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Chapter 3

ELEMENTS OF GROUP 3

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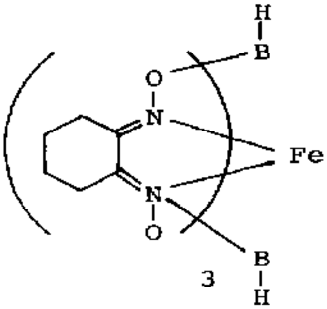
3.1 BORON

3.1.1 Boranes

A combination of valence ionisation potentials and core binding energies was used to probe the bonding in the adducts $BH_3.L$, where $L = NH_3$, NMe_3, CO, CNMe, PF_3 or PMe_3. π-back-bonding is only significant for L = CO or PF_3. The stabilisation of the Lewis base lone pair on coordination to BH_3 is correlated with the proton affinity of the Lewis base.[1]



(1)

(1) is prepared by the reaction of cyclohexanedione oxime with anhydrous $FeBr_2$ and $NaBH_4$ in MeCN. νB-H is at 2490 cm^{-1}, i.e. terminal. The terminal B-H bonds are chemically very unreactive, presumably due to the steric constraints of the encapsulating ligand.[2] CNDO calculations have been performed, for the processes (1) and (2), where $pz = N_2C_3H_3$, pyrazolyl, showing

$$R_2BH + Hpz \rightarrow R_2Bpz + H_2 \qquad \ldots(1)$$

$$2R_2Bpz \rightarrow R_2B(\mu\text{-}pz)_2BR_2 \qquad \ldots(2)$$

that for R = H both steps are energetically favourable. For $R = \frac{1}{2}MeN(CH_2)_2NMe$ only the first step is favoured, although (3) is

$$R_2Bpz + Hpz \rightarrow R_2B(\mu\text{-}pz)_2H \qquad \ldots(3)$$

favoured in this case.[3]

The first direct report has been made of the $^{11}B-^{11}B$ coupling constant for diborane, i.e. ±3.8±0.5Hz.[4] $PtBr_2$ promotes cage growth and dehydro-coupling reactions between B_2H_6 and small polyhedral boranes and carbaboranes. The products are either larger single-cage compounds or bridge-substituted diborane-polyhedral carbaborane or borane complexes. Such a reaction between B_2H_6 and 1,5-$C_2B_3H_5$ gives the new <u>arachno</u>-carbaborane 5,6-$C_2B_6H_{12}$.[5]

Microwave spectra have been obtained for B_2H_5Cl and 3 isotopic species; these gave the following structural parameters: r(B...B) 1.776±0.003Å; r(B-Cl) 1.766±0.004Å; ∠B-B-Cl 121.1±0.1°. The distance between the bridge hydrogens was estimated to be 2.03 ±0.03Å.[6] $B_2H_4.2NMe_3$ is isolated as a decomposition product (at 0°C) of $B_3H_7.NMe_3$. It was characterised by ^1H and ^{11}B n.m.r. spectroscopy.[7] The reaction (4) gave the new adduct $B_4H_7.2PMe_3{}^+BF_4{}^-$.[8]

$$B_4H_8.2PMe_3 + Ph_3C^+BF_4^- \rightarrow B_4H_7.2PMe_3{}^+BF_4^- + Ph_3CH \qquad ...(4)$$

Re-calculation of the stable geometries for the possible transient intermediates B_3H_9 and B_4H_{12} suggest that these should be of C_{3v}, C_{2v} symmetries respectively, not D_{3h}, D_{4h} as previously thought.[9] B_5H_9 and B_2H_6 undergo hydrogen isotope exchange with deuteriated aromatic hydrocarbons. Lewis acid-catalysed H/D exchange between C_6D_6 and the apical H atom of B_5H_9 gives 1-DB_5H_8 at ambient temperature. Uncatalysed exchange gives 1,2,3,4,5-$D_5B_5H_4$ at 45°C, B_5D_9 at 120°C.[10] MNDO semi-empirical M.O. calculations only predict the observed structure of B_5H_9 as the most stable form on the addition of polarisation functions (d-orbitals on B) and correlation correction (Møller-Plesset perturbation of the SCF wavefunction to orders 2 and 3). The possibility that some of the less-stable structures could be transition states for B_5H_9 rearrangements was explored.[11] Halopentaboranes(9) can be converted to the parent B_5H_9 in high yields by $^nBu_3SnH$. With $^nBu_3SnD$, DB_5H_8 is produced, with the D statistically distributed between 3 hydrogen environments in the pentaborane cage.[12]

The kinetics of gas-phase thermolysis of B_6H_{10} were followed by mass-spectrometry. The decomposition is a second-order process, with an activation energy of 79.7±3.7 kJ.mol^{-1}. The rate of reaction was less than previously thought, with the main products as H_2 and a non-volatile solid. The mechanism is believed to involve a $\{B_{12}H_{20}\}^{\ddagger}$ activated complex, and possibly $\{B_{12}H_{16}\}$.[13]

Selectively ^{10}B-labelled $\mathrm{3\text{-}MeB_6H_{11}}$ was prepared from $\mathrm{1\text{-}MeB_5H_8}$ and 96% ^{10}B-labelled $\mathrm{B_2H_6}$. B(1), B(2) and B(6) of the product have 46±5% ^{10}B; B(3), B(4) and B(5) are isotopically normal.[14]

^{10}B and ^{11}B n.q.r. spectra of $\mathrm{B_{10}H_{14}}$ were obtained and assigned, correcting earlier reports.[15] A new procedure for the preparation of $\mathrm{6,6'\text{-}(B_{10}H_{13})_2O}$ also gave $\mathrm{6\text{-}B_{10}H_{13}OH}$, fully characterised by ^{1}H, ^{11}B n.m.r., and mass spectroscopy. Both compounds react with *cis*-$\mathrm{PtCl_2L_2}$ (where L = $\mathrm{PMe_2Ph}$ or $\mathrm{PPh_3}$) to give 3 platinaboranes: *arachno*-$\mathrm{L_2PtB_8H_{12}}$; *nido*-$\mathrm{L_2PtB_{10}H_{12}}$ and $\mathrm{Pt_2(\mu\text{-}\eta^3\text{-}B_6H_9)_2L_2}$. The last has a centrosymmetric 14-vertex structure with two $\mathrm{B_6H_9}$ units above and below an almost linear P-Pt-Pt-P system. The $\mathrm{B_6H_9}$'s are symmetrically trihapto. $\mathrm{6,6'\text{-}(B_{10}H_{13})_2O}$ with *cis*-$\mathrm{NiCl_2(PMe_2Ph)_2}$ gives, among other products, a new species: *closo*-$\mathrm{(PhMe_2P)_2NiB_9H_7Cl_2}$.[16]

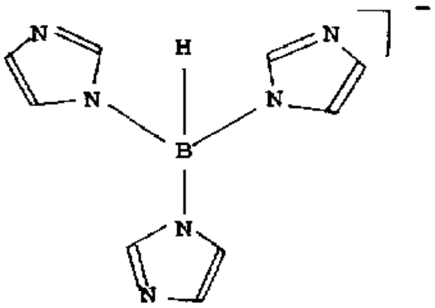
$\mathrm{1,10\text{-}B_{10}H_8(N_2)_2}$ with $\mathrm{CO/CH_4}$ mixtures or CO in benzene at 130°C give $\mathrm{B_{10}H_8(CO)_2}$ substituted by Me, Ph respectively, i.e. $\mathrm{MeB_{10}H_7(CO)_2}$ (two isomers), $\mathrm{Me_2B_{10}H_6(CO)_2}$ (one isomer), $\mathrm{PhB_{10}H_7(CO)_2}$ (two isomers). Thus C-H activation has occurred.[17] A study was made of oxidative fusion or coupling reactions of $\mathrm{B_5H_8^-}$ to $\mathrm{B_{10}H_{14}}$ or $\mathrm{2,2'\text{-}(B_5H_8)_2}$ in the presence of $\mathrm{FeCl_2/FeCl_3}$; of $\mathrm{B_5H_8^-}$ to $\mathrm{B_{10}H_{14}}$ alone in the presence of $\mathrm{RuCl_3}$; and of $\mathrm{1\text{-}XB_5H_7^-}$ (X = D or Me) to $\mathrm{2,4\text{-}B_{10}H_{12}D_2}$, $\mathrm{2,2\text{-}(1\text{-}CH_3B_5H_7)_2}$ with $\mathrm{RuCl_3}$ or $\mathrm{FeCl_2/FeCl_3}$. $\mathrm{B_{10}H_{13}^-}$ gives *n*- and *i*-$\mathrm{B_{18}H_{22}}$ on treatment with $\mathrm{RuCl_3}$/THF and subsequent exposure to air. Fusions of square-pyramidal cobaltaboranes give a good route to, for example, $\mathrm{Cp_2Co_2B_8H_{10}}$ isomers.[18]

The reaction of $\mathrm{K^+B_6H_9^-}$ with $\mathrm{FeCl_2/FeCl_3}$ in $\mathrm{Et_2O}$ produces $\mathrm{B_{12}H_{16}}$, the first neutral $\mathrm{B_{12}}$ hydride. The cage skeleton is conjuncto-type, with open $\mathrm{B_6}$ and $\mathrm{B_8}$ units joined along a common B-B edge, and their open faces on opposite sides of the molecule. There are 10 terminal and 6 bridging hydrogens, with 2 of the borons only having bridging hydrogens attached. $\mathrm{B_{12}H_{16}}$ with KH/THF forms $\mathrm{B_{12}H_{15}^-}$.[19]

The crystal and molecular structures of $\mathrm{1,2'\text{-}}$(*nido*-$\mathrm{B_{10}H_{13})_2O}$ have been determined, and they confirm earlier n.m.r. data. The intercluster B-B *conjuncto* linkage is 169.6(4)pm long.[20]

3.1.2 Borane Anions and Metallo-derivatives

The complex $\mathrm{MoF(N_2C_6H_4Me\text{-}p)_2[HB(C_3H_3N_2)_3]}$ forms monoclinic crystals, space group $P2_1/n$.[21] Several octahedral transition-metal complexes have been reported for the hydrotris(imidazolyl)-borate anion, (2).[22]



(2)

The total energy, B-H equilibrium distance, symmetric stretching wavenumber and SCF vertical ionisation potentials have been calculated for BH_4^- using the variational cellular method.[23] Non-empirical M.O. calculations of the relative energies of uni-, bi- and tridentate forms of $LiBH_4$ were carried out in the SCF approximation, using a 6-31G** basis set. These gave the tridentate form as having lowest energy, then bi-, then unidentate.[24]

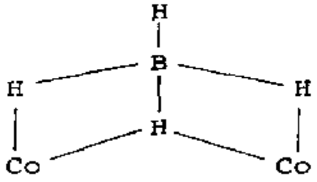
BH_3Cl^- is formed, as the $[(Ph_3P)_2N]^+$ salt, by the reaction of Cl^- with B_2H_6 in CH_2Cl_2 at -78°C; (5). It was characterised by

$$\tfrac{1}{2}B_2H_6 + Cl^- \rightarrow BH_3Cl^- \qquad \ldots(5)$$

i.r. and n.m.r. spectra. The crystal structure confirms the approximately tetrahedral geometry at boron, and shows that the B-Cl bond is unusually long (200.3pm).[25] Crystals of $[Th(BH_3Me)_4]_2.OEt_2$ are monoclinic, space group $P2_1/c$, while those of $[Th(BH_3Me)_4OC_4H_8]_2$ are also monoclinic, but space group $P2_1/n$. The thorium atoms are bridged by two BH_3Me ligands via one of the hydrogens of each BH_3 group. N.m.r. and i.r. data suggest that the dimers break up in solution.[26]

$Mg(BH_4)_2.nNH_3$, where n = 2 or 6, have been isolated, characterised by i.r. spectroscopy, and their thermal decompositions studied.[27] The crystal structure of $Zr_3S_3(S^tBu)_2(BH_4)_4(THF)_2$ shows that there are 3 tri- and one bidentate BH_4^- ligands.[28] $[Hf\{N(SiMe_2CH_2PMe_2)_2\}]_2(\mu\text{-}H)_3(BH_4)_3$, on the other hand, contains three different BH_4^- ligands, one tri-, one bi- and one unidentate. N.m.r. shows that there is rapid exchange between the 3 types in solution.[29] $Ta(BH_4)_2H_2(PMe_3)_4$ can be prepared from $TaCl_2H_2(PMe_3)_4$ and $LiBH_4$ in the presence of PMe_3. I.r. and n.m.r. spectra were consistent with bidentate BH_4^-. Reaction of the complex with CO gave $Ta(BH_4)(CO)_3(PMe_3)_3$, with unidentate BH_4^-.[30]

The red, crystalline complex $Fe(H)(H_2BH_2)(tppme)$, where tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane, has Fe-H(B) distances of 158(11), 165(10)pm; (Fe)H-B, 132(12), 118(10)pm, and (H)B-H 110(9), 108(13)pm.[31] $[Co(BH_4)\{Ph_2P(CH_2)_5PPh_2\}]_2$ forms triclinic crystals, space group $P\bar{1}$. Two Co(I) atoms are bridged by phosphine ligands and BH_4 in a hitherto unknown way. Each BH_4 group chelates to each Co using one common H, leaving one terminal H uninvolved, (3).[32]

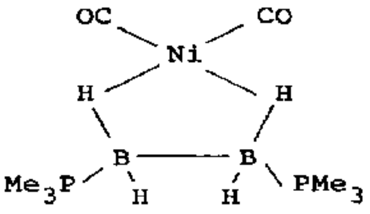


(3)

CO_2 reacts with $(L\text{-}L)(Ph_3P)Cu(BH_4)$, where L-L = phen or 3,4,7,8-tetramethylphen, in the presence of free PPh_3. In non-protic solvents, $[(L\text{-}L)(Ph_3P)_2Cu][HB(O_2CH)_3]$ (for L-L = phen only) and $[(L\text{-}L)(Ph_3P)_2Cu][H_2B(O_2CH)_2]$ are formed. In protic solvents, however, covalent formato complexes are produced.[33] An ether adduct of lanthanum hydroboratozincate is obtained by the reaction of Zn and lanthanum hydroborates in ether. The i.r. spectrum shows that the hydroborate is bidentate.[34] $Zn(BH_4)_2$ and AlH_3 in Et_2O form solid ZnH_2 and (according to i.r. data) $AlH_2(BH_4)$ in solution.[35] $U(BH_4)_4$ and CpTl or $C_5H_6/C_6H_5CH_3$ give $CpU(BH_4)_3$. The crystal structure shows that the U-B distance is characteristic of tridentate BH_4^- ligands.[36]

I.r. spectra and other physicochemical properties were reported for complexes of macrocyclic polyethers with alkali metal boranes, $[M(L)]B_nH_m$, where M = Na, K; L = e.g. dibenzo-18-crown-6; B_nH_m = BH_4, B_3H_8.[37] N.m.r. data for the adduct

$Ni(CO)_2[B_2H_4.2PMe_3]$ (from $Ni(CO)_4$ and $B_2H_4.2PMe_3$) are consistent with the novel coordination type (4).[38]



(4)

High-field (360MHz) ^1H n.m.r. spectra of $B_3H_8^-$ and a number of mono- and di-substituted derivatives show that the spectral line shapes are best interpreted on the basis of partial quadrupolar relaxation.[39] The crystal structures of $[(Ph_3P)_2N]^+$ salts of $[B_3H_7NCBH_3]^-$, $[(B_3H_7)_2CN]^-$ and $[Ag(CNB_3H_7)_2]^-$ show that the effective anion symmetries are C_s, D_{2h} and C_2 respectively.[40]

