)_3.THF + 3Hg \qquad (28)$$

it melts at 81°c.[195]

3.2.3 Compounds containing Aℓ-N or Aℓ-P Bonds

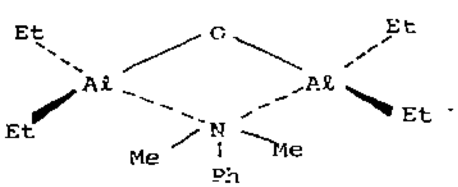
The compounds $X_2A\ell NMe_2$, where X = Br or I, can be prepared by reactions (29), in benzene solution. Both are structurally anal-

$$H_2A\ell NMe_2 + HgX_2 \longrightarrow Hg + H_2 + X_2A\ell NMe_2 \qquad (29)$$

ogous to the chloro-compound. Crystal structure determinations show that they are dimers, with a planar, four-membered, $A\ell_2N_2$, ring, all of the atoms being four-coordinate. The Aℓ-N bond distance is 1.94Å; for the Aℓ-Br, Aℓ-I and N-C bonds the distances are 2.26Å, 2.49Å, 1.50-1.55Å.[196]

Aluminium and gallium tri-iodides react with IN_3 to form I_2MN_3 (M = Aℓ or Ga). These react with liquid bromine to give the bromo-analogues. Their i.r. spectra were reported and partly assigned. νM-N modes were seen near 490 cm^{-1} (M = Aℓ), or 430 cm^{-1} (M = Ga).[197]

Tetra-alkylalumoxanes, $R_4Aℓ_2O$, where R = Et or i-Bu, react with nitrogen-containing donor molecules, e.g. NMe_2Ph, PhHC=N-n-Bu or PhCN, to give adducts. They are generally 1:1, and monomeric. Their structures, based on ^1H n.m.r. evidence, are thought to be (58).



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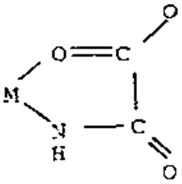


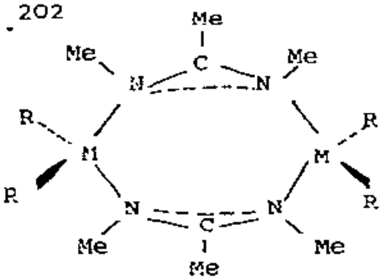
(59)

The ^1H n.m.r. spectrum of $(HAℓNCHMePh)_6$ is consistent with the presence of a closed hexameric cage structure.[199]

Complex anions of Aℓ, Ga, In or Tℓ with oxamic acid, $[M(C_2HO_3N)_3]^{3-}$, have been prepared. Their infrared spectra suggest that coordination has taken place via the carboxyl oxygen and the amidic nitrogen, after ionisation of one of the amidic hydrogens as shown in (59).[200]

Dimethylaluminium- and dimethylgallium-N,N'-dimethylacetamidine exist as dimers, with a puckered eight-membered ring. The M-N bond distances within each ring are almost equal (1.925Å for M = Aℓ, 1.979Å for M = Ga), as are N-C distances (ca. 1.33Å in each case).[201]

Vibrational spectral studies of a number of such derivatives: $[R_2M(N_2MeCMe)]_2$, where M = Aℓ or Ga, R = Me or Et; M = In, R = Me, confirm these results. The symmetry of the ring is probably C_{2h}, (60).[202]



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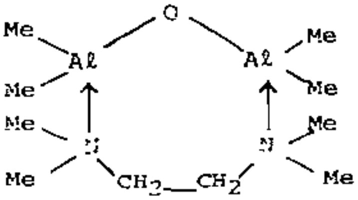


(61)

Infrared and mass spectra of tetramethylalumoxane-N,N,N',N'-tetramethylethylenediamine show that it is a monomer, (61), in the gas phase.[203]

Gas-phase electron diffraction results were used to obtain the molecular structure of $Me_3A\ell PMe_3$. The following bond lengths were found: Aℓ-C, 1.973(3)Å; Aℓ-P, 2.53(4)Å; P-C, 1.822(3)Å. The PAℓC and AℓPC angles were 100.0(1.3)° and 115.0(0.7)° respectively.[204]

3.2.4 Compounds containing Aℓ-O or Aℓ-Se Bonds

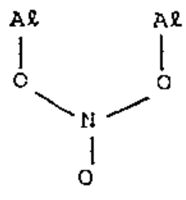
Lattice vibrations of boehmite, γ-AℓOOH, show that the true space group must be Cmc2, (C^{12}_{2v}), rather than the Cmcm (D^{17}_{2h}) indicated as statistical symmetry by diffraction.[205]

Ranges in which sodium aluminate solution exists mainly as (a) NaOH, with monomeric $A\ell(OH)_4^-$ or (b) NaOH, with dimeric $A\ell_2O(OH)_6^{2-}$ have been estimated from water-activity measurements. The former condition applies at aluminium concentrations of 1-4 M dm^{-3}, the latter at 2-7 M dm^{-3}.[206]

Single-crystal Raman spectra have been obtained for $[A\ell(OH_2)_6]C\ell_3$ and its deuteriate. All of the Raman bonds predicted by factor group analysis are seen. The symmetric stretch, ν_1, of $A\ell O_6$ is at 524 cm^{-1} (the alternative assignment at 701 cm^{-1} gives less satisfactory force constants). ν_3 of $A\ell O_6$ is probably at about 670 cm^{-1}.[207]

Rates and activation parameters have been determined for the formation of mono-complexes of $A\ell(DMSO)_6^{3+}$ with pyridine, bipyridyl and terpyridyl. Reactions with the last two ligands proceed in respectively two and three distinct stages.[208]