Borane anions react with Ru(II) complexes (such as $RuCl_2(PPh_3)_2$) to give new polyhedral ruthenaborane clusters. Thus, *arachno*-$B_3H_8^-$ gives the colourless, four-vertex *arachno*-$[(OC)(Ph_3P)_2HRu\text{-}B_3H_8]$. *Nido*-$B_5H_8^-$ forms the pale yellow, 5-vertex *nido*-$[(OC)(Ph_3P)_2RuB_4H_8$, and the 6-vertex *nido*-$[(OC)(Ph_3P)_2RuB_5H_8]$. Some 6-ruthena-*nido*-decaboranes were produced from *arachno*-$B_9H_{14}^-$ and *nido*-$B_9H_{12}^-$.[41]

X-ray diffraction studies gave the detailed molecular structure of $(OC)(Ph_3P)_2HIrB_3H_7$ (monoclinic, space group $P2_1/n$). This contains a four-vertex 'butterfly' cluster, IrB_3, with the iridium at the 'hinge' position. This can be interpreted in terms of a capped-octahedral, seven-orbital, eighteen-electron, d^4 Ir(V) complex, with metal-borane bonding chiefly by three 2-electron, 2-centre Ir-B bonds.[42]

A review has been given of solvent-induced shifts in ^{11}B n.m.r. spectra of a range of metallaboranes and metallacarbaboranes, e.g. $2\text{-}(\eta^5\text{-}C_5H_5)CoB_4H_8$, $1,2,3\text{-}LFeEt_2C_2B_4H_4$ ($L = \eta^6\text{-}C_6H_6$ or $\eta^6\text{-}C_8H_{10}$) and $1,2,3\text{-}(\eta^8\text{-}C_8H_8)TiEt_2C_2B_4H_4$.[43]

The 1:1 reaction of B_5H_9 and NaCN gives $Na[B_5H_9CN]$. Excess B_5H_9 leads to the formation of $B_9H_{14}^-$. $Na[BH_3CN]$ gives only the latter.[44]

An improved synthesis of $2,2,2\text{-}(OC)_3\text{-}2\text{-}MnB_5H_{10}$ involves the reaction of $Mn_2(CO)_{10}$ with $2B_5H_9$ and 100atm. pressure of H_2, in the presence of heterogeneous catalysts, especially 5% Ru on a carbon support. $2,2,2\text{-}(OC)_3\text{-}2\text{-}ReB_5H_{10}$ is prepared similarly from $Re_2(CO)_{10}$. Both were characterised by ^{11}B n.m.r.[45] $(Ph_2PCH_2)_2CuB_5H_8$ is prepared directly from $(Ph_2PCH_2)_2CuI$ and KB_5H_8. N.m.r. spectra show that the product has a static structure in solution. It was suggested that all 2,3-μ-metallopentaboranes have similar structures.[46] $(Ph_3P)AuB_5H_8$ forms triclinic crystals, space group $P\bar{1}$. The Au is attached to two basal B atoms of the square-pyramidal B_5H_8 cage, and is virtually coplanar with the B(1)B(2)B(3) face.[47]

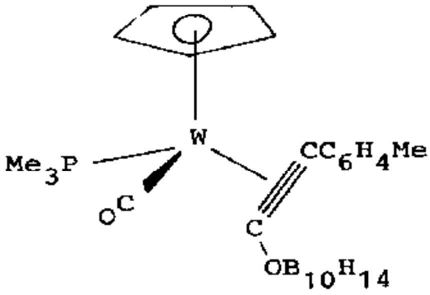
MNDO calculations on $B_6H_6^{\;2-}$, $B_6H_7^{\;-}$ and B_6H_8 demonstrate increased preference for a capped square-pyramidal cluster geometry, compared to octahedral, for increased protonation.[48] Cluster bond enthalpies, E_L(B-B) and orders $\bar{n}$(B-B) were estimated for $B_nH_n^{\;2-}$ (n = 6, 8-12), and compared with bond-index-based bond enthalpies, E_I(B-B). The latter approach suggests that all are of comparable stability, the former that n = 6, 10, 12 are more stable than n = 8, 9, 11. For n = 5, the former calculations suggest that the ion would be unstable, while for n = 7 a stability comparable with n = 8 was suggested.[49]

$M_2B_6H_6.xH_2O$, where M = Li^+-Cs^+, Me_4N^+, Bu_4N^+, Ph_4P^+; x = 0-7, were prepared. They are quite stable towards hydrolysis, heat and oxidation.[50] $(Bu_4N)_2B_6H_6$ and $NaBPh_4$ in MeOH give a convenient synthesis of anhydrous $Na_2B_6H_6$.[51]

New syntheses of 2,5;6,10;8,10-tri-μ-hydro-nonahydro-*nido*-nonaborate(1−), $B_9H_{12}^{\;-}$, salts gave crystals suitable for X-ray analysis. This shows the anion to have a *nido*-nine vertex cage structure, based in a parent bicapped square antiprism with one 5-connected vertex removed. The pentagonal open face is symmetrically bridged by 3 (μ-H) atoms. The polyhedron has effective C_s symmetry.[52]

Mer-$ReCl_3(PMe_2Ph)_3$ with excess $(Et_4N)B_9H_{14}$ gives 6,6,6,6-$(PMe_2Ph)_3$H-*nido*-6-ReB_9H_{13} (40% yield) and 6,6,6,6-$(PMe_2Ph)_3$H-9-(OEt)-*nido*-6-ReB_9H_{12}. These, and a number of other minor products are all air-stable, coloured crystalline solids. N.m.r. data were consistent with *nido*-structures for all.[53] *Arachno*-$B_9H_{14}^{\;-}$ and $RuCl_2(PPh_3)_3$ form the orange, 10-vertex 1,1,1-(Ph_3P)HCl-1-RuB_9H_7-3,5-$(PPh_3)_2$. The structure of this is based on an "*isocloso*" C_{3v} 1:3:3:3 RuB_9 stack, with the nine-coordinate metal occupying the unique six-connected apical position. Suggestions were made as to the possible electronic configuration. Similar results were reported for the 11-vertex $1,1-(Ph_3P)_2-1-RuB_{10}H_8-2,5-(OEt)_2$, from $RuCl_2(PPh_3)_3$ and closo-$B_{10}H_{10}^{2-}$ in refluxing ethanolic chloroform.[54] $B_9H_{13}X^-$, where X = H, NCS, NCSe, $NCBPh_3$, $NCBH_3$ or $NCBH_2NCBH_3$, and $[Cu(PPh_3)_2]BH_4$ react to give $Cu(PPh_3)_2(B_9H_{13}X)$. Several of these are fluxional in solution, down to −50°C.[55]

The previously-proposed mechanism for the formation of $B_{10}H_{10}^{2-}$ by the thermolysis of BH_4^- was shown to be incorrect.[56] Electrochemical and n.m.r. (^1H, ^{11}B) studies have been carried out on $B_{10}H_{13}L^-$, where L = PPh_3, py, quinuclidine, piperidine, CN^-, SMe_2, and also on $B_{10}H_{12}LL'$, where L,L' = py, PPh_3 or CN^-. The SMe_2 compound was thought to have a different structure from the others, with fluxional SMe_2 behaviour.[57]



(5)

Decaborane(14) reacts with carbonyl(η⁵-cyclopentadienyl)(η²-4-methylphenylketenyl)(trimethylphosphine)tungsten to produce (5), characterised by X-ray diffraction and spectroscopic data.[58] Two-dimensional COSY $^{11}B-^{11}B$ measurements on nido-$Me_2TlB_{10}H_{12}$ correlates individual ^{11}B doublet components associated with particular ^{205}Tl spin states. It is thus possible to determine the relative signs and magnitudes of the various intercluster coupling constants, $^nJ(^{205}Tl-^{11}B)$.[59]

$(C_5Me_5)RhB_{10}H_{11}Cl(PMe_2Ph)$ has a novel nido-7-metallaundecaborane structure, with one BHB and two RhHB bridging H atoms, compared to the usual two BHB bridging H atoms. The three bridging hydrogens undergo exchange ($\Delta G^{\ddagger}$ ca. 33kJ.mol^{-1}). The results suggest that the parent nido-$B_{11}H_{14}^-$ has a conventional BHB bridge, styx 3730 structure, rather than one with an H_3^+

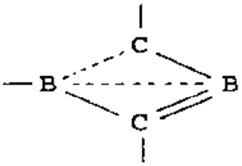
triangle perpendicular to the molecular axis.[60] Dissolving *nido*-[(η^5-C_5Me_5)$RhB_{10}H_{11}Cl(PMe_2Ph)$] in CH_2Cl_2 in the presence of H_2= gives an open 12-vertex oxametalladodecaborane, (η^5-C_5Me_5)$RhOB_{10}H_9Cl(PMe_2Ph)$. This is the first non-carbon-containing open 12-vertex polyhedral boron cluster compound, and the first boron cluster compound to contain an oxygen atom bound solely to boron in a contiguous cluster position.[61]

$AuBr_2(S_2CNEt_2)$ and 7,7-(PMe_2Ph)-*nido*-7-$PtB_{10}H_{12}$ gives a 52% yield of μ-2,7-($SCSNEt_2$)-7-(PMe_2Ph)-*nido*-7-$PtB_{10}H_{11}$. The structure is that of a *nido*-7-platina-undecaborane with an exopolyhedral N,N-diethyldithiocarbamate bridging the B(2) and Pt(7) positions to form a $\overline{\text{Pt-B-S-C-S}}$ five-membered ring.[62] $B_{10}H_{14}$ and Et_3PAuMe give the triple-cluster complex $(H_{12}B_{10}Au)(AuPEt_3)_4(AuB_{10}H_{12})$, whereas Cy_3PAuMe gives $Cy_3PAuB_{10}H_{13}$.[63]

Electron-counting in large closo-boranes, e.g. $B_{32}H_{32}{}^q$, where q = +4, -2, -8, has been considered in terms of the pairing principle in Stone's tenser surface harmonic (TSH) theory.[64]

3.1.3 Carba- and other Non-metal Heteroboranes

A number of $C_2B_2H_4$ isomers have been studied by *ab initio* M.O. methods. Several have experimentally known analogues, but there are no representatives yet reported for the global energy minimum, (6). The most stable $(CH)_2(BH)_2$ form is tha puckered 1,3-diboretene, (7).[65]



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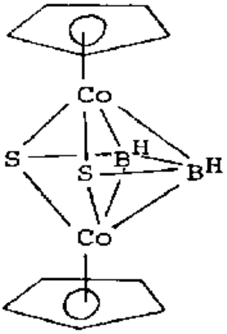
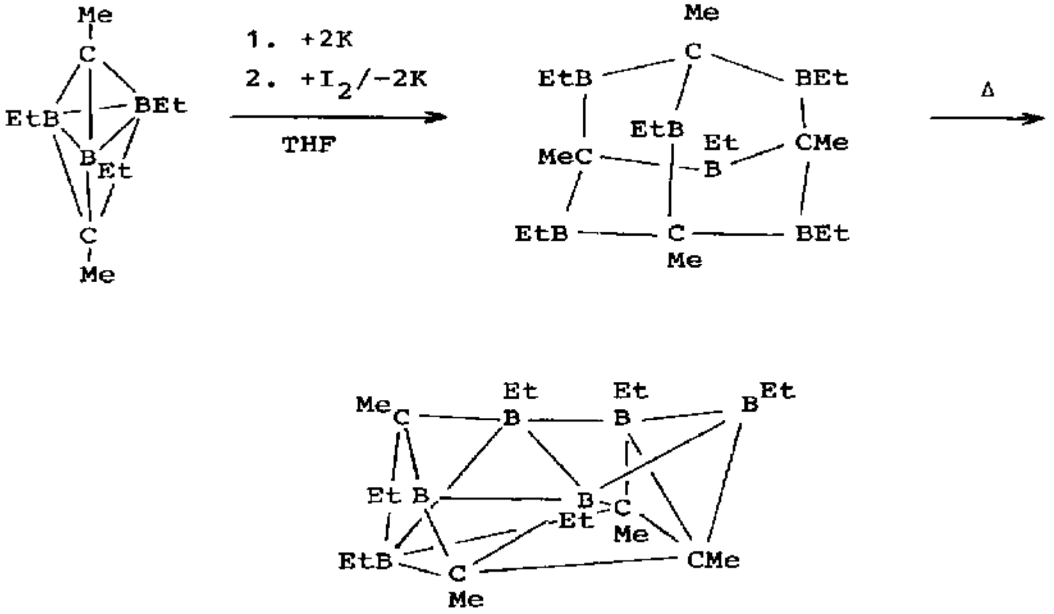


(8)

(7)

Thermally-generated cobalt atoms with cyclopentadiene, B_5H_9 and either COS or H_2S give several sulphur-containing clusters, especially the new species (*8*), a triple-decker sandwich.[66]

Evidence was found from n.m.r. for the dimerisation of a C_2B_3 *closo*-carbaborane(5) to a C_4B_6 adamantane, and its subsequent isomerisation to a fluxional C_4B_6 carbaborane(10), equation (6).[67]



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Quantitative yields were reported in preparations of air-stable 2-Me_3Si-3-R-2,3-$C_2B_4H_6$ and $[R(H)C{=}CSiMe_3]_3B$, where R = H, Me or $SiMe_3$.[68] Kinetic studies were made on the rearrangements of the *B*-monochloro derivatives of *closo*-2,4-$C_2B_5H_7$ and on the rearrangement of 5,6-Cl_2-*closo*-2,4-$C_2B_5H_5$. It was possible to characterise all of the *B*,*B*'-Cl_2-*closo*-2,4-$C_2B_5H_5$ isomers for the first time.[69] Synthetic routes were reported for all of the *B*-X-*closo*-2,4-$C_2B_5H_6$ and *B*,*B*'-X_2-*closo*-2,4-$C_2B_5H_5$, where X = Br or I, isomers, except for 1,7-Br_2-2,4-$C_2B_5H_5$. Isomer equilibrium measurements show that the stabilities of the *B*-monobromo isomers are in the sequence: 3-Br > 5-Br > 1-Br-2,4-$C_2B_5H_6$, but for the *B*-monoiodo isomers they are: 5-I > 3-I > 1-I-2,4-$C_2B_5H_6$. For the dihalo-species, the stability sequences are: (X = Br) 3,5- ≳ 5,6- > 1,3- > 1,5- > 1,7-; (X = I) 5,6- > 3,5- > 1,5- ≳ 1,3- > 1,7-.[70] Halogen exchange was observed between *B*-halo-derivatives of *closo*-2,4-$C_2B_5H_7$ and $NR_4^+X^-$, but only when the "reagent" halide is smaller than the "leaving" halide. Increase in the (cage)boron-halogen bond energy is the main driving force.[71]

^{11}B and ^{1}H n.m.r. spectra of CB_8H_{14} and $CB_8H_{13}^-$ were assigned unambiguously using decoupling and COSY techniques. Both species contain unsymmetrical bridging hydrogens. The endo-H attached to the carbon is involved in exchange with all 3 bridging hydrogens in $CB_8H_{13}^-$, but not in $C_2B_8H_{14}$.[72]

A phase transition was found at 188K by Raman spectroscopy in the temperature range 15-470K for the plastic solid carbaborane p-$C_2B_8H_{10}$.[73] BH_4^- reduction of nido-5,6-$C_2B_8H_{12}$ is a convenient synthesis of arachno-6,9-$C_2B_8H_{14}$. Electrophilic halogenation of the latter gives 1-X-6,9-$C_2B_8H_{13}X$, where X = Cl, Br or I.[74] Stereoselective addition of HX (where X = F, Cl, Br or I) to unsaturated nido-[6,9-$C_2B_8H_{10}$]$^{2-}$ gives a series of arachno-5-X-6,9-$C_2B_8H_{13}$ compounds. HF/H_2O gave dimeric 5,5'-O-(6,9-$C_2B_8H_{13}$)$_2$. All were characterised by ^{1}H and ^{11}B n.m.r.[75]

MNDO calculations for 1-SB_9H_9, and photoelectron spectra, enabled cluster-bonding M.O.'s to be assigned. The electronic structure was very similar to those of $B_{10}H_{10}^{2-}$, 1,10-$B_{10}H_8(N_2)_2$[76] and 1,10-$C_2B_8H_{10}$. The bonding in 1-$SB_{11}H_{11}$ was also analysed.