Addition of $A\ell_2Me_6$ to MNO_3, where M = K, Rb, Cs, NMe_4 or NEt_4, in benzene produces $M[A\ell_2Me_6(NO_3)]$. The crystal structure of the potassium salt shows that the nitrato-group is bridging, (62). If dibenzo-18-crown-6 is added to this species $K[A\ell Me_3(NO_3)].7C_6H_6$ is obtained, in which the NO_3 is unidentate (Aℓ-O distance of 1.930(7) Å).[209]



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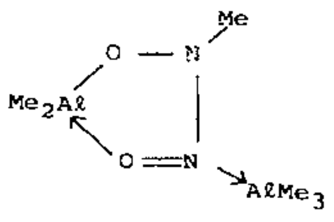

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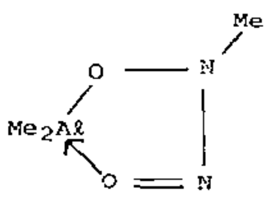
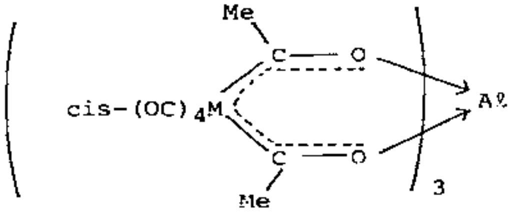


(64)

Nitric oxide reacts with trimethylaluminium to form "Me_3AlNO" and "$Me_3Al(NO)_2$". Infrared and n.m.r. spectra, and the results of hydrolysis experiments suggest that they are, in fact, (63) and (64) respectively.[210]

^{13}C n.m.r. spectral data were tabulated for (65), where M = Mn or Re, R = Me; M = Re, R = $PhCH_2$ or Me_2CH, as well as for some related boron complexes.



(65)

Alkoxyaluminium compounds, $(RO)AlCl_2$, where R = Me, Et, n-Pr, i-Pr, n-Bu or t-Bu, react with $MeAlCl_2$ with evolution of gases (RMe, RCl), producing alumoxane systems, Al-O-Al. The sequence of reactivities is as follows:

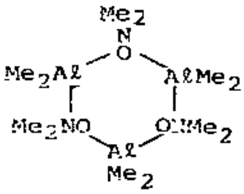
$$\text{t-Bu} \gtrsim \text{i-Pr} > \text{n-Bu} > \text{n-Pr} \gg \text{Et} \ggg \text{Me}.$$

This suggests that the formation of a carbocation from the RO- group must play a significant part in the mechanism.[212]

The complex $[Ta\{H_2Al(OC_2H_4OMe)_2\}(Me_2PC_2H_4PMe_2)_2]_2$ contains an approximately square pyramidal P_4Ta-μ-H_2-Al group; Al_2O_2 bridge units are also present.[213]

The compound $[Me_2AlONMe_2]_3$ contains a six-membered ring, (66). The crystal structure shows that this is in the skew-boat conformation. The following average bond lengths were determined: Al-O, 1.867Å; Al-C, 1.961Å; N-O, 1.477Å; N-C, 1.459Å.[214]

Alkaline earth metals react with aluminium iso-propoxide, with $HgCl_2$ as a catalyst, to give the corresponding double alkoxides: $[M\{Al(O\text{-}i\text{-}Pr)_4\}_2]_n$, where n = 1, M = Mg; n = 2, M = Ca, Sr or Ba. Treatment of these with excess of a tertiary alcohol produces $M[Al(O\text{-}i\text{-}Pr)(OR)_3]_2$, M = Mg, Ca or Sr, or $Ba[Al(O\text{-}i\text{-}Pr)_2(OR)_2]$, where R = t-butyl or t-amyl.[215]



(66)

New salts $M_2[A\ell(C\ell O_4)_5]$, where M = Na or K, have been reported - formed by the interaction of $MA\ell C\ell_4$ with $HC\ell O_4$ or $MC\ell O_4/HC\ell O_4$ mixtures. The infrared spectra show shifts and splitting of the $C\ell O_4^-$ modes characteristic of $A\ell-C\ell O_4$ covalent bonding.[216]

The electron density distribution in crystals of $CoA\ell_2O_4$ shows that the net charges on the atoms are: Co, +1.5e; Aℓ, +2.8e; O, 1.8e. Thus the bonding is very largely ionic.[217]

Aluminite, $A\ell_2(OH)_4(SO_4).7H_2O$, forms monoclinic crystals, space group $P2_1/c$. The complex ion $[A\ell_4(OH)_8(H_2O)_6]^{4+}$ is present, built up from four edge-sharing aluminium octahedra polymerised in chains. These are connected to SO_4^{2-} ions by a three-dimensional, hydrogen-bonded system. The formula of this substance should therefore be written as $[A\ell_2(OH)_4(H_2O)_3]SO_4.4H_2O$.[218]

The crystal structure of $A\ell(H_2PO_4)(HPO_4)(H_2O)$ shows that it contains macromolecular units of that formula, built up from $A\ell(O)_5(H_2O)$ octahedra which share vertices with $P(O)_2(OH)_2$ and $P(O)_3(OH)$ tetrahedra. Neighbouring layers are linked by hydrogen bonds.[219]

The crystal structure of aluminium tris(dihydrogen phosphate), on the other hand, shows the presence of isolated $A\ell O_6$ octahedra stacked, by corner-sharing with $O_2P(OH)_2$ tetrahedra, to give columns parallel to the $\underline{c}$ axis. The columns are linked by hydrogen-bonding. The heavy atoms have an almost centrosymmetric arrangement, but the symmetry is lowered by the positions of the protons.[220]

The structural differences between the low-temperature form of anorthite, $Ca_{0.98}Na_{0.02}A\ell_{1.98}Si_{2.03}O_8$, and that quenched from 1530°c have been discussed. The latter has partial Aℓ/Si disorder.[221]

The crystal structure of the metastable phase of $5CaO.3A\ell_2O_3$ shows that the crystals are orthorhombic, but that the space group is $Cmc2_1$, not $C222_1$ as previously reported. The structure consists of alternating twisted sheets of $A\ell O_4$ tetrahedra and calcium atoms lying perpendicular to [001]. The tetrahedra are linked via corners to give a network of five-membered rings.[222]

A solid-state reaction occurs at 1700°c in the $BaO-Fe_2O_3A\ell_2O_3$ system to yield single crystals of $Ba_2Fe_{11}A\ell_{11}O_{34}$, space group $P6_3/mmc$. It is isotypic with $Na_2O.11A\ell_2O_3$ (structure of β-alumina).[223]

$CaA\ell_2Se_4$ and $SrA\ell_2Se_4$ can be prepared by heating stoichiometric mixtures of the elements. Both are orthorhombic, space group Cccm. They are isostructural, with a structure closely related to that of $T\ell Se$.[224]

3.2.5 Aluminium Halides

Co-condensation of oxygen atoms with $A\ell X$, where X = F or $C\ell$, in an Ar matrix leads to formation of $OA\ell X$. The following stretching wavenumbers were seen in the infrared spectra (^{16}O isotope): X = F, $\nu A\ell{=}O$, 1148 cm^{-1}; $\nu A\ell{-}F$, 740 cm^{-1}; X = $C\ell$, $\nu A\ell{=}O$, 1090 cm^{-1}; $\nu A\ell{-}C\ell$ 490.5 cm^{-1}.[225]

Aluminium chloride reacts with the perchlorates $MC\ell O_4$, M = Na, Li or NBu_4, in 1,2-dimethoxyethane (DME), to form $MA\ell C\ell_4$ and an insoluble species formulated as $A\ell C\ell_2(C\ell O_4).2DME$.[226]

Fourier-transform infrared spectroscopy was used to obtain infrared data for the first time on $A\ell C\ell_4^-$ in chloroaluminate melts $MA\ell C\ell_4$ where M = Li, Na or K.[227]

Potassium tetrachloroaluminate forms monoclinic crystals, space group $P2_1$. Discrete K^+ and $A\ell C\ell_4^-$ ions are present, although the latter are slightly distorted from tetrahedral geometry. The structure is a slightly deformed version of that of $(NO)A\ell C\ell_4$, i.e. $BaSO_4$ type.[228]

The analogous ammonium salt forms orthorhombic crystals, space group Pnma, isostructural with $NH_4C\ell O_4$. The $A\ell{-}C\ell$ bond lengths are very close to those in other chloroaluminates. Spectroscopic results (i.r.,Raman, ^1H n.m.r.) suggest that the NH_4^+ is rotating freely.[229]

Quartz glass is attacked by $A\ell_2C\ell_6$ vapour at temperatures above 300°c to give gaseous $SiC\ell_4$. At lower temperatures oxygen is incorporated as the gaseous oxide chloride $A\ell_4OC\ell_{10}$, about 300°c as crystalline $A\ell OC\ell$, and at even higher temperatures as $A\ell_2O_3$.[230]

Raman spectra of liquid mixtures of $A\ell C\ell_3$ and 1-butylpyridinium chloride, at room temperatures and molar ratios between 0.75:1.0 and 2.0:1.0, show that the association equilibrium constant for $A\ell_2C\ell_7^-$ ion formation, equation (30), is significantly larger than in $A\ell C\ell_3$-$MC\ell$ melts, where M = alkali metal cation.[231]

$$2A\ell C\ell_4^- + A\ell_2C\ell_6 \longrightarrow 2A\ell_2C\ell_7^- \qquad (30)$$

^{23}Na, $^{27}A\ell$ and $^{35}C\ell$ n.m.r. studies on fused (Na K)$A\ell_2C\ell_7$ at 170°c show that the structure is essentially ionic $M^+A\ell_2C\ell_7^-$.[232] $TiC\ell_4$ in the presence of gaseous $A\ell_2C\ell_6$ forms the species $TiA\ell C\ell_6$ and $TiA\ell_3C\ell_{11}$ in the gaseous phase. In condensed phases the stable species is $TiA\ell_2C\ell_8$.[233]

Spectrophotometric and potentiometric measurements on the $KC\ell$-$FeC\ell_3$-$A\ell C\ell_3$ system at 300°c suggest that the two most likely melt

$$A\ell C\ell_4^- + FeC\ell_4^- \longrightarrow FeA\ell C\ell_7^- + C\ell^- \qquad (31)$$

$$FeA\ell C\ell_7^- \longrightarrow FeA\ell C\ell_6 + C\ell^- \qquad (32)$$

reactions are (31) and(32), with pK values of 6.75 ± 0.03 and 6.53 ± 0.06 respectively.[234]

The electronic spectra of Pd(II) dissolved in $A\ell_2C\ell_6$, $A\ell_2C\ell_6$-$KC\ell$ eutectic or in $KA\ell C\ell_4$ are all similar, suggesting square-planar four-fold coordination in all cases. The temperature dependence of the spectra is consistent with the presence of centrosymmetric species.[235]