The salt Cs^+[nido-7-(p-C_6H_4NCS)-9-I-7,8-$C_2B_9H_{11}$]$^-$ crystallises in the monoclinic space group $P2_1/c$.[77] Salts of $B_{10}H_{10}CH^-$ with alkali metal or R_4N^+ cations have been prepared. I.r. spectra and solubility in water at 25°C were reported.[78] The new derivatives 7-L-7-$CB_{10}H_{12}$, where L = $Me_2C{=}NH$, $(CH_2)_5C{=}NH$, PhCH=$(PhCH_2)N$, $HOOCCH_2NH_2$, CH_3CONH_2, $(CH_2)_6N_4$ or $(CH_3)_2S$, were prepared, and characterised by i.r., ^{1}H and ^{11}B n.m.r. spectroscopy.[79]

Optimum procedures were determined for the thallation of 1,2-, 1,7- and 1,12-closo-dodecaboranes(12).[80] Improved and simplified procedures have been reported for a high-yield preparation of 9-iodo-o-carbaborane; by the treatment of o-carbaborane with I_2 and $AlCl_3$ in CH_2Cl_2.[81]

3.1.4 Metallo-heteroboranes

$(\eta^6\text{-}C_8H_{10})Fe\{[Ph(CH_2)_3]C_2B_4H_5\}$ and Al/$AlCl_3$ give $[\eta^6\text{-}C_6H_5(\overline{CH_2)_3]Fe(C}_2B_4H_5)$, containing a trimethylene group bridging benzene and carbaborane ligands. Reaction of this with CH_3OH forms nido-$[\eta^6\text{-}C_6H_5(\overline{CH_2)_3]Fe(C}_2B_3H_5)$.[82]

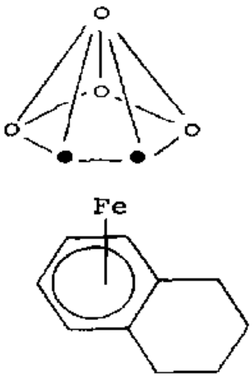
Closo-1,2,3-$(\eta^6\text{-}C_6R_6)Fe(Et_2C_2B_4H_4)$, where R = H or Me, and

$1,2\text{-}(NMe_2)_2(CH_2)_2$ produce *nido*-$(\eta^6\text{-}C_6R_6)Fe(Et_2C_2B_3H_5)$. For R = H, deprotonation of this with KH, followed by metal-promoted oxidative fusion, gives $(\eta^6\text{-}C_6H_6)Fe(Et_4C_4B_6H_6)$, shown to have an 11-vertex FeC_4B_6 cage. Reaction of $(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)$ with biphenyl in vacuo at 200°C forms $(\eta^6\text{-}C_6H_5\text{-}C_6H_5)Fe(Et_2C_2B_4H_4)$. Treatment of this with more of the Fe precursor gives $(Et_2C_2B_4H_4)Fe(\eta^6\text{-}C_6H_5\text{-}C_6H_5\text{-}\eta^6)Fe(Et_2C_2B_4H_4)$.[83]

Thermally-generated Co atoms, with B_6H_{10}, bis(trimethylsilyl)-acetylene and cyclopentadiene give as major products: 5:1',2'-$[1\text{-}(\eta\text{-}C_5H_5)Co\text{-}2,3\text{-}(Me_3Si)_2C_2B_4H_3][B_2H_5]$; $1\text{-}(\eta\text{-}C_5H_5)Co\text{-}4,6\text{-}(Me_3Si)_2\text{-}C_2B_6H_6$ and $1\text{-}(\eta\text{-}C_5H_5)Co\text{-}4,5\text{-}(Me_3Si)_2C_2B_6H_6$, with smaller amounts of $5\text{-}(\eta\text{-}C_5H_5)Co\text{-}1,8\text{-}(Me_3Si)_2C_2B_5H_5$ and $1\text{-}(\eta\text{-}C_5H_5)Co\text{-}2,3\text{-}(Me_3Si)_2\text{-}C_2B_4H_4$. The crystal structure of the first species shows it to have a unique bridged structure with a *closo*-$1\text{-}(\eta\text{-}C_5H_5)Co\text{-}2,3\text{-}(Me_3Si)_2C_2B_4H_3$ sandwich complex having an exopolyhedral B_2H_5 group bound to the B(5) cage atom by a B-B-B three-centre bond i.e. it is a bridge-substituted organometallic derivative of diborane.[84]

Several seven-vertex phosphinohalometallacarbaboranes of Fe, Co and Ni have been reported, e.g. $1,5\text{-}(Ph_3P)_2\text{-}1,2,3\text{-}Ni(Et_2C_2B_4H_3)$, with phosphines attached to Ni and B, and $1,1\text{-}(Ph_2PCH_2)_2\text{-}1\text{-}Cl\text{-}1,2,3\text{-}M(Et_2C_2B_4H_4)$, where M = Co or Fe. All were characterised by single-crystal X-ray diffraction and various spectroscopic measurements. The MC_2B_4 cages all have the normal 7-vertex *closo* (pentagonal bipyramidal) geometry.[85] $K_2(R_2C_2B_4H_5)$ (where R = H or Me) react with $(Ph_3P)_2CuBr$ or $(Ph_2PCH_2)_2CuI$ to form $(Ph_3P)_2CuC_2B_4H_7$, $(Ph_3P)_2CuMe_2C_2B_4H_5$, $(Ph_2PCH_2)_2CuC_2B_4H_7$, and $(Ph_2PCH_2)_2CuMe_2C_2B_4H_5.\frac{1}{2}CH_2Cl_2$. All were characterised by ^1H and ^{11}B n.m.r., and have *nido*-pentagonal pyramidal geometry, with the Cu^I having replaced a bridging hydrogen in the parent carbaborane.[86] The polycyclic arene complexes of ferracarbaboranes, (**9**)-(**12**), where o = BH, ● = CEt, have been reported and characterised.[87]

$3,1,2\text{-}(\eta\text{-}C_6H_6)RuC_2B_9H_{11}$ and ethanolic KOH in refluxing ethylene glycol give a polyhedral contraction reaction, to form $1,2,4\text{-}(\eta\text{-}C_6H_6)RuC_2B_8H_{10}$ and $2,5,6\text{-}(\eta\text{-}C_6H_6)RuC_2B_7H_{11}$ in low yield. The latter forms triclinic crystals (space group $P\bar{1}$) with a 10-membered, *nido*-decaborane-like structure, and the Ru in the closed portion of the polyhedron. $(\eta\text{-}C_6H_6)OsCl_2.NCMe$ and $Tl[3,1,2\text{-}TlC_2B_9H_{11}]$ in THF give $3,1,2\text{-}(\eta\text{-}C_6H_6)OsC_2B_9H_{11}$. This is



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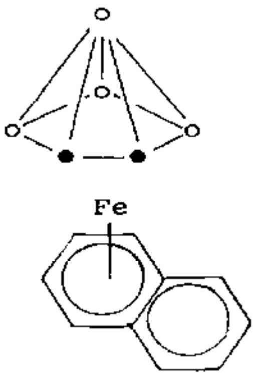

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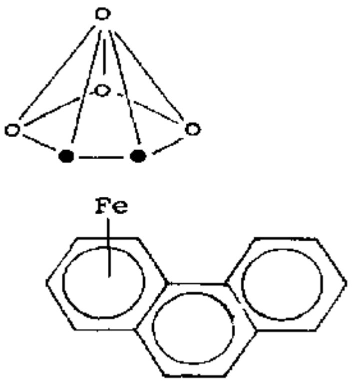

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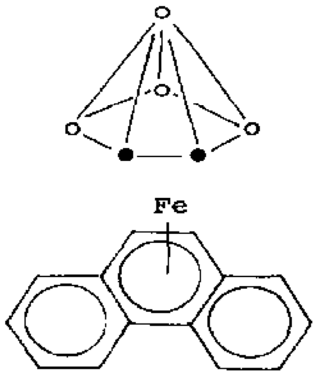


(12)

the first reported (π-arene)osmacarbaborane.[88]

The reaction of $Et_4C_4B_8H_8^{2-}$ with $CoCl_2$ in THF gives $(Et_4C_4B_8H_8)_2Co_2$ and $(Et_4C_4B_8H_7)_2Co_2$. Two-dimensional n.m.r. showed the former to consist of a pair of 14-vertex closo-$Co_2C_4B_8$ polyhedra sharing a common Co-Co edge, a previously unknown geometry in metallacarbaborane chemistry. The same reaction followed by addition of $B_5H_8^-$ gave several products including the former of the two above, and also, e.g. $(Et_4C_4B_8H_8)Co(Et_4C_4B_8H_7O-C_4H_8)$, $(Et_4C_4B_8H_7)_2CoH$ etc. $(Et_4C_4B_8H_8)_2Co_2$ and I_2/acetone react to form $(Et_4C_4B_8H_7)_2(OCMe_2)_2CoH$, in which the carbaborane ligands are bridged by an acetone molecule, with B-O-B bridging.[89]

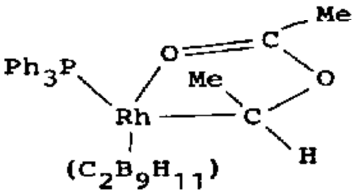
A number of mixed-ligand Co and Fe complexes have been prepared which are derived from $Et_4C_4B_8H_8^{2-}$ and $Et_2C_2B_4H_5^-$, e.g. treatment of $Et_4C_4B_8H_8^{2-}$ with $CoCl_2$ or $FeCl_2$ in THF, followed by addition of $Et_2C_2B_4H_5^-$ gave as the main product $(Et_2C_2B_4H_4)M(Et_4C_4B_8H_7-OC_4H_8)$ (M = Co,Fe). In these a <u>closo</u>-MC_2B_4 and a <u>nido</u>-MC_4B_8 cage are joined at a common M vertex. The 13-vertex MC_4B_8 has the shape of a 14-vertex <u>closo</u>-polyhedron (a bicapped hexagonal antiprism) with a missing equatorial vertex.[90] The complex $[N(PPh_3)_2][W(\equiv CR)(CO)_2(\eta-1,2-C_2B_9H_9Me_2)]$, where R = C_6H_4Me-4, reacts with $[M(CO)_2(NCMe)_2(\eta-C_9H_7)]^+BF_4^-$, where M = Mo or W, to give the dimetal complexes $[MW(\mu-CR)(CO)_3(\eta-C_9H_7)(\eta-C_2B_9H_9Me_2)]$.[91]

Protonation of <u>closo</u>-3,3,3-$(CO)_3$-3,1,2-$ReC_2B_9H_{10}$-1-CH_2OR (where R = H or Me) or <u>closo</u>-3,3,3-$(CO)_3$-3,1,2-$ReC_2B_9H_{10}$-1-$CR{=}CH_2$ produces stable carbenium cations in the zwitterionic complexes <u>closo</u>-3,3,3-$(CO)_3$-3,1,2-$ReC_2\overset{-}{B}_9H_{10}$-1-$\overset{+}{C}RR'$, where R = R' = H or Me; R = H, R' = Me.[92]

$Fe(cod)(\eta^5-C_5H_5)$ reacts with 2,3-Me_2-2,3-$C_2B_9H_9$ and the appropriate arene to give moderate yields of icosahedral 2,4-dicarba-1-ferraboranes with η^6-bonded benzene, toluene, o-xylene or naphthalene ligands e.g. <u>closo</u>-[1-$(\eta^6-C_6H_5Me)$2,4-Me_2-1,2,4-$FeC_2B_9H_9$]. $RuCl_2(\eta^6-C_6H_6)_2$ and $Tl(TlC_2B_9H_{11})$ form <u>closo</u>-[3-$(\eta^6-C_6H_6)$-3,1,2-$RuC_2B_9H_{11}$].[93] A variety of icosahedral metallacarbaboranes can undergo isomerisation under mild experimental conditions when reduced over sodium amalgam e.g. 3,1,2-$MC_2B_9H_{11}$, where M = $(\eta^6-C_6H_6)Ru$, CpCo or CpRh.[94]

$NiCl_2$ reacts with $[Cb_2Ni^{III}]Na$, where Cb = π-(3)-1,2-$C_2B_9H_{11}$, in the presence of L(=py or bipy) to form $[Cb_2Ni^{III}]_2Ni^{II}.4L$.[95] $Tl^+[3,1,2-TlC_2B_9H_{11}]^-$ and $PdCl_2(tmen)$, where tmen = $Me_2N(CH_2)_2NMe_2$, produce 3-(tmen)-3,1,2-$PdC_2B_9H_{11}$, with a "slipped" structure. The diamine can be readily replaced to give a series of 3-L_2-3,1,2-$PdC_2B_9H_{11}$ complexes.[96]

Bidentate and unidentate acetato derivatives of rhodacarbaboranes have been reported, e.g. $(PPh_3)(\eta^2-CH_3COO)RhC_2B_9H_{11}$, $(PPh_3)_2(\eta^1-CH_3COO)RhC_2B_9H_{11}$, and also chelated, stable species (<u>13</u>).[97]



(<u>13</u>)

Protonation of [*closo*-3,3-(η^4-bicyclo[2.2.1]hepta-2,5-diene)-1,2-Me_2-3,1,2-$RhC_2B_9H_9$]$^-$ with CF_3CO_2H/CD_2Cl_2 at -78°C gives an isolated fluxional intermediate, which isomerised on standing to 3-(η^2-vinyl)-3-(η^4-cyclopentenyl)-1,2-Me_2-3,1,2-$RhC_2B_9H_9$. Thermolysis of this at 40°C in C_6H_6 gave *closo*-3-(η^5-C_5H_4Et)-1,2-Me_2-3,1,2-$RhC_2B_9H_9$.[98] [*Nido*-7-(R)-9-(R')-7,9-$C_2B_9H_{10}$]$^-$, where R = Me, R' = Ph, and $(PPh_3)_3RhCl$ in refluxing ethanol produces *closo*-2,2-$(PPh_3)_2$-2-H-1-(Me)-7-(Ph)-2,1,7-$RhC_2B_9H_9$, rather than the expected *exo*-*nido* tautomer.[99] CF_3CO_2H in CH_2Cl_2 at -73°C protonates [*closo*-3,3-(η^4-1,5-cyclooctadiene)-1,2-Me_2-3,1,2-$RhC_2B_9H_9$$^-$, via an unstable intermediate, to form an unusually stable 16-electron rhodium(III) complex: *closo*-3-(η^3-C_8H_{13})-1,2-Me_2-3,1,2-$RhC_2B_9H_9$. This is not stabilised by any obvious M-H-C interactions.[100]