Mass-spectrometric measurements on the vapour over $CuC\ell$(solid)/ $A\ell_2C\ell_6$ showed that $Cu_3A\ell C\ell_6$ and $Cu_2A\ell_2C\ell_8$ are the principal components. Enthalpy and Entropy changes associated with their formation were estimated. The molecules probably have a cubic structure, based upon that on $Cu_4C\ell_4$.[236]

Spectrophotometric measurements on the $PdBr_2(s)/A\ell_2Br_6(g)$ system suggest that one predominant species is present, equation (33), for

$$PdBr_2(s) + A\ell_2Br_6(g) \longrightarrow PdA\ell_2Br_8(g) \qquad (33)$$

which $\Delta H = 8.27$ kcal. mol.$^{-1}$. The complex is believed to have D_{2h} symmetry, and to contain square planar Pd.[237]

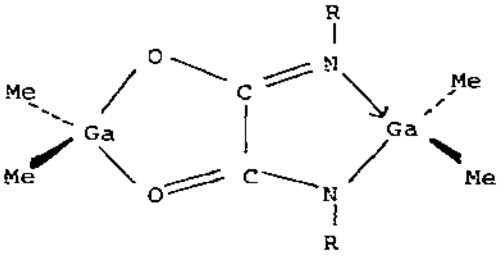
3.3 GALLIUM

3.3.1 Compounds containing Ga-C Bonds

$GaMe_2(BH_4)$ can be prepared from trimethylgallium and diborane, but a better reaction is between $GaMe_2Cl$ and $LiBH_4$ in the absence of solvent at $-15^\circ C$. Characterisation of the product was based on molecular weight determination, mass-, vibrational- and ^1H n.m.r.-spectra. The infrared spectrum of the gas was consistent with the formulation $Me_2Ga(\mu\text{-}H)_2BH_2$, of C_{2v} symmetry, i.e. four-coordinate gallium linked to bidentate BH_4. This appears to persist in the condensed phases, although the vibrational spectra of the solid suggest increased polarisation in the sense $GaMe_2^+BH_4^-$.[238]

Trimethylgallium reacts with acetic acid at a molar ratio of 1:2 to produce $MeGa(OOCMe)_2$. The crystal structure of this shows that the monomers are linked by bridging acetate groups into a layer structure. The structure contains both four- and five-coordinate gallium atoms, being bonded to bridging acetates in the former, and to both bridging and terminal acetates in the latter. The vibrational spectrum agrees with this, although only one ^1H n.m.r. resonance due to acetate groups is seen at room temperature. Thus an exchange process is rapid (on the n.m.r. time scale) in solution at this temperature.[239]

Trimethylgallium, with N,N'-dimethyloxamide, forms two isomeric N,N'-bis(dimethylgallium)-N,N'-dimethyloxamide complexes. These are, respectively, cis, (67), and trans, (68), with respect to the central oxamide C-C bond, and they belong to the point groups C_{2v} (cis) and C_{2h} (trans).[240]



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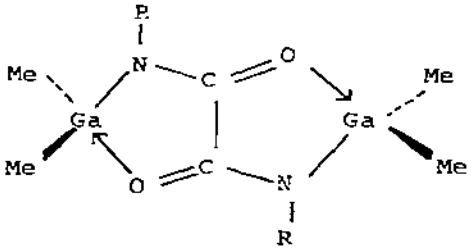
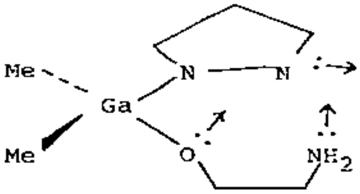


(68)

3.3.2 Compounds containing Ga-N or Ga-P Bonds

The anionic tridentate ligand $[MeGa(N_2C_3H_3)_3]^-$ has been prepared. It acts as a six-electron chelating ligand to transition metal cations, M^{2+}, forming ML_2 complexes with an octahedral MN_6 skeleton. The tridentate bonding was confirmed by a determination of the crystal structure of $[MeGa(N_2C_3H_3)_3]Mo(CO)_2(\eta^3-C_3H_5)$.[241]

Dimethyl(ethanolamino)(1-pyrazolyl)gallate can act as a tridentate ligand also, (69). Crystal structures of two complexes of this ligand with Ni(II) were reported.[242]



(69)

^{35}Cl N.q.r. studies on $R_3P.GaCl_3$, where R = Me or Ph, show that the phosphines are very good donors towards $GaCl_3$. The crystal structure of Me_3PGaCl_3 reveals that it adopts the staggered conformation.[243]

3.3.3 Compounds containing Ga–O, Ga–S or Ga–Se Bonds

The adducts $L.GaBr_3$ have been reported, where L = pyridine-N-oxide, 2- 3- or 4-picoline-N-oxide, 4-chloropyridine-N-oxide or 4-nitropyridine-N-oxide. All show decreases in νNO on coordination, showing that the ligands are bound to the gallium via the oxygen atom. Tentative assignments to νGaO were made in the 400–450 cm^{-1} range.[244]

Gallium(III) and indium(III) can be extracted from aqueous thiocyanate media by dibutylphenylacylphosphonate, HDBPP, as the complexes $M(NCS)_3(HDBPP)_3$. The ligand bonds only via the P=O grouping.[245]

^{71}Ga and ^{31}P Fourier-transform n.m.r. spectra have been obtained for gallium/phosphate systems. The data were consistent with the formation of several types of complex, with different stoichiometries, e.g. $GaH_3PO_4^{3+}$, $GaH_2PO_4^{2+}$, together with a complex of the dimeric $H_5P_2O_8^-$.[246]