Rh(cod)(PR_3)Cl, where R = Ph, Et or Me, and [*nido*-7-R'-7,8-$C_2B_9H_{11}$]$^-$, where R' = H, Ph or 7'-*nido*-7',8'-$C_2B_9H_{11}$$^-$, form bimetallic rhodacarbaborane clusters containing Rh-Rh bonds, supported by Rh-H-B interactions. These determine the stereospecificity of the reactions, e.g. only one (of 6) isomer of $[Rh(PPh_3)C_2B_9H_{11}]_2$ is formed.[101] Deprotonation of 3 neutral *closo*-hydrido complexes, $[(L)_2$-H-$RhC_2B_9H_{11}]$, where L = PPh_3, CO or η^2-C_2H_4, under carefully-controlled conditions produces the corresponding isomeric [*closo*-$L_2RhC_2B_9H_{11}$]$^-$ species. The product with L = PPh_3 has a *closo*-structure similar to that in the parent hydrido complex. The RhP_2 plane lies approximately perpendicular to the least-squares plane passing through the bonding face of the carbaborane ligand.[102]

Ditertiary phosphines(L), $R_2P(C_2B_{10}H_{10})PR'_2$ (R = R' = Ph, NMe_2; R = Ph, R' = NMe_2) and $AuBr_2^-$ give three-coordinate complexes AuBrL, and the dimeric two-coordinate complex $(AuBr)_2\{Ph_2P(C_2B_{10}H_{10})PPh_2\}$. There was some evidence for the existence in solution of other 2-, 3- and 4-coordinate species.[103] The crystal structure of $AgB_{11}CH_{12}.2C_6H_6$ shows that two carbaborane anions are associated with each Ag^+ via terminal B-H bonds. The results support the idea that $B_{11}CH_{12}^-$ is a poor σ-donor, and possibly a novel non-coordinating anion.[104]

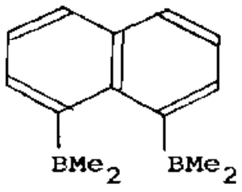
Preparations have been reported for several rhodium(I) complexes of 1,2-bisdiphenylphosphino-1,2-dicarbadodecaborane(dppb) e.g. RhCl(X)(dppb), where X = CO or PPh_3. Possible catalytic properties of these were examined.[105]

3.1.5 Compounds containing B-C Bonds

A study of the laser-initiated thermal synthesis of BEt_3 from B_2H_6/C_2H_6 mixtures showed this to be a convenient method of synthesis.[106] $(Me_2PhSi)_3CBF(OH)$, produced by the hydrolysis of $(Me_2PhSi)_3CBF_2$, is the first fully-characterised organofluorohydroxyborane. Coordination at the boron is approximately planar.[107]

A simple preparation has been reported for di-isopropyl(chloromethyl)boronate, $ClCH_2B(O^iPr)_2$, i.e. from (chloromethyl)lithium and tri-isopropylborate.[108] Three new preparative routes have been reported for methylboronic acid, $MeB(OH)_2$, and its anhydride, trimethylboroxin, $(MeBO)_3$.[109]

(14) has a very high affinity for H^-, because it readily forms a chelated complex with H^- that has unusual thermodynamic stability.[110] $Me_2Si(NH^tBu)_2$ is used as a starting material to prepare $Me_2Si(N^tBu)_2MX$, where M = B, Al, Ga or In, X = Me; $Me_2Si[N(^tBu)MX_2]_2$, where M = Al, Ga or In, X = Me or Cl; and $Me_2Si(NH^tBu)N(^tBu)MX_2$, where M = B, Al, Ga, In or Tl, X = Me or Cl.[111]



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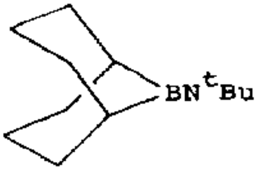


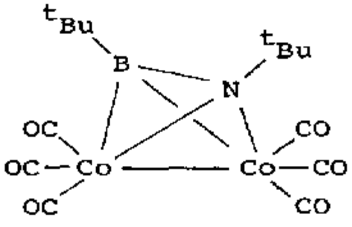
(15)

E.s.r. of the radical (15) shows that the unpaired electron occupies an orbital located in the C_2BNC plane.[112] Pyridine and 2,4-lutidine form 1:1 coordination compounds with dibutylboron triflate, 9-(((trifluoromethyl)sulphonyl)oxy)-9-borabicyclo[3.3.1]-nonane or 9-(((trifluoromethyl)sulphonyl)oxy)-9-borafluorene. 2,6-lutidine, however, gives borenium(1+) triflates with the first two reagents. The three bases form neutral addition compounds with dibutylboron chloride, 9-chloro-9-borabicyclo-[3.3.1]nonane and 9-chloro-9-borafluorene.[113]

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

The complex (16) is synthesised from $Co_2(CO)_8$ and $^tBuB{\equiv}N^tBu$.

Its structure shows an analogy with Co-alkyne complexes.[114] Photoelectron spectra were recorded for NH_2BF_2, $NHMeBF_2$ and NMe_2BF_2; their first ionisation potentials were 11.47, 10.45 and 9.49eV respectively.[115]



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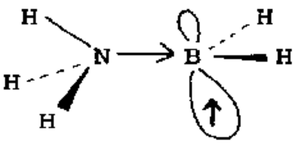


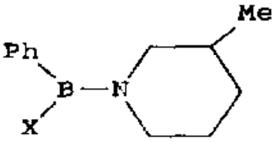
(17)

E.s.r. studies on the radical (17), an inorganic analogue of the ethyl radical, show that the bond angle at B is smaller than that at the equivalent position in the ethyl radical.[116] The rotational barrier for H_3B-NH_3 was studied at the Hartree-Fock level. A 6-31G* basis set sugested a barrier to rigid rotation of 1.85 kcal.mol^{-1}.[117] Thermal decomposition mass spectra of poly(aminoborane) show ions with -BH_2NH_2- units up to 9 atoms in length. The XPS spectrum suggests equal numbers of B and N atoms, each in a single type of environment i.e. a large cyclic structure.[118]

Tris(dichloroboryl)amine was prepared according to equation (7).

$$BCl_3(Xs) + (Me_3Sn)_3N \rightarrow N(BCl_2)_3 + 3Me_3SnCl \qquad \ldots(7)$$

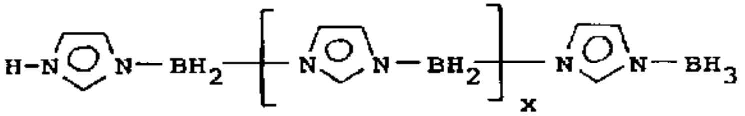
$N(BBr_2)_3$ and $N(BF_2)_3$ are prepared from this by transhalogenation. N.m.r. showed that $N(BF_2)_3$ has a planar skeleton, and mass spectra showed that the iminoboranes X_2B-N=BX have high stability in the gas phase.[119]



(18)

It has proved possible to use variable-temperature ^{13}C n.m.r. to obtain reliable activation parameters ΔH^* and ΔS^* for restricted rotation about the B-N bond in the aminoboranes (18, X = F or Br).[120] Rotational barriers (ΔG^*) about the $>$B-NMe$_2$ bond were determined for PhB(NMe$_2$)NH^{t}Bu and PhB(NMe$_2$)NHSiMe$_3$ by the same technique (values of 11.86, 13.5 kcal.mol^{-1} respectively).[121]

$H_3B.\overline{P(OCMe_2CH_2)_2N}.BH_3$ forms monoclinic crystals, space group P2$_1$/n. The B-P (187.3pm) and B-N (165.5pm) distances both confirmed the dibasic character of the ligand. N.m.r. data show that the B-N and B-P bonds are preserved in solution.[122] Imidazole-borane eliminates H$_2$ in ether solution over 1-2 weeks, leaving the air-stable polymer (19). The polymerisation was catalysed by excess diborane.[123]



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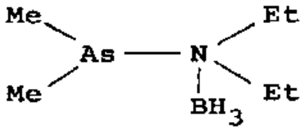

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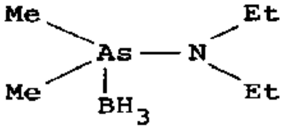
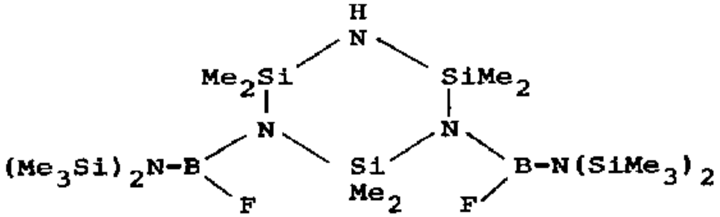


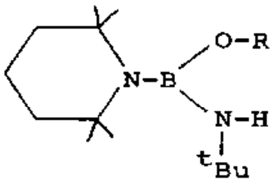
(21)

New 1:1 addition compounds of borane and aminoarsines have been described and characterised by ^{1}H, ^{11}B and ^{13}C n.m.r., i.e. (20) and (21).[124] Preparations and characterisations were reported for several fluoroboryl- and fluoroboranediyl-cyclosilazanes, e.g. (22).[125]



(22)

$Hg[N(SCF_3)_2]_2$ and BX_3, where X = Br, SCF_3 or Cl, react to form $B[N(SCF_3)_2]_3$. This is thermally stable, and a very weak Lewis acid. Preparations were also reported for $[(CF_3S)_2N]_2BX$, where X = Cl or Br, and $(CF_3S)_2NB(N_3)_2$.[126] (t-Butylimino)(2,2,6,6-tetramethylpiperidino)borane adds on ROH across the BN triple bond to form (27, where R = Me, ^{i}Pr, ^{t}Bu, Ph or $C_6H_2Me_3$). The relative rates of addition were chiefly governed by steric factors.[127]



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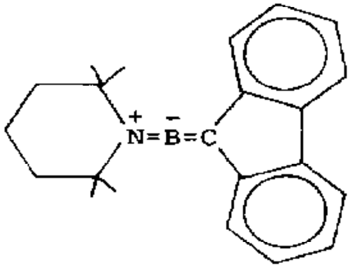

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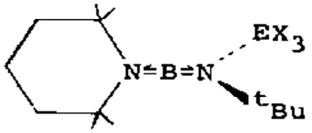
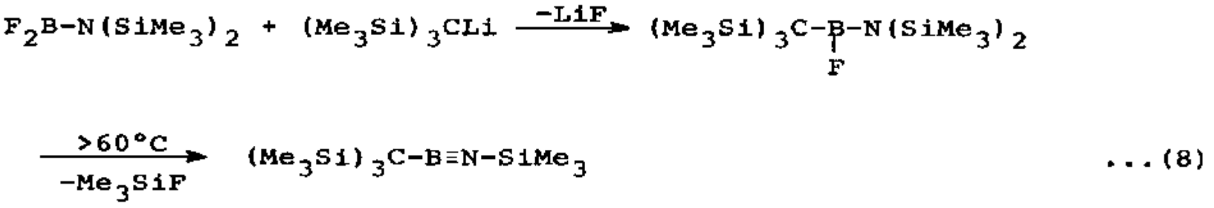


(25)

A stable 1-aza-2-bora-allene system has been prepared, (24), in which stability is conferred by the bulky substituents.[128] (tert-Butylimino)(2,2,6,6-tetramethylpiperidino)borane forms adducts with $AlCl_3$, $AlBr_3$ and $GaCl_3$, (25, EX_3 = $AlCl_3$, $AlBr_3$, $GaCl_3$), which retain two-coordinate boron.[129]

$^{t}Bu(Me_3Si)N{=}B{\equiv}N{-}^{t}Bu$, an amino-imino borane, is prepared by the gas-phase elimination of $FSiMe_3$ from the corresponding diaminoborane. It is stable at −30°C, but dimerises at room temperature; a number of its reactions were reported.[130] A new iminoborane has been prepared, equation (8). It is stable for

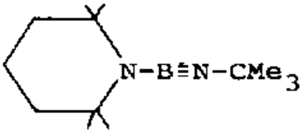


$$F_2B\text{-}N(SiMe_3)_2 + (Me_3Si)_3CLi \xrightarrow{-LiF} (Me_3Si)_3C\text{-}\underset{\displaystyle F}{\underset{|}{B}}\text{-}N(SiMe_3)_2$$

$$\xrightarrow[-Me_3SiF]{>60°C} (Me_3Si)_3C\text{-}B{\equiv}N\text{-}SiMe_3 \qquad \ldots(8)$$

months at room temperature due to the effect of the $(Me_3Si)_3C$ group.[131]

(26) adds $ROSO_2CF_3$ (where R = H or Me) to give the three-coordinate borane derivatives (27). Me_3SiI or $Me_3SiOSO_2CF_3$, on the other hand, form the two-coordinate species, (28, where X = I or SO_3CF_3).[132] Infrared and Raman spectra were reported for



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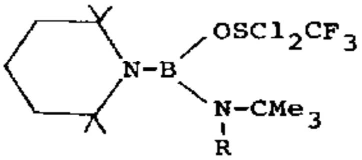

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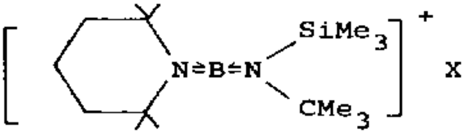
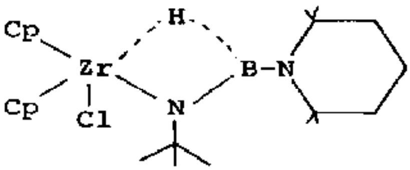


(28)

$Me_3CB{\equiv}NCMe_3$ and its ^{10}B isotopomer. The fundamental wavenumbers were assigned on the basis of a linear chain and staggered t-butyl groups (C_{3v} symmetry). There was evidence for Fermi resonance perturbing the $^{11}B{\equiv}N$ stretch.[133]

2:1 adducts (derived from $C_4H_4N_2.2BX_3$, where X = F or Br) were identified for unsubstituted, 2-methyl-, 2,3-dimethyl and 2,6-dimethylpyrazines. A 1:1 adduct could be identified only for 2,6-dimethylpyrazine.[134] Preparations were reported for the following boron-analogues of α-aminoacids: $R_3N.BH_2CO_2H$, where R = Et, ^nPr, ^nBu or ^sBu, by two alternative paths from $R_3N.BH_2CN$. They were characterised by i.r. and n.m.r. spectroscopy.[135]



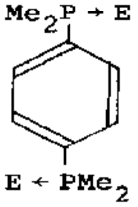
(29)

The novel system (29), reminiscent of a μ-H-metallaborane, is prepared by the reaction of $Cp_2Zr(H)Cl$ with the parent iminoborane.[136] An empirical relationship was derived for the ^{11}B n.m.r. chemical shift for methyl-substituted pyrazine-boranes.[137] Several borane adducts of pyridazine, pyrimidine, pyrazine and some of their methyl derivatives have been prepared and characterised by i.r., ^1H and ^{11}B n.m.r. spectroscopy.[138]

Convenient, high-yield syntheses have been developed for $Me_3PBH_2PMe_2(=X)$, where X = O or S. Both compounds are readily metallated at one of the PMe_3 methyl groups to give $Li[CH_2(CH_3)_2PBH_2P(CH_3)_2(=X)]$.[139] $Na[Fe(CO)_2(C_5Me_5)]$ reacts with Ph_2PCl to give $(C_5Me_5)(CO)_2Fe{-}PPh_2$, which forms a borane adduct with $BH_3.THF$: $(C_5Me_5)(CO)_2Fe{-}PPh_2{-}BH_3$. The B-P bond is longer than expected (194.9pm).[140] The following related adducts were also reported: $Cp(CO)_2(L)N{-}PPh_2{-}BH_3$, where M = Mo or W, L = CO or PMe_3.[141]

The adducts $(Ph_2P)_2(CH_2)_n.(BH_3)_2$ and $(Ph_2P)_2(CH_2)_n.BH_2I$, where n = 2, 3 or 4, were isolated for borane and iodoborane with bis(diphenylphosphino)alkanes. A relationship was found between the length of the carbon chain and the ^{11}B n.m.r. chemical shift.[142]

The borane adduct (to P) of diphenyl-2,6-dioxa-1,3-diazo-6-phospha-2-cycloöctyl-2 forms monoclinic crystals; space group $P2_1$.[143] The complexes (30), where E = BH_3, BEt_3, $AlMe_3$, $AlEt_3$ or $GaMe_3$, have been studied. The borane adducts are reduced by K in THF to form persistent anion radicals. For Al, such radicals are only observed <240K, while for gallium, reduction produces only Ga metal.[144]



(30)

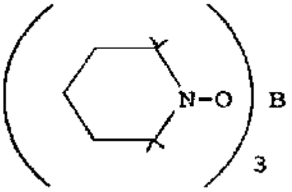
Detailed vibrational assignments, from i.r. and Raman spectra, were made for $MeAsH_2.BX_3$,[145] and $Me_2AsH.BX_3$,[146] where X = Cl, Br or I. In all cases C_s symmetry was appropriate.