$LiGaO_2.6H_2O$ forms monoclinic crystals, belonging to the space group C2. The structure is better described as $[GaO_2.2H_2O]^-.[Li.4H_2O]^+$, rather than as $[Ga(OH)_4]^-[Li.4H_2O]^+$.[247]

$M_6[Ga_2O_6]$, where M = K or Rb, can be prepared from the constituent oxides. Both are isotypic with $K_6Fe_2O_6$, and belong to the space group C2/m. The hitherto unknown Na_3GaO_3, space group Imcm or I2cm, and $Cs_6[Ga_2O_6]$, $P2_1/a$, were also prepared.[248]

Single crystals of $Bi_2Ga_4O_9$ and $Bi_2Ga_2Fe_2O_9$ have been prepared from appropriate oxide mixtures under the influence of a CO_2 laser. The former is one of the few Ga^{3+} compounds in which the gallium is octahedrally, as well as tetrahedrally coordinated. In the latter the Ga^{3+} is only tetrahedrally coordinated, showing the preferential occupation of tetrahedral holes by the gallium.[249]

The three ordered synthetic feldspars $SrGa_2Si_2O_8$, $BaGa_2Si_2O_8$ and $BaGa_2Ge_2O_8$ all belong to the space group I2/c.[250]

$LaGaOS_2$ forms orthorhombic crystals, space group Pmca. The structure is very compact, with all of the oxygen and sulphur atoms bonded simultaneously to lanthanum and gallium.[251]

Infrared and Raman spectroscopic data have been obtained for single crystals of α-Ga_2S_3. The spectra were consistent with approximate C^6_{2h} crystal symmetry. Frequencies were assignable to both external and internal modes of the GaS_4 groups.[252]

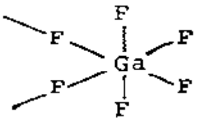
It was found that β-Ag_9GaSe_6 formed cubic crystals, space group $P2_13$. $GaSe_4$ tetrahedra were present, of C_3 symmetry; three GaSe distances were 2.367(6)Å, the fourth 2.363(9)Å.[253]

The crystal structure of TℓGaSe shows that large Ge_4Se_{10} tetrahedra are present, composed of four corner-linked $GeSe_4$ tetrahedra. The $Tℓ^+$ ions are situated in straight lines, parallel to the edges of the Ga_4Se_{10} groups. The Tℓ is six-coordinated by the selenium, giving trigonal prismatic $TℓSe_6$ units.[254]

3.3.4 Gallium Halides

Co-condensation of GaF with oxygen atoms in an argon matrix produces OGaF. The infrared spectrum shows νGaO at 943 cm^{-1}, and νGaF at 690 cm^{-1} (both figures referring to $^{16}O^{69}GaF$).[255]

$BaGaF_5$ has been isolated from the BaF_2-GaF_3 system. It crystallises in the space group $P2_12_12_1$, and contains chains based on the unit (70).[256]



(70)

All of the compounds $GaX_3.SbX_3$ (where X = Cℓ,Br or I) are formed in the solid state, but $GaX_3.SbX'_3$ (where X ≠ X') do not exist. The $GaC\ell_3$-SbI_3 system is a simple eutectic, whereas in GaI_3-$SbC\ell_3$ complete halogen exchange occurs.[257]

The crystal structure of $Me_4Sb^+GaC\ell_4^-$ shows that the ions are isolated from one another, and only very slightly distorted. The average Ga-Cℓ bond length is 2.172Å.[258]

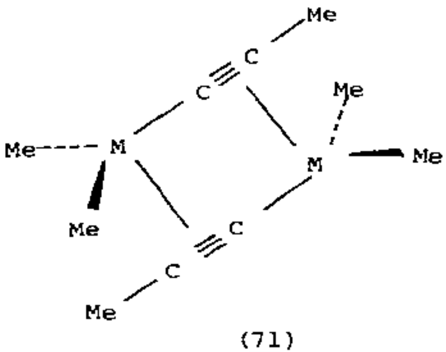
The rates of phenyl ring rotation in gallium chloro-complexes of p-tetraphenylporphyrins have been measured by variable-temperature ^1H n.m.r. spectroscopy. The rates of rotation found were the fastest to date for any metallotetraphenylporphyrin complexes.[259]

The lower halides of gallium, Ga_2X_4 (where X = Cℓ, Br or I) and Ga_4I_6, are prepared conveniently by the reduction of the appropriate gallium(III) halide by gallium metal in benzene at 60°c. For the iodide system excess of the gallium metal is required to produce Ga_4I_6.[260]

3.4 INDIUM

3.4.1 General

The reaction of NaC≡CMe with Me_2MX, where M = Aℓ, Ga or In, and X = Cℓ or Br, produces dimethylpropynylmetal derivatives. Infrared, Raman, ^1H and ^{13}n.m.r. spectra were recorded, showing that they are dimeric in solution, the structure probably being (71). A similar π-interaction was revealed by the crystal structure of the indium compound, which is polymeric, and contains the unit (72).[261]



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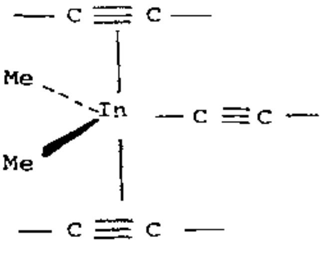


(72)

Li_2In has been found to be isotypic with Li_2Ga, belonging to the space group Cmcm. The indium atoms form zig-zag chains. $Li_{13}In_3$, on the other hand, belongs to a new structure type. It is face-centred cubic, space group Fd3m. It can best be described as an ordered variant of a body-centred cubic form, containing isolated indium atoms.[262]

The phase analysis of the Li-In-Pb system revealed the formation of the following cubic phases (the value of a, in Å, is given in parentheses): $Li_{10.66}In_{4.01}Pb_{1.33}$ (6.75); $Li_{10.66}In_{3.21}Pb_{2.13}$ (6.77); $Li_{11.73}In_{1.07}Pb_{3.20}$ (6.73). The structures are all believed to be based upon a modified NaTℓ-type lattice.[263]

E.m.f. measurements on liquid In/Hg amalgams, in the cell In/$InC\ell_3$/amalgam, were used to deduce values of ΔG, ΔH and ΔS for the process In+Hg amalgam at various indium concentrations.[264]

3.4.2 Compounds containing Bonds between Indium and Elements of Group 4

The vapour pressures of pure indium, and of $In+In_2O$ mixtures over the mixture $In+MgIn_2O_4+MgO$ have been measured by the Knudsen effusion technique in the temperature range 1095-1300K. The results were used to determine the free energy of formation of the inverse spinel $MgIn_2O_4$ from its component oxides, i.e. $-6190+0.6T(\pm 400)$ cal., at TK.[265]

The mixed oxide $In_2Te_3O_9$ forms orthorhombic crystals, space group Pbnm. The structure is built up from sheets of TeO_3^{2-} anions, with InO_6 octahedra linked in parallel chains.[266]

$K_{0.72}(In_{0.72}Sn_{0.28})O_2$ exists as hexagonal crystals, belonging to the space group P$\bar{6}$m2. The structure contains sheets of $(MO_2)_n$ stoichiometry, (M = In or Sn), containing linked octahedral units, in which the indium and tin atoms are statistically distributed over two non-equivalent positions.[267]

A new quenchable high-pressure modification of In_2S_3 has been obtained at 35 kbar and 500°C. The new form has been named ϵ-In_2S_3, its crystals belong to the space group R$\bar{3}$c, and it is isotypic with Lu_2S_3 (corundum-type structure).[268]

Orthorhombic crystals are formed by La_3InS_6, which belong to the space group $P2_12_12_1$. The indium atoms are present in both four-coordinate (In-S = 2.44Å) and six-coordinate (In-S = 2.61Å) sites.[269]

Crystal structure determinations have been carried out on $Pb_4In_9S_{17}$ and $Pb_3In_{6.67}S_{13}$. The crystals belong to the space groups Pbam and B2/m respectively. In both cases the indium atoms are approximately octahedrally coordinated by six sulphur atoms with In–S distances in the range 2.46 to 2.92Å.[270]

Similar studies have also been carried out on indium phosphorus chalcogenides, yielding the following information: $\mathrm{InPS_4}$, tetragonal, space group $I\bar{4}$; $\mathrm{In_4(P_2S_6)_3}$, monoclinic, space group $P2_1/c$; $\mathrm{In_4(P_2Se_6)_3}$, orthorhombic, space group Pba2.[271]

Four different phases were identified in the intercalation substitution system $\mathrm{Na_xIn_xSn_{1-x}S_2}$, where $1 > x > 0$. They existed in the following ranges: (2) $1 \gtrsim x > 0.63$; (b) $0.60 > x > 0.43$; (c) $x \sim 0.40$; (d) $x \sim 0.20$.[272]

X-ray diffraction was used to determine the crystal structure of the low-temperature form of $\mathrm{In_2Se_3}$. The crystals belong to the space group $P6_1$, while the structure was a distorted form of the wurtzite structure, in which the indium atoms were either tetrahedrally- or five-coordinated.[273]

$\mathrm{In_2Te_5}$(II) forms monoclinic crystals; space group C2/c. The structure contains planar sheets, perpendicular to C*, which are similar to those found in $\mathrm{In_2Te_5}$(I), consisting of chains of four-membered In–Te rings, with each indium atom tetrahedrally coordinated. The average In–Te distance was found to be 2.849(5)Å.[274]

3.4.3 Indium Halides

Previous ambiguities in the interpretation of X-ray diffraction data on $\mathrm{InF_3.3H_2O}$ have been resolved. The coordination about the indium is octahedral, as previously thought, but the orientations of the octahedra were revised to account more satisfactorily with the observed results.[275]

Twenty-two fluoroindates, $\mathrm{M_xIn_nF_{3n+x}}$, have been isolated and characterised by solid-state reactions in $\mathrm{MF{-}InF_3}$ systems, where M = alkali metal, Tℓ or $\mathrm{NH_4}$. The species found were as follows: $\mathrm{MInF_4}$ (M = K, Rb, Cs or Tℓ); $\mathrm{M_3InF_6}$ (M = Rb, Cs, Tℓ or $\mathrm{NH_4}$); $\mathrm{MIn_2F_7}$ (M = K, Rb or $\mathrm{NH_4}$); $\mathrm{MIn_3F_{10}}$ (M = Rb, Cs, Tℓ or $\mathrm{NH_4}$); $\mathrm{M_2In_3F_{11}}$ (M = Rb, Tℓ or $\mathrm{NH_4}$); $\mathrm{M_4In_3F_{13}}$ (M = Rb or Tℓ); $\mathrm{M_5In_3F_{14}}$ (M = K or $\mathrm{NH_4}$).[276]

$\mathrm{Rb_2In_3F_{11}}$ forms monoclinic crystals, space group $P2_1/m$. The structure is built up from parallel sheets of edge- and corner-sharing pentagonal bipyramids (as in $\alpha\text{-}\mathrm{U_3O_8}$), joined together by infinite, parallel chains of corner-sharing octahedra.[277]