3.1.7 Compounds containing bonds between Boron and Elements of Group 6

Non-empirical calculations have been made of the potential surface of the rearrangement $\mathrm{B{-}O{-}O} \rightarrow \underset{\mathrm{B}}{\mathrm{O{-}O}} \rightarrow \mathrm{O{-}B{-}O}$.[147] Similar calculations were reported for the potential barriers to isomerisation in the systems HBO-BOH, HAlO-AlOH and LiBO-BOLi.[148]

An improved preparation has been developed for icosaborane oxide,

$(B_{10}H_{13})_2O$, i.e. dehydration of $(H_3O)_2B_{10}H_{10}$. New Raman data were given for the oxide, especially νB-H-B bands (1850-2100 cm^{-1}).[149] U.v. and i.r. spectra were reported for a series of boron β-diketonates, and also luminescence properties.[150]



(31)

Several methods have been devised for the preparation of piperidine-N-oxyboranes and their 2,2,6,6-tetramethyl analogues, such as (31).[151] All of the series $(Me_3SiO)_nB(O^iPr)_{3-n}$, where n = 0-3, were detected as products of trimethylsilylation of boric acid by $Me_3SiCl/(Me_3Si)_2O$ in the presence of n-propanol.[152] Solutions of hydroxofluoroborates in acetic and peroxyacetic acids were studied by ^{11}B and ^{19}F n.m.r. OH groups are replaced by acetate and peroxyacetate ions.[153]

The equilibrium diagram of the $LiBO_2$-CdO system has been studied at CdO concentrations of up to 85%. Two compounds were detected: $Li_3CdB_3O_7$ and $LiCdBO_3$.[154] Vibrational assignments were proposed for sinhalite, $MgAlBO_4$, on the basis of ^{10}B-^{11}B and ^{24}Mg-^{26}Mg isotopic shifts.[155] Evidence was found for the compounds $3Na_2O.2V_2O_5.3B_2O_3$ and $Na_2O.2V_2O_5.B_2O_3$ in the $NaBO_2$-V_2O_5 system.[156] KLi_2BO_3 has been prepared for the first time. It forms orthorhombic crystals (space group Pnma-D_{2h}^{16}) and is very sensitive to atmospheric moisture.[157]

$Co_2[BO(OH)_2](OH)_3$ forms orthorhombic crystals also, space group Pnma, containing only trigonally-coordinated boron atoms. This is the first example of a structure containing the singly-charged $BO(OH)_2^-$ unit.[158] The behaviour of magnetite on heating with H_3BO_3 or $Na_2B_4O_7$ has been followed. With H_3BO_3 at 600°C, Fe_3BO_6 is formed, with a structure based on tetrahedral BO_4 groups; at 700°C, $FeBO_3$ is formed, containing isolated three-coordinate BO_3 groups.[159] $Ln_7BP_2O_{17}$, where Ln = La-Dy, can be obtained by solid-phase reactions; single crystals were obtained for the Pr and Nd compounds.[160]

Solubility measurements were reported for the systems: lithium(sodium,potassium)monoborate-aromatic amine-H_2O (at

25°C);[161] B_2O_3-calcium propionate-H_2O (at 60°C).[162]

Homilite, $Ca_2(Fe_{0.90}Mn_{0.03})B_2Si_2O_{9.86}(OH)_{0.14}$, forms monoclinic crystals (space group $P2_1/a$). It contains sheets built up of alternating SiO_4 and BO_4 tetrahedra.[163] Crystals of $Ni_5TiB_2O_{10}$ are orthorhombic, space group Pbam; all of the B atoms are triangularly coordinated.[164]

Guanidinium tetraborate(2-) dihydrate, $(C_3H_6N)_2[B_4O_5(OH)_4].2H_2O$, forms triclinic crystals, space group $P\bar{1}$. Discrete anions are present, containing two tetrahedral and two trigonal boron atoms, with average B-O distances of 147.5, 136.9pm respectively.[165]

Solubility isotherms in the H_3BO_3-CaB_4O_7-H_2O and H_3BO_3-CaB_6O_{10}-H_2O systems were studied at 50°C. Several species were identified in the former, but the latter is simple eutonic.[166] The systems $(NH_4)_2B_4O_7$ or $(NH_4)B_5O_8$ with aniline, N,N-dimethyl- or N,N-diethylaniline and H_2O are all simple eutonic.[167] Salting out of alkali metal tetraborates in aqueous solutions of aromatic amines increases as the hydration of the cation is reduced.[168] Solubilities were also studied in lithium(sodium,potassium)pentaborate - EDTA - water systems at 25°C.[169]

Boric acid and hexamethylene tetramine give a polyborate derivative, $C_6H_{12}N_4.2\cdot 5B_2O_3.4H_2O$, containing a cyclic anion with three- and four-coordinated boron atoms.[170] Ethylenediamine gives a very similar species, en.$2\cdot 5B_2O_3.4H_2O$.[171] Thermal phase transformations of ulexite, $NaCa[B_5O_6(OH)_6].5H_2O$, show the formation of tri- and monohydrates, and finally calcium metaborate and sodium triborate.[172] The anion in monoclinic crystals of $CaNaB_5O_9$ (space group $P2_1/c$) forms complex metaborate sheets built up from B_5O_9 units. Each B_5O_9 unit contains BO_4 (2) and BO_3 (3) groups in two rings.[173] Discrete $(B_5O_{10})^{5-}$ ions are present in $CaNa_3B_5O_{10}$ crystals (triclinic; space group $P\bar{1}$), each contains two 6-membered rings. Each ring has two triangular BO_3 groups, and the rings are joined by a shared tetrahedral BO_4 group.[174]

Thermal decomposition of synthetic aksaite, $Mg[B_6O_7(OH)_6].2H_2O$, was followed by high-temperature X-ray diffraction and thermogravimetry. Two stable end-products are crystalline MgB_4O_7 and amorphous B_2O_3.[175] $Fe_3B_7O_{13}Cl$ has been shown to have bond lengths and angles very similar to those for the isostructural $Fe_{2.4}Mg_{0.6}B_7O_{13}Cl$.[176] The boracite $Cu_3B_7O_{13}I$ (cubic; space group $F\bar{4}3c$) has a structure comparable with those of other cubic boracites.[177] I.r. spectra and some X-ray diffraction studies have been reported for $Pb_4Bi_3B_7O_{19}$.[178]

$K_6[UO_2\{B_{16}O_{24}(OH)_8\}].12H_2O$ forms monoclinic crystals, space group $P2_1/n$. Isolated anions are present, comprising a ring of 16 B atoms enclosing one uranium atom.[179] $K_5H\{Cu_4O[B_{20}O_{32}(OH)_8]\}.33H_2O$ gives triclinic crystals (space group $P\bar{1}$). The anion contains the largest-known isolated borate ion, with 20 boron atoms. Each anion contains the boron atoms in a porphyrin-like ring, enclosing four copper atoms in a near-planar Cu_4O unit.[180]

Solid-state ^{11}B n.m.r. was used to study the structures of various phases in the systems B-S, B-Se, B-S-Se and B-Te. In B-S, BS_2 is seen at higher S:B ratios, together with B_2S_3 at lower ones. In B-Se, only BSe_2 (and a B-B bonded subselenide) is seen, and no B_2Se_3. No binary B/Te compounds were detected.[181]

3.1.8 Boron Halides

A theoretical study of the relative stabilities of the known molecules XBO (where X = F or Cl) and their unreported isomers BOX suggests that the latter are potentially stable. The bonding was similar to that in the XBS/BSX analogues.[182] *Ab initio* calculations of the Lewis acidity of BF_3 and BCl_3 show (agreeing with experiment) that the order is $BF_3 < BCl_3$.[183] Pure rotational transitions have been measured for the $\nu_3(E')$ state of $^{11}BF_3$ by infrared-microwave double resonance, using a tunable diode laser.[184] $K[BF_3(OOH)]$ has been prepared and characterised by i.r. and n.m.r. spectroscopy; its thermal decomposition was also studied.[185]

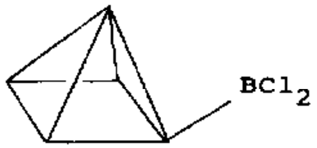
$(OC)_5ReFBF_3$ is a useful source of monomeric complexes $(OC)_5ReX$, where X = SCN, SeCN, ONO_2, NO_2, O_2CH or CN, and also ligand-bridged derivatives such as $(OC)_5Re(oxalato)Re(CO)_5$.[186]

Tetrachlorodiborylmethane can be made according to equation (9).

$$2BCl_3 + CH_2(AlCl_2)_2 \rightarrow CH_2(BCl_2)_2 + Al_2Cl_6 \qquad \ldots(9)$$

Halogen exchange produces the analogous BBr_2 and (for the first time) BI_2 compounds.[187]

2-(Dichloroboryl)pentaborane(9), (32), is prepared by the treatment of μ-$(Cl_2B)B_5H_8$ with an ether, followed by reaction of the resulting 2-$(Cl_2B.OR_2)B_5H_8$ with BX_3 (X = F or Cl). It was



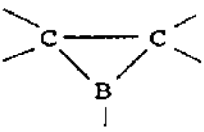
(32)

characterised by its i.r., mass, ^{11}B and ^{1}H n.m.r. spectra. This completes the syntheses of all 3 possible isomers of (dichloroboryl)pentaborane(9).[188]

B_4Cl_4 undergoes reactions which change the cage geometry in a variety of different ways. Thus, with Me_3SnH, B_4H_{10} is produced; $LiBH_4$ gives B_5H_9 and B_6H_{10}, while B_2H_6 gives a range of derivatives $B_{10}H_nCl_{14-n}$, where n = 8-12.[189]

3.1.9 Boron-containing Heterocycles

Ab initio calculations have been carried out on the effects of first-row substituents (Li, BeH, BH_2, CH_3, NH_2, OH or F) on the structures and stabilities of boranes, boriranes (33a) and borirenes (33b). Due to both σ- and π-effects bonds of CH_3, NH_2, OH or F to B are considerably stronger than those to C. The chief factor in stabilising borirenes is the large resonance energy (47 kcal.mol^{-1}).[190]



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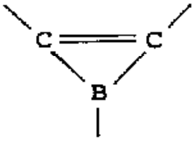
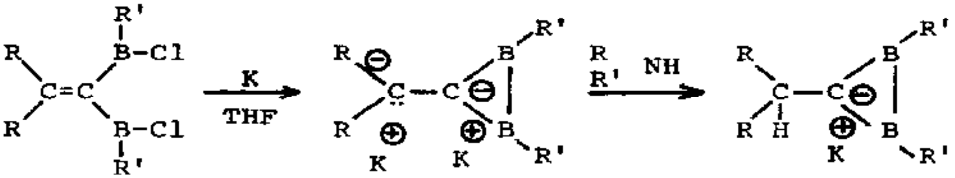


(33b)

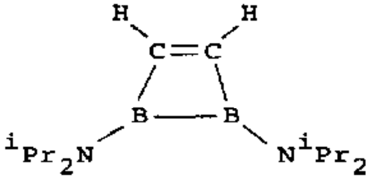
The first three-membered ring anions containing two boron and



...(10)

one carbon atom have been isolated as potassium salts, equation (10), where R = $SiMe_3$, R' = ^tBu.[191]

Several routes have been devised to the first 1,2-dihydro-1,2-diborete, (34), with a planar C_2B_2 ring. This rearranges at 120°C to the thermodynamically more stable 1,3-dihydro-1,3-diborete.[192]



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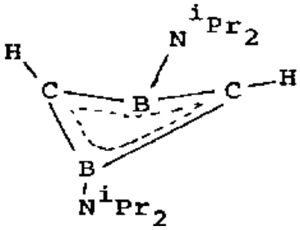

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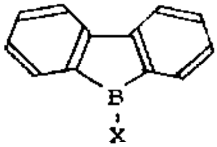
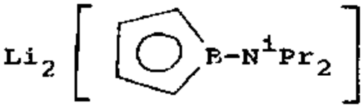


(36)

O,O'-mercurated diphenyl and boron halides give a convenient, high-yield synthesis of the 9-halo-9-borafluorene derivatives, (36; X = Cl, Br or I).[193] (37) is a versatile reagent for producing [1-(di-isopropylamino)borole]metal complexes. Examples quoted included (38) and (39).[194]



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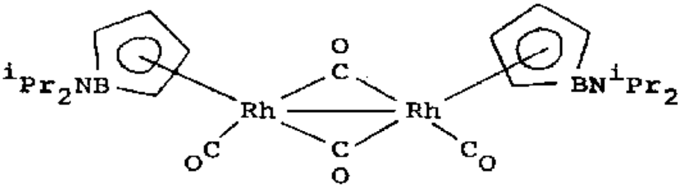

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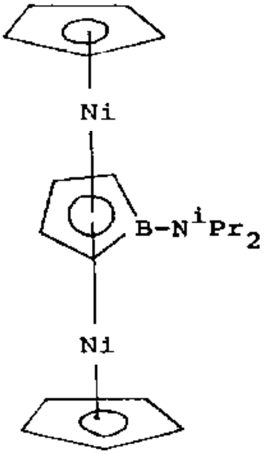

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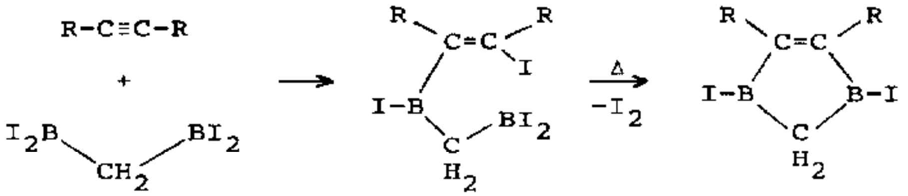
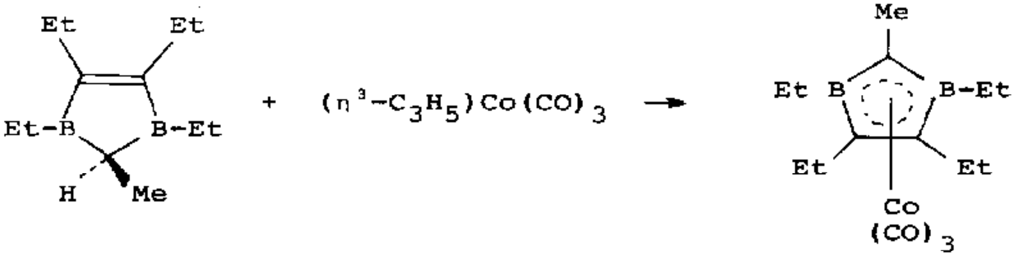