The equilibria (34) have been examined, when M = Mg, Ca or Mn;

$$\mathrm{MC\ell(s) + nInC\ell_3(g) \longrightarrow MIn_nC\ell_{2+3n}(g)} \qquad (34)$$

two complexes are formed (n = 1 or 2). When M = Cu, however, only $CuInC\ell_5$ is detected.[278] $M_3In_2C\ell_9$ (where M = Cs, Rb, Tℓ or In), and $Cs_3In_2Br_{9-x}C\ell_x$ where x = 7 or 8, all form crystals which are isotypic with $Cs_3T\ell_2C\ell_9$. $Cs_3In_2Br_{9-x}C\ell_x$ (where x = 3, 6 or 7) belong to the $Cs_3Cr_2C\ell_9$ type of structure. Note that $Cs_3In_2Br_2C\ell_7$ is dimorphic.[279]

3.5 THALLIUM

3.5.1 Thallium(III) Compounds

A number of $R_2T\ell$- derivatives containing a thallium-transition metal bond have been prepared by various routes, e.g. $R_2T\ell-ML_n$, where $ML_n = M'(CO)_2L'cp$ (M' = Mo or W; L' = CO or PPh_3); $Cr(CO)_3cp$; $Fe(CO)_2cp$; $Co(CO)_4$. A typical reaction is shown in (35), M' = Mo

$$Ph_2T\ell Br + NaM(CO)_2L'cp \longrightarrow Ph_2T\ell{-}M(CO)L'cp + NaBr \qquad (35)$$

or W; L' = CO or PPh_3).[280]

Disproportionation of $RT\ell X_2$ (where R = alkyl or aryl; X = CH_3COO^-) does not occur at room temperature, i.e. the equilibrium concentrations of $R_2T\ell X$ and $T\ell X_3$ are too small to detect. In the presence of $P(OMe)_3$, however, $T\ell X_3$ is removed from the equilibrium, leading to significant disproportionation.[281]

The crystal structure of $T\ell[N(SiMe_3)_2]_3$ shows that it is isomorphous with the aluminium and iron(III) analogues. The Si_2N groups are twisted out of the plane defined by the metal and the three nitrogen atoms.[282]

TℓOBr can be prepared by the reaction of $T\ell_2CO_3$ with liquid bromine. It forms orthorhombic crystals, belonging to the space group Pmmn, isomorphous with InOBr (i.e. belonging to the FeOCℓ structure-type).[283]

The observed reaction kinetics for the interaction of Tℓ(III) with hydrogen peroxide can be rationalised in terms of one-electron reactions of mono- and di-(hydrogenperoxo)thallium(III) species with H_2O_2.[284]

The hydrated thallium(III) nitrate, $T\ell(NO_3)_3.3H_2O$, forms rhombohedral crystals, space group $R\bar{3}$. The thallium atom is nine-coordinate, with three unsymmetrically-bidentate nitrate groups (Tℓ-O distances 2.299(8)Å, 2.637(10)Å), and three water molecules (Tℓ-O distance 2.293(17)Å). The water molecules are ideally situated for transfer to an organic substrate when thallium(III) nitrate is used as an oxidant in solution.[285]

Thallium(III) acetate, on the other hand, forms monoclinic crystals, space group C2/c. The thallium is chelated by the three acetate groups (Tℓ-O distances in the range 2.26 to 2.34Å) and it also forms two further, weak, bonds (at 2.57Å) with adjacent molecules along the c axis. The thallium therefore adopts a distorted eight-coordination.[286]

Heating a mixture of Na_2O and $T\ell_2O$ (Na:Tℓ ratio of 5.4:1) at 620°c for7 days leads to the formation of $Na_5T\ell^{(III)}O_4$. This forms orthorhombic single crystals, isotypic with Li_5GaO_4. Thermal decomposition of these produces, first, the previously unknown $Na_3T\ell O_3$, and, finally, $NaT\ell O_2$.[287]

The diarylthallium compounds $R_2T\ell(O_2CR)$, where R = C_6F_5, p-$MeOC_6F_4$, p-HC_6F_4, m-HC_6F_4 or o-HC_6F_4, all have associated structures, with bridging carboxylate groups. Except when R = o-HC_6HF_4 heating led to decarboxylation, and it was possible to isolate the dioxan adducts $R_3T\ell(\text{dioxan})_2$. The ease of decarboxylation was in the sequence R = $C_6F_5 \lesssim$ p-$MeOC_6F_4$ > p-$HC_6F_4 \sim$ m-HC_6F_4 >> o-HC_6F_4.[288]

Palladium(II) oxide reacts with $T\ell NO_3$ or $T\ell_2O_3$ at 550°c to form $T\ell Pd_3O_4$. The Pd/O skeleton forms a cage unit with cubic and rhombicuboctahedral spaces occupied by $T\ell^{3+}$, $T\ell^+$ respectively. Thus this is a thallium(III) thallium(I) oxopalladate(II). The analogous platinum(II) compound was also reported.[289]

Neutron powder-diffraction shows that $T\ell Pd_3O_4$ is cubic, belonging to the space group Fm3m, and a = 9.5807Å.[290]

(DL-Tryptophanato)dimethylthallium(III) monohydrate forms monoclinic crystals, space group $P2_1/c$. Centrosymmetric dimers are present: $(Me_2T\ell)_2$(D-tryptophan)(L-tryptophan). The coordination about the thallium atom is very irregular.[291]