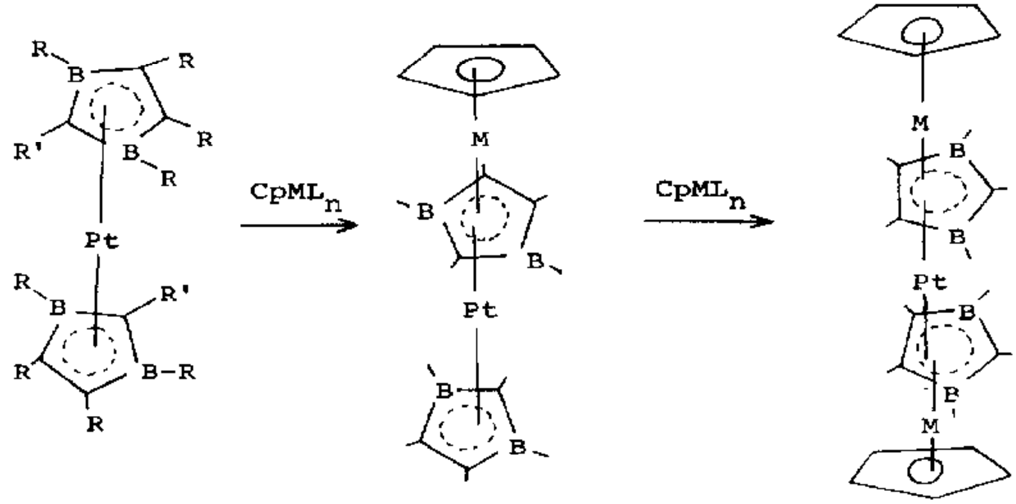
...(11)

The reaction sequence (11) produces some new 4,5-dialkyl-1,3-di-iodo-2,3-dihydro-1,3-diboroles (R = Me or Et). The iodines can also be replaced by Cl, OEt, SMe, NMe_2, Me, Et or Ph.[195]



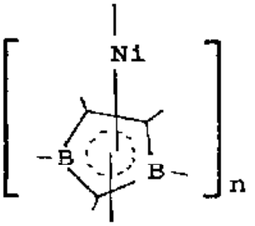
...(12)

The complex produced as a result of reaction (12) has the heterocycle acting as a three-electron ligand.[196] New unsymmetrical triple- and tetra-decker species have been prepared according to the scheme (13), where ML_n = $Fe(C_8H_{12})$, $Co(C_2H_4)_2$ or Ni(CO). Note that the triple-decker complexes are isolable for M = Co, Ni only, the tetra-decker for M = Fe, Ni only.[197]



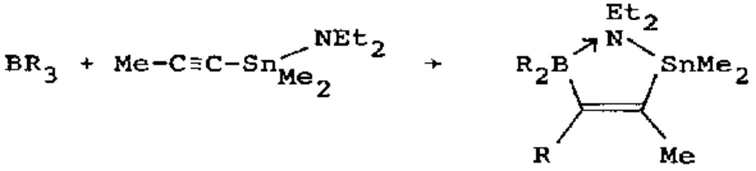
..(13)

Syntheses of 'multi-decker' sandwich complexes have been extended as far as a hexa-decker unit, $CpCo[C_3B_2Ni]_3C_3B_2CoCp$.[198] Such complexes have also been reviewed including semi-conducting polymers containing the stacking unit (40).[199]



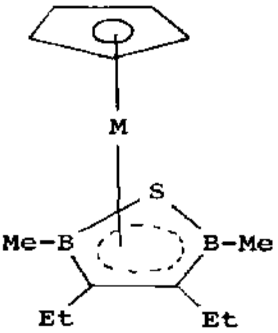
(40)

New, highly-reactive heterocyclic compounds have been prepared by equation (14), where R = Me or Et. Both N→B and Sn–N bonds are readily attacked by H-acidic groups.[200]



...(14)

Several sandwich complexes have been reported which contain 2,5-dihydro-1,2,5-thiadiborole derivatives as ligands, e.g. (41, where M = Co or Ni).[201] Irradiating a 2:1 mixture of 3,4-diethyl-2,5-dimethyl-1,2,5-thiadiborolene and $Fe(CO)_5$ produces (42), with non-parallel ring ligands.[202]



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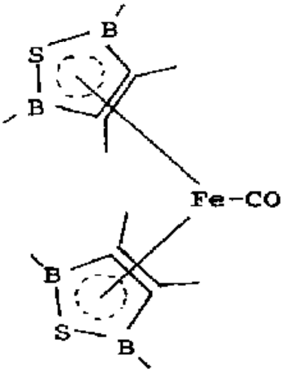

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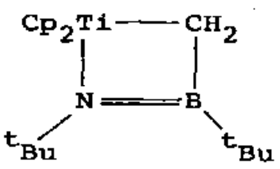
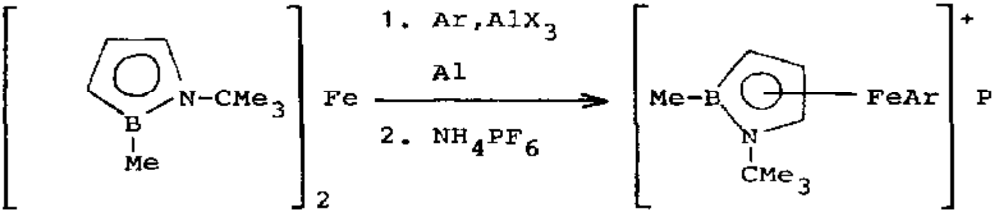


(43)

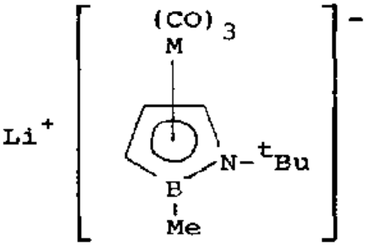
The iminoborane ^{t}BuB≡N^{t}Bu and the short-lived titanaethene $H_2C{=}TiCp_2$ undergo [2+2]-cycloaddition with formation of (43).[203] The novel boron-nitrogen stannocene, $(^t\mathrm{Bu}\overline{\mathrm{N{-}BMe{-}CHMe{-}CH{=}CH}})_2\mathrm{Sn}$ has two dihydro-1,2-azaborolyl rings at an angle of 46.5°. Two diastereoisomers can be detected by ^{1}H n.m.r.[204]

Bis(1-tert-butyl-2-methyl-η^5-1,2-azaborolinyl)iron can be converted to cationic Fe-arene complexes, equation (15), where X =



..(15)

Cl or Br; Ar = benzene, toluene, o-xylene or mesitylene. The structures were confirmed by X-ray diffraction, ^{1}H, ^{11}B and ^{13}C n.m.r. spectroscopy.[205] 1-t-Butyl-2-methyl-1,2-azaborolinyllithium and $M(CO)_6$, where M = Cr, Mo or W, form (44). These give M-M'Me_3 adducts with M'Me_3Cl (where M' = Ge, Sn or Pb). All have pentahapto azaborolinyl rings.[206]



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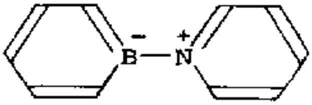

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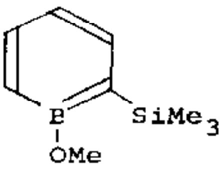
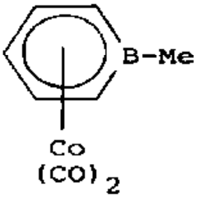


(46)

Pyridine-borabenzene, (45), is prepared by the elimination of methoxytrimethylsilane from (46) in the presence of pyridine at 60°C. The two rings are twisted by 43.3°. The corresponding pyridine-2-boranaphthalene was also reported.[207] The properties and preparations were given for the borabenzene complexes (47), (48) and (49, R = Me or Ph).[208]

Pyridine-borabenzene reacts with $(MeCN)_3M(CO)_3$, where M = Cr, Mo or W, to form (50). X-ray crystal structure determinations prove the η^6-coordination of the borabenzene ring.[209]



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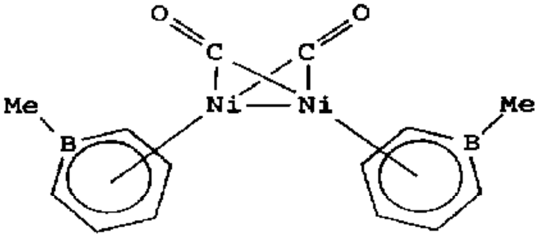

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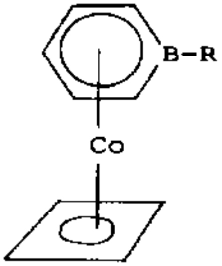

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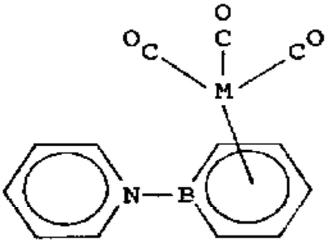
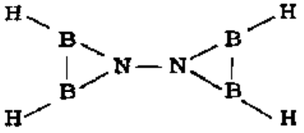


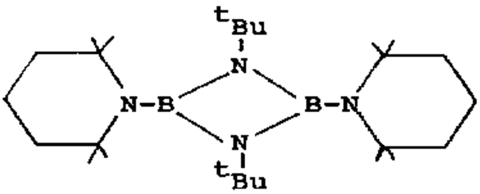
(50)



(51)

Both 1-amino-1,2,3-azadiboriridine and bis(1,2,3-azadiboriridin-1-yl) were calculated, using *ab initio*, to prefer conformations with coplanar lone-pair orbital axes on adjacent nitrogen atoms. The latter molecule was predicted to prefer a fully-coplanar (D_{2h}) structure, (51).[210] α,β-unsaturated ortho-thienylazides and $PhBCl_2$ give good yields of 1,2-dihydro-1-phenyl-2-chloro-, thieno[b]- or thieno[c]-[1.2]azaborines.[211]

N-organyl-*B*-*t*-butyl-borazines, $(-B^tBu-NR-)_3$, or -diazaboretidines, $(-B^tBu-NR'-)_2$, were prepared from ^tBuLi and the corresponding *B*-fluoroborazines. The ring size was determined by the steric requirements of the N-substituents.[212] An X-ray structure analysis of (52) shows that the planar B_2N_2 four-membered ring is diamond-shaped, with the 6-membered rings approximately orthogonal to it.[213]



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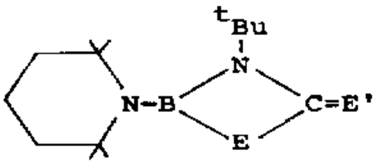
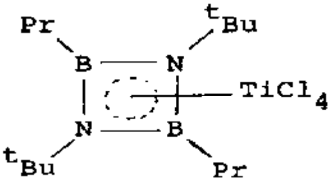


(53)

(*Tert*-butylimino)(2,2,6,6-tetramethylpiperidino)borane forms [2+2]-cyclo-addition products with CO_2, COS, CS_2, CSe_2, i.e. (53), where E = E' = O, S or Se; E = S, E' = O.[214] Preparations have been reported for the new complexes (54) and (55, M = Ti, n = 2; M = V, n = 1). X-ray analyses all show significant interaction between B atoms and Cl ligands. There is probably poor M → ring back-bonding by these metals with few d-electrons.[215]



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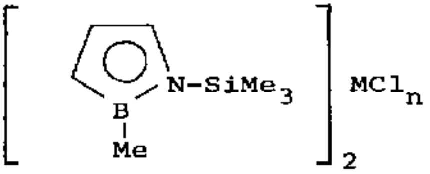

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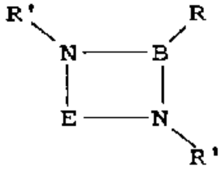
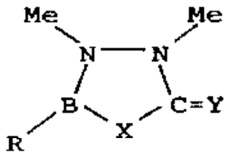


(56)

1,3,2,4-Diazaphospha-(or -sila-)-boretidines, (56), where E = Me(S)P, Me(O)P, Me_2Si; R = Me, Et, Ph, F, Cl or Br; R' = Me or ^{t}Bu, are accessible via thermal decomposition of $E(NR'BR_2)_2$ or from organoboron dihalides or boron trihalides and $E(NR'Li)_2$. N.m.r. data are consistent with the presence of a highly-strained ring system.[216]



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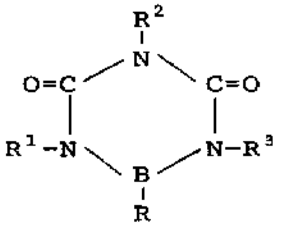
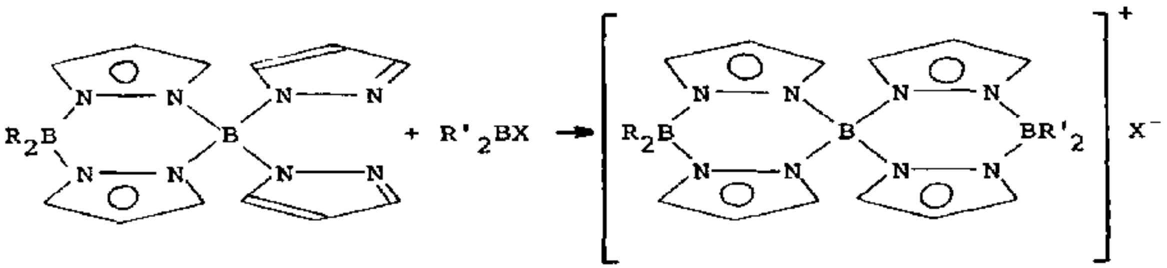


(58)

CO_2, COS and CS_2 form [2+2]-cycloadducts with tetraazadiborinanes i.e. (57), where R = Me, Ph; X = Y = O or S; X = O, Y = S. An X-ray structure for R = Ph, X = Y = S reveals a planar, five-membered ring.[217] Several members of the hitherto little-known series (58), i.e. B-N analogues of substituted uracils, have been reported.[218]

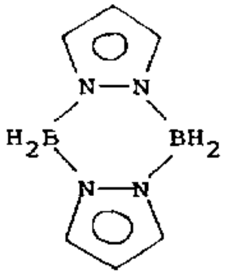
The reaction (16) was used to prepare polyboron spiro-cations, where R = R' = H or Et; R = H, R' = Et.[219] The unsymmetrical pyrazabole, $Ph_2B(\mu\text{-}pz)_2BH_2$, where pz = $N_2C_3H_3$, pyrazolyl, was prepared from $K[Ph_2B(pz)_2]$ and $Me_3N.BH_2I$. Subsequent treatment



...(16)

with Br_2 gave $Ph_2B(\mu\text{-}pz)_2BBr_2$. $H_2B(\mu\text{-}pz')BH_2$, where Hpz' = 3,5-dimethylpyrazole, and Br_2 gave $Br_2B(\mu\text{-}pz')_2BBr_2$, which reacted in turn with Kpz to form $(pz)_2B(\mu\text{-}pz')_2B(pz)_2$, the first species with two different pyrazolyl units attached to one boron.[220]

Stepwise bromination of the pyrazabole (59) was studied using BBr_3 or Br_2. 4-Bromo-, 4,8-dibromo- (as a mixture of cis and trans isomers) and 4,4,8,8-tetrabromopyrazabole were all identified. The B_2N_4 ring of the parent compound is in the boat conformation, but in the tetrabromo-derivative it is planar.[221]



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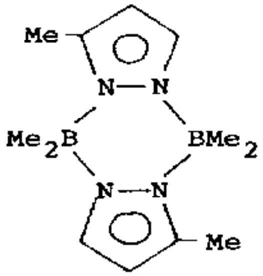

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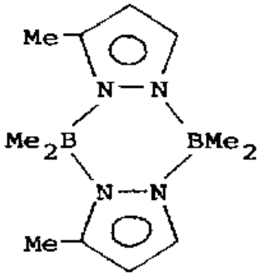

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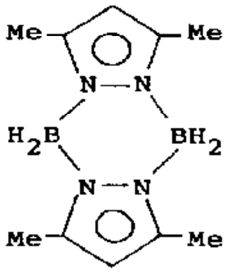
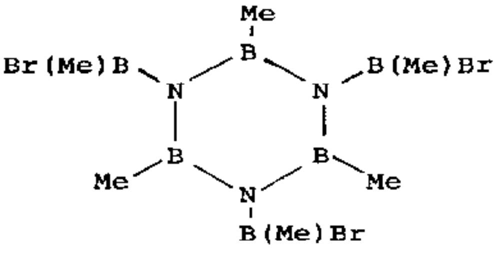


(62)

Several boron derivatives of 3-methylpyrazole were reported, e.g. (60), (61).[222] The crystal structures for 1,3,5,7-tetramethylpyrazabole, (62), and related species all show a pronounced boat conformation for the B_2N_4 ring, but the exact conformation was sensitive to substituent and packing effects.[223]

The reaction of MeMgI with *B*,*B'*,*B"*-trichloro-*N*,*N'*,*N"*-tri-*o*-tolyl borazine gave *cis*-$(o\text{-}CH_3C_6H_4NBMe)_3$ together with *B*-hydroxy by-products. The expected *trans*-isomer is not produced for steric reasons.[224] *N*-borylated borazines have been reported, e.g. $N(SnMe_3)_3$ and $MeBBr_2$ or BCl_3 gave (63), (64) respectively. N.m.r.



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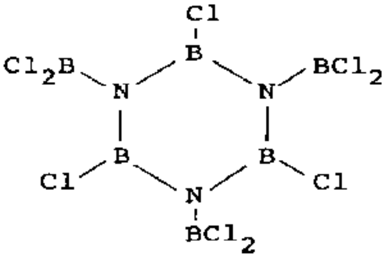

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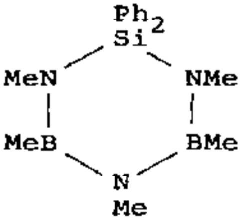

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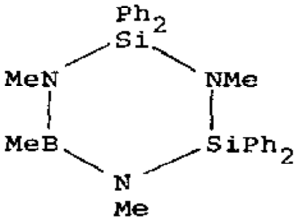
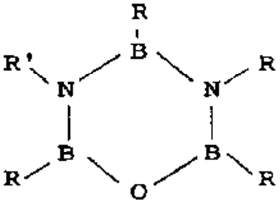


(66)

and i.r. spectra show that the boryl groups are strongly twisted with respect to the borazine ring.[225]

The crystal structures of (65) and (66) show that both have approximately planar cyclic structures. The average B-N bond lengths are practically identical (144pm). N.m.r. data (^{1}H, ^{11}B, ^{13}C and ^{27}Si) are consistent with planar rings in solution also.[226] $[RhCl(LL')]_2$ and $Me_3B_3N_3Me_3$, with $AgPF_6$ in CH_2Cl_2 form hexamethylborazinerhodium(I) complexes, $[Rh(Me_3B_3N_3Me_3)(LL')]^+$, where LL' = 1,5-cyclo-octadiene, norbornadiene etc., L = L' = CO, ethene. The complexes are very labile and undergo rapid ring-ligand exchange with both σ- and π-donor ligands.[227] Several methods have been developed for synthesising derivatives of (67) and (68).[228]



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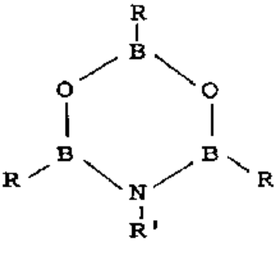

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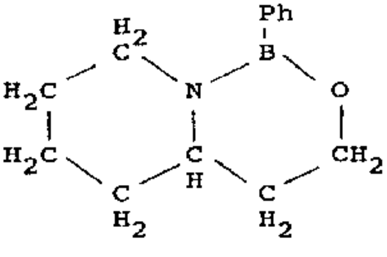
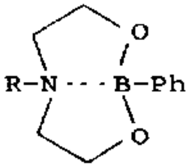


(69)

Preparations have been reported for a number of heterocyclic boranes containing a tertiary nitrogen atom, e.g. (69).[229] ^{11}B and ^{15}N n.m.r. were used to investigate the eight-membered ring compounds (70), where R = H, Me, Et, ^iPr, ^nBu, ^iBu, ^tBu. A good correlation was found between hydrolytic stability and $\delta^{11}B$ shifts.[230]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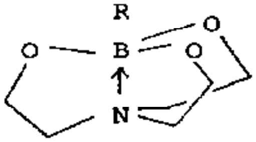
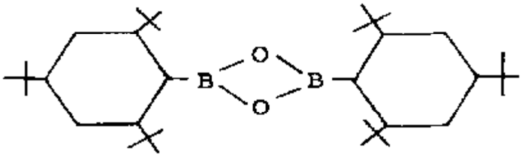

(71)

^{15}N-^{11}B coupling constants were measured for a series of boratranes, (71).[231] 1,3-Dibora-2,4-dioxetane, (72), can be prepared by hydrolysis and dehydration of (2,4,6-tri-t-butylphenyl)dimethoxyborane.[232] A convenient synthesis of catecholatoborane, (73), involves ball-milling $NaBH_4$ and 2,2'-o-phenylenedioxybis(1,3,2-benzodioxaborole) in Et_2O in the presence of small amounts of LiCl. $NaBH_4$ and catecholatoborane in diglyme give high yields of B_2H_6.[233]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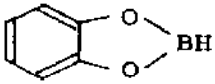
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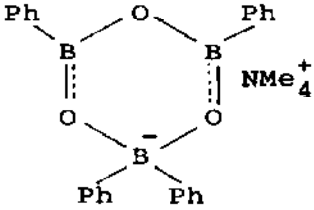
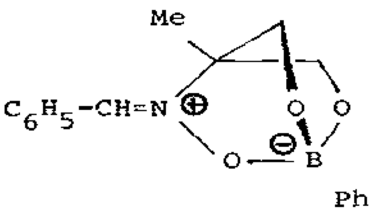

(74)

The crystal structure of (74) shows that the B_3O_3 ring is non-planar, with a flattened O(1)-envelope conformation.[234] The crystal structures of (75) and (76) show that in the former, the bicyclic structure results from intramolecular O→B coordination (O-B distance 160.4(7)pm). This is the first such system characterised. In the latter, there is no O→B interaction, due to the weakened nitrone basicity.[235]

(77), where R = Et, ^nBu or F; X = Cl or Br, have been prepared, and some of their spectroscopic properties studied.[236] X-ray



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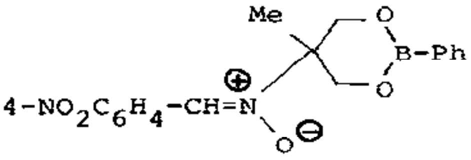
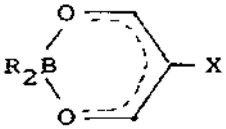


(76)

structure determinations have been reported for (78) and (79). They show significant differences in C-O bond lengths which can relate to shifts in electronic spectra observed for various chelates of 1,3-diketones and related compounds.[237]



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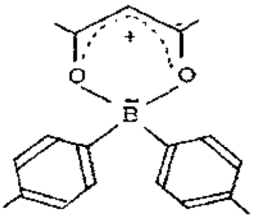

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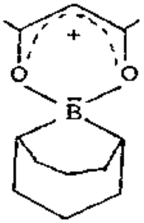
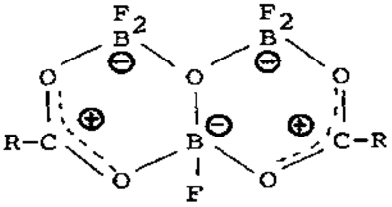


(79)

Bicyclic di-acyloxy-pentafluoro-μ_3-oxotriboranes, (80), where R = Me, Et or ^{n}Pr, have been prepared by reaction of bicyclic acyloxyfluoroboranes with BF_3. The structure was confirmed by X-ray diffraction for the compound with R = Et.[238] The dioxaborinane derivatives, (81), where R^1 = CO_2H, CN, CO_2Me, OMe; R^2 = n-C_6H_{13}, n-C_4H_9O or n-$C_8H_{17}O$, were synthesised by a method including a palladium-catalysed coupling stage. They provide a new series of liquid crystalline compounds.[239]



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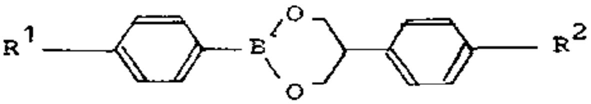
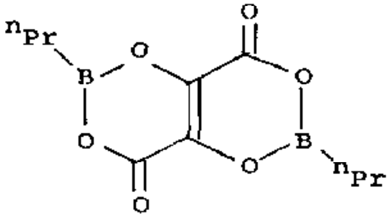
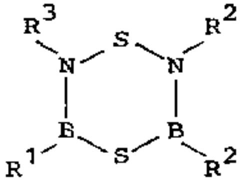


(81)

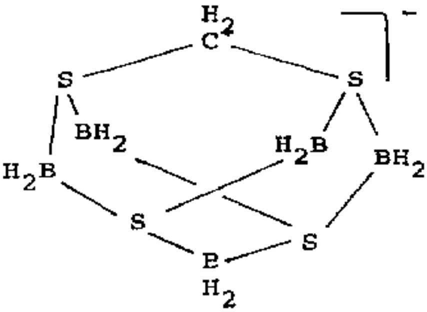
Reversible polymerisation/depolymerisation processes were followed for (<u>82</u>) by matrix-isolation and thin-film infrared and ultraviolet spectroscopy.[240] 1,3-disubstituted sulphur di-imides react with 1,2,4-trithia-3,5-diborolanes to give a wide range of 1,4-dithia-2,6-diaza-3,5-diborinanes, (<u>83</u>).[241] CS_2 and $B_3H_8^-$ form a new anion $[CH_2(BH_2)_5S_4]^-$, with an adamantane-like CB_5S_4 skeleton, (<u>84</u>).[242]



(<u>82</u>)



(<u>83</u>)



(<u>84</u>)

3.1.10 <u>Metal Borides</u>

LCAO-MO calculations have been performed on the electronic structure and chemical bonding for titanium boride nitrides and a ternary Ti-N-B alloy.[243]

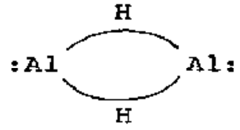
The ternary borides $Mg_2Ru_5B_4$ and $Mg_2Ru_{13}B_{11}$, both of which are orthorhombic; space group Pbam, are prepared by heating the components in sealed tantalum ampoules. $Mg_2Ru_5B_4$ is homeotypic with $Sc_2Ru_5B_4$, containing BRu_6 trigonal prisms, connected by faces and edges to give pentagonal channels filled by chains of Mg atoms.[244]

3.2 ALUMINIUM

3.2.1 Aluminium Hydrides

High-resolution ^{1}H n.m.r. spectra of liquid ^{i}Bu$_2$AlH and its solutions reveal the presence of a higher molecular weight oligomer, as well as the commonly-accepted trimeric form. There was some evidence for the presence of monomer and dimer at low concentrations.[245] $\mathrm{Ni(C_2H_4)_3}$ and $\mathrm{M[M'HR_3]}$, where M = Li, Na; M' = Al, Ga; R = Me, Et or ^{i}Bu, form $\mathrm{[R_3M'{-}H{-}Ni(C_2H_4)_2]^-}$. The σ-donor strength of $\mathrm{R_3AlH^-}$ was compared to that of other σ-donors by using ^{13}C n.m.r.[246] In a related reaction, Ni(CDT), where CDT = trans,trans,trans-1,5,9-cyclododecatriene, and $\mathrm{M[AlHR_3]}$, where R = Me, Et or ^{i}Bu, M = Li or Na, form $\mathrm{[R_3Al{-}H{-}Ni(CDT)]^-}$.[247]

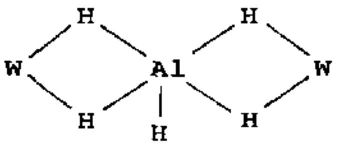
Both MNDO and ab initio MO calculations for various possible structures of $\mathrm{Al_2H_2}$ suggested that a dibridged structure, (85), should be preferred to classical forms.[248]



(85)

$\mathrm{NaAlH_2(OCH_2CH_2OMe)_2}$ remains unchanged in benzene solution, but the presence of donors causes disproportionation to other members of the series $\mathrm{NaAlH_{4-x}(OCH_2CH_2OMe)_x}$, where x = 0-4.[249] Semi-empirical SCF-MO calculations were performed for the radical ions $\mathrm{AlR_3}^{\pm}$, $\mathrm{Al_2R_6}^{\pm}$, where R = H or Me. Methylation gives an increased angle at the Al. $\mathrm{Al_2Me_6}^-$ has C_s symmetry, like a weak complex of $\mathrm{AlMe_2}$ and $\mathrm{AlMe_4}^-$.[250]

The crystal structure determination for $\mathrm{[Cp_2Ti(\mu\text{-}H)_2Al(\mu\text{-}H)(\eta^1{:}\eta^5\text{-}C_5H_4)TiCp(\mu\text{-}H)]_2.C_6H_5CH_3}$ showed the compound to be polycyclic, with two four-membered $\mathrm{(TiH_2Al)}$, two 6-membered $\mathrm{(\overline{Ti(\mu\text{-}C_5H_4)Al(\mu\text{-}H)Ti(\mu\text{-}H)})}$, and one 8-membered $\mathrm{(\overline{Ti(\mu\text{-}H)Ti(\mu\text{-}H)Al(\mu\text{-}H)Al(\mu\text{-}H)})}$ rings.[251] In $\mathrm{[(\eta^5\text{-}C_5Me_5)_2TiH_2AlH_2]_2}$, from $\mathrm{(\eta^5\text{-}C_5Me_5)_2TiH_2BH_2}$ and $\mathrm{LiAlH_4}$, the Ti-Al link involves 2 hydrogen bridges, and dimerisation is achieved by $\mathrm{AlH_2Al}$ bridges. The aluminium has a distorted trigonal bipyramidal coordination polyhedron. The above compound decomposes in solution to $\mathrm{[(\eta^5\text{-}C_5Me_5)_2Ti]_2AlH_5}$, also containing five-coordinate aluminium.[252]

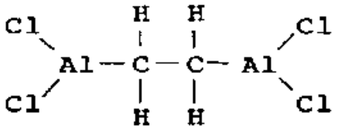


(86)

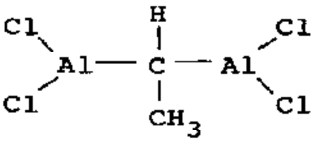
$WCl_4(PMe_3)_3$ reacts with $LiAlH_4/Et_2O$, followed by addition of $Me_2N(CH_2)_2NMe_2$, to form $(Me_3P)_3H_3W(\mu\text{-}H)_2Al(H)(\mu\text{-}H)_2WH_3(PMe_3)_3$, characterised by X-ray diffraction and n.m.r. This is the first aluminium polyhydride with a formally AlH_5^{2-} bridge, (86).[253] The crystal structure of $(dmpe)_2Mn(\mu\text{-}H)_2AlH(\mu\text{-}H)_2AlH(\mu\text{-}H)_2Mn(dmpe)_2$, where dmpe = 1,2-bis(dimethylphosphino)ethane, shows the dimeric structure, which is centrosymmetric, with two *cis*-octahedral $MnH_2(dmpe)_2$ units bridged by a $AlH(\mu\text{-}H)_2AlH$ unit via $Al(\mu\text{-}H)_2Mn$ linkages. The hydrogen atoms in the Al-H-Mn bridge are closer to Mn than to Al. The aluminium is trigonally-bipyramidally coordinated, with the terminal hydrogen in an equatorial position.[254]