Another thallium(III) compound to form monoclinic crystals is $T\ell(S_2CNEt_2)_3$, space group A2/a. It is isostructural with the gallium and indium analogues. The average Tℓ-S distance is 2.66_5 Å.[292]

3.5.2 Thallium(I) Compounds

Cyclopentadienylthallium(I)-d_5 can be prepared conveniently from C_5H_6, D_2O and $T\ell_2SO_4$ at room temperature. It is a useful source material for a number of (C_5D_5)-metal compounds.[293]

S.C.F. molecular-orbital calculations on $C_5H_5T\ell$, using the theory of effective potentials, shows that bonding is mainly due to the highest filled m.o. pair (of E_1 symmetry), based on pd^2 hybrids of Tℓ and p-orbitals of carbon atoms interacting in π-symmetry with respect to the C_5 axis of the molecule.[294]

^{13}C n.m.r. studies on $T\ell[C_5H_4CH(Me)Ph]$, and K^+ and Fe derivatives of the same ligand, together with ^{19}F n.m.r. studies on a similar series of compounds with $C_5H_4C_6H_4F$-m or -p, suggest that the $T\ell^+$ compounds exist in THF solution chiefly as tight ion-pairs. There is no covalent Tℓ-(ring) interaction.[295]

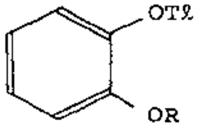
MTℓO, where M = K, Rb or Cs, are formed from mixtures of the appropriate oxides at 500-600°c. The oxothallates(I) crystallise in a monoclinic layer lattice (space group C^3_{2h}). The structures are closely related to that of $T\ell_2O$.[296]

Complexing of $T\ell^+$ with the crown ether dibenzo-18-crown-6 has been studied by n.m.r., fluorescence and pulse radiolysis. The data reveal a strong interaction between the $T\ell^+$ and the aromatic fragments.[297]

$T\ell^{(I)}H_5(PO_4)_2$ forms monoclinic crystals, belonging to the space group C2/c. The $T\ell^+$ ion is six-coordinated, and the average Tℓ-O distance is 3.048(2)Å.[298]

Thallium(I) sulphite can be prepared by passing SO_2 through a saturated solution of $T\ell_2CO_3$ in inert solvents. The crystals are orthorhombic, space group Pnam. The structure is disordered, but related to those of $T\ell_2SO_4$ and $T\ell_2S_2O_3$. The thallium atoms statistically all have the same coordination number.[299]

The preparation of the new thallium(I) compounds (<u>73</u>) have been reported, where R = H, Me, Et, Ph etc. Some infrared spectral assignments were given, together with data on their u.v. spectra.[300]



(<u>73</u>)

The thallium(I) tetramolydate, $T\ell_2Mo_4O_{13}$, forms orthorhombic crystals, space group Pbca. The anions form a sheet structure, with $Mo_8O_{26}^{4-}$ units, containing the $T\ell^+$ ions. There are two types of

$T\ell^+$ present, (a) six-coordinate, with five oxygen atoms at 2.69-2.86Å distance, and a sixth oxygen at 3.08Å; (b) seven-coordinate, with six oxygen atoms lying 2.81-2.99Å from the thallium, the seventh at 3.08Å. In each case one oxygen is very weakly bound, and so it is difficult to define the coordination numbers unambiguously.[301]

X-ray diffraction shows that the crystals of the thallium tantalate $T\ell_{4.62}Ta_{11.08}O_{30}$ are trigonal, and that they belong to the space group $R\bar{3}m$. The structure is based upon a covalent framework $Ta_{11}O_{30}$, with $T\ell^+$ ions in the cavities.[302]

Anhydrous thallium(I) sulphide can be precipitated from nitric acid solutionsof thallium(I) species, by H_2S. DTA measurements showed two polymorphic transitions, at 300°c and 450°c.[303]

The first mixed alkali metal-thallium(I) sulphides have been reported, e.g. $K_4T\ell_2S_3$, $Rb_4T\ell_2S_3$, $K_7T\ell S_4$. All were isolated from the $K_2S-T\ell_2S$ or $Rb_2S-T\ell_2S$ systems. The first two are hexagonal, the third is monoclinic. The last structure is based on the CaF_2 type, i.e. they are derived from "K_8S_4" by replacement of one K^+ by $T\ell^+$.[304]

The following phases were identified in the Tℓ-V-S system: $T\ell_3VS_4$, $T\ell V_5S_8$, $T\ell_xV_6S_8$ and $T\ell_2V_2S_5$.[305]

The chloroform adduct of thallium(I) diethylthiocarbamate, $[T\ell(S_2CNEt_2)]_2.CHC\ell_3$ forms monoclinic crystals, space group $P2_1/c$. The thallium atoms are four-coordinate, with the Tℓ-S distances in the range 2.9-3.5Å in the dimeric, centrosymmetric units $(T\ell S_2CNEt_2)_2$. Each thallium atom also interacts with a further sulphur, in another unit (3.7-3.8Å), and (weakly) with two chlorine atoms (Tℓ-Cℓ, 3.9-4.5Å) of the chloroform molecules.[306]

$T\ell_6Ag_2I_{10}$ is produced by heating a stoichiometric mixture of $T\ell I+AgI+I_2$ at 400°c _in vacuo_, or by refluxing a 3:1 mixture of TℓI and AgI in 67% aqueous HI solution. The crystals belong to the space group $P\bar{6}2c$. The structure is built up from $T\ell_6I_6$ units in chains parallel to the c axis, Ag_2 pairs and I_4^{2-} polyiodide ions are also present.[307]

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