3.2.2 Compounds containing Al-C Bonds

Ab initio M.O. calculations have been reported for the Al + C_2H_2 potential energy surface, especially the barrier to rearrangement between *cis*-AlHCCH (observed by e.s.r. at 4K) and $AlCCH_2$ (predicted global energy minimum). A large (39.1 kcal) barrier was found, clearly prohibiting the isomerisation at 4K.[255] E.s.r. studies of the reaction of Al atoms with buta-1,3-diene in adamantane at 77K show the formation of two major paramagnetic products: σ-bonded aluminium cyclopentene and an aluminium substituted-allyl.[256]



(87)



(88)

Aluminium is dissolved by $C_2H_4/AlCl_3$ to give (87) and (88). The presence of ethylaluminium dichloride gives $Et(Cl)Al\text{-}C_2H_4\text{-}AlCl_2$ and/or $Cl_2Al\text{-}C_2H_4\text{-}Al(Cl)\text{-}C_2H_4\text{-}Al(Cl)Et$. All of these compounds react further with olefins giving elimination of alkylaluminium dichloride or dialkylaluminium chloride.[257]

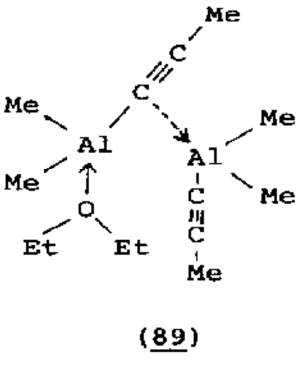
$[AlMe_2(NHR')]_m$ has been isolated, for R' = Ph, C_6H_4Me-o, C_6H_4Me-p or $C_6H_3Me_2$-2,6. X-ray diffraction for the C_6H_4Me-o compound shows that it crystallises as trans-dimers, with aromatic rings approximately perpendicular to the $(AlN)_2$ plane. In solution, all 4 appear to exist as mixtures of two forms (possibly a dimer and a trimer). Heating the amido-compounds produces the imido-species $[AlMe(NR')]_n$. R' = Ph exists with n = 6 and a cage structure of S_6 symmetry in the solid.[258] ^{13}C n.m.r. was used to probe the donor abilities of pyridine and piperidine towards $AlEt_2Cl$.[259]

Al_2Me_6 and ytterbium bis[bis(trimethylsilyl)amide] react to give $Yb[N(SiMe_3)_2]_2[AlMe_3]_2$. The crystal structure shows 4 Yb-Me-Al and 2 Yb-Me-Si interactions.[260]

The reactions of dialkylaluminium acetylacetonates with Lewis bases proceed according to (17), where R = Me, Et, or ^iBu; B =

$$3R_2Al(acac) + 2B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2R_3Al.B + Al(acac)_3 \qquad ...(17)$$

Et_2O, thf, py, dmso or hmpt. Only strong bases can shift the equilibrium completely to the right. k_1 depends upon R ($^iBu<Et<Me$).[261]



(89)

2:1 complexes are formed between dimethylalkynylaluminium and Et_2O or acetone. The suggested structure for the Et_2O adduct is (89).[262] Ethyl bromide and aluminium powder react under the influence of ultrasound, to give $Et_3Al_2Br_3$. This reacts in turn with trialkyl borates to form trialkylboranes in good yields.[263] Several complexes of the form $MX_2.nRAlY_2$ have been synthesised and characterised, e.g. M = Mg, Ca, Sr, Ba; X = Cl, Br, I; R = Me, Et; Y = Cl, Br, I; n = 1-4.[264]

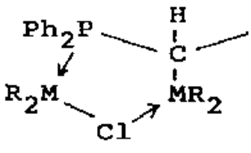
$R_{3-n}AlCl_n$, where n = 0 or 1, R = Me, Et, ^{i}Pr, ^{i}Bu or CH_2Ph, react with 2-pyridylmethanol to produce RH and dimeric $[R_{2-n}X_n\overline{AlOCH_2\text{-}2\text{-}C_5H_4N}]_2$. Both aluminium atoms are five-coordinate, with a planar, four-membered Al_2O_2 ring. N.m.r. data show that in solution, above 25°C, there is also a species containing four-coordinate Al.[265] $CpFe(CO)_2Y$, where Y = SPh, PPh_2 or SO_2Ph, form adducts with $AlMe_3$, $AlMe_2Cl$ and $AlBr_3$. For Y = SPh these react with nucleophiles (L) to give $[CpFe(CO)_2L][PhS(AlR_3)_2]$.[266]

The relative reactivities of Al-Al and Al-C bonds in $Al_2{}^iBu_4$ have been examined. H_3O^+ gives 100% cleavage of both Al-Al and Al-C bonds, but Al-Al is more reactive than Al-C towards HCl. $Al_2{}^iBu_4$ and B_2H_6 react to give an insoluble material, possibly $Al_2(BH_2)_4$.[267]

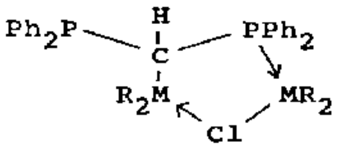
New aluminium and gallium complexes have been prepared by reaction (18), where M = Al or Ga; R = Me or Et. They have

$$Ph_2PCHLiPPh_2 + 2R_2MCl \rightarrow (Ph_2P)_2CH(MR_2)_2Cl \qquad ...(18)$$

unusual structures and show fluxional behaviour, involving the two forms (<u>90</u>) and (<u>91</u>).[268]

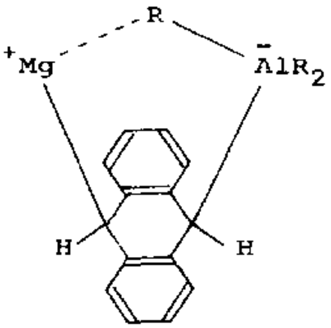


(<u>90</u>)

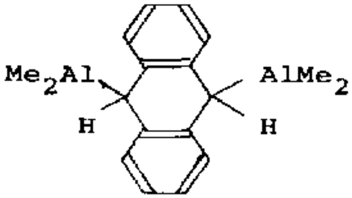


(<u>91</u>)

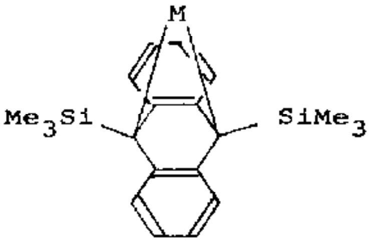
Trimesitylaluminium is formed as a THF adduct from $AlCl_3$ and solutions of $Mg[C_6H_3(CH_3)_3]Br$ or $Mg[C_6H_3(CH_3)_3]_2$ in THF. It is quite easy to remove THF to give the solvate-free species. $Al[C_6H_3(CH_3)_3]Cl_2$ and $Al[C_6H_3(CH_3)_3]_2Cl$ were also reported (as THF adducts).[269] "Anthracene-magnesium" reacts with AlR_3 (where R = Me or Et) in toluene, to give (<u>92</u>), where R = Me or Et. The methyl species and $MeAlCl_2$ form (<u>93</u>).[270]



(92)



(93)



(94)

The presence of a five-membered ring, with aluminium occupying axial positions at C9 and C10, was proved by X-ray diffraction for (94), where M = EtAl(thf).[271]

3.2.3 Compounds containing Al-N or Al-P Bonds

The electronic structures have been calculated for the hypothetical $Al(NR_2)_2^+$, where R = H or Me, and compared with the boron analogues (recently synthesised for large R). The rotational barriers about the Al-N bond are lower than for B-N. The positive charge would be much more localised on Al than on B for the boron analogue.[272] Li and Al in liquid NH_3 form $LiAl(NH_2)_4$, which gives monoclinic crystals (space group $P2_1/n$). The structure is a new variant of the $GaPS_4$-type structure. Thermal decomposition at 220°C gives very finely-divided AlN.[273]

The decomposition of $AlCl_3.NH_3$ to $AlCl_3 + NH_3$ has been investigated in basic $MCl-AlCl_3-NH_3$ (where M = Na or K) mixtures in the temperature range 500-600°C. Greater stability was found in the NaCl-$AlCl_3$ than in the KCl-$AlCl_3$ melts.[274] Infrared spectra of $AlCl_3.NH_3$ and $AlCl_3.ND_3$ gave assignments for all infrared-active fundamentals, together with an indirect assignment for the Al-N torsion, i.e. there is restricted rotation about the Al-N bond.[275]

The following crystal and molecular structures were determined: $Me_2Si(N^tBu)_2(AlPh_2)_2$, bicyclic, with two four-membered rings and a short common Al-N edge (197.5(6)pm); $Me_2Si(N^tBu)(N^tBuH)AlCl_2$, containing an intramolecular Al-N bond, which gives a cyclic structure (four-membered ring, Si + 2N + Al); and $[Me_2Si(N^tBu)_2InMe]_2$, which has a polycyclic structure built up from 3 four-membered rings sharing common edges.[276]

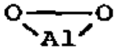
The Al-C bond of Al(TPP)Et, where TPP = tetraphenylporphinato, is cleaved homolytically by photolysis (visible light) in benzene in the presence of excess 2,4,6-tri-<u>t</u>-butylnitrosobenzene. The products are ethyl radicals and spin adducts of Al(TPP).[277]

Neutral phosphinomethylaluminium compounds are prepared by reaction (19), where X = PMe_2, $SiMe_3$. They were characterised

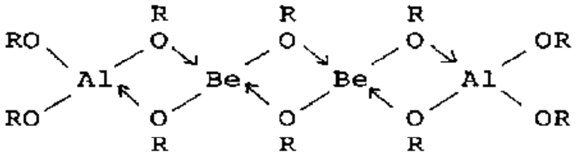
$$AlCl_3 + 3Li[C(PMe_2)_2X] \xrightarrow[-3LiCl]{THF} Al[(PMe_2)_2CX]_3 \qquad ...(19)$$

as octahedral aluminium phosphine complexes by ^1H, ^{13}C, ^{31}P and ^{27}Al n.m.r.[278]

3.2.4 Compounds containing Al-O or Al-S Bonds

Al + O_2 in an argon matrix at 18K react to give AlO. The <u>X</u>-state vibrational fundamental is seen at 975cm^{-1} (confirmed by ^{18}O experiments).[279] The potential surface of the process O-Al-O +  → Al-O-O has been studied by non-empirical methods. Equilibrium geometric parameters were calculated for alternative isomers.[280] An *ab initio* study has been made of the potential surface and vibrational spectrum of Al_2O (using an MO-LCAO-SCF method). The equilibrium configuration was calculated to be linear ($D_{\infty h}$).[281]

Alkanolamines, R^1R^2NXOH (R^1 = H, Me or Et; R^2 = H, Me or Et; X = $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CHMe-$ or $-C_6H_4CH_2CH_2-$) and aluminium isopropoxide react to give $Al(O^iPr)_{3-n}(OXNR^1R^2)_n$, where n = 1, 2 or 3. All are believed to be tetramers.[282] Isopropoxyberyllium tetraisopropoxyaluminate dimerises to (<u>95</u>), where R =



(95)

O^iPr.[283] It is possible to prepare the mixed [Si(IV),Al(III)] μ-oxo-isopropoxide $Me_2SiO_2Al_2(O^iPr)_4$ by the reaction of aluminium isopropoxide and dimethyldiacetoxysilane.[284]

Infrared and Raman spectra of polycrystalline dawsonite compounds $MAl(OH)_2CO_3$, where M = Na, K or NH_4, were assigned on the basis of the factor groups D_{2h}^{28} (M = Na, K) or D_{2h}^{17} (NH_4). O-Al modes are responsible for main features in the 250-700 cm^{-1} range.[285] Evidence was found for the formation of $Al(OH)_3F^-$ in the $Al(OH)_4^-$-F^- system, and $Ga(OH)_2S^-$ in the $Ga(OH)_4^-$-HS^- system.[286]

The cation in $[AlCl_2(\text{benzo-15-crown-5})]^+[AlCl_3Et]^-$ contains seven-coordinate aluminium. The five Al-O distances are in the range 2.06 - 2.30Å, with Al-Cl at 2.202(5) and 2.197(7)Å.[287] The liquidus diagram of the $AlCl_3$-THF system reveals the formation of three intermediate compounds, $AlCl_3.nTHF$, where n = 1, 2 or 3.[288] The solvation of Al^{3+} by DMF is followed by Raman spectroscopy in the δOCN region.[289] ^{27}Al n.m.r. was used to investigate the preferential solvation of Al^{3+} in a DMF-Me_2SO mixed solvent system.[290]

Potentiometry and ^{27}Al n.m.r. were used to follow equilibria in the Al^{3+}-oxalic acid (H_2L)-OH^- system. There was evidence for $[AlL_n]^{3-2n}$, where n = 1, 2 or 3, $Al_3(OH)_3L_3$ and $[Al_2(OH)_2L_4]^{4-}$. $[AlHL]^{2+}$ was detected in strongly acid solutions.[291] A potentiometric study has been made of complexation of Al^{3+} by 5-sulphosalicylic, 2,5-dihydroxybenzoic, 3,4-dihydroxybenzoic or 2,3-dihydroxy-naphthalene-6-sulphonic acids.[292] Solubilities and composition of phases were determined for the system $Al(HCOO)_3$-$HCOOH$-H_2O at 50°C. Aluminium formate is salted out by formic acid.[293]

Care is needed in using $Al(H_2O)_6^{3+}$ as a reference in ^{27}Al n.m.r., as second coordination sphere effects can be detectable. It is best to use dilute aqueous $AlCl_3$ or $Al(ClO_4)_3$.[294] Automated potentiometric titrations were used to study the hydrolytic behaviour of Al^{3+} in 0.10 $mol.dm^{-3}$ $NaNO_3$ at 25°C. The species detected were $Al(OH)^{2+}$, $Al(OH)_2^+$, $[Al_3(OH)_4]^{5+}$ and a high molecular weight polymer.[295] The formation of aluminium(III) hydroxide particles was followed by small-angle X-ray scattering.[296]

$AlPO_4$-21 with clathrated en or pyrrolidone forms a structure with Al and P forming ribbons of edge-shared 3- and 5-membered rings along [101], joined along [010] via four-membered rings to give corrugated sheets of $[Al_2P_2O_7H_{20}]$ or $[Al_2P_2O_7OH]$.[297] Potentiometric equilibrium studies were made on Al^{III} and Ga^{III} complexes of the Schiff bases of 2-amino-3-phosphonopropionic acid and pyridoxal 5'-phosphate.[298]

^1H (and ^{205}Tl) n.m.r. was used to study the structural characteristics of the hydrates $MH(SO_4)_2.nH_2O$, where M = Al, Ga, In or Tl, and their thermal decomposition.[299] Solubility was studied in the $Mg(NO_3)_2$-$Al(NO_3)_3$-H_2O system at 25°, 50° and 75°C.[300] The new barium aluminate glycolate $BaAlO_8C_{6.75}H_{14.75}$ contains a novel aluminate anion, formed by edge-sharing of two distorted trigonal bipyramids. The crystals are orthorhombic, Cccm.[301]

$Rb_2O.Al_2O_3.4SiO_2$ forms a tetragonally distorted b.c.c. lattice. Heating to 400°C gives a transition to a cubic form.[302] Solubility and phase compositions were studied at 25°C in the system $Al(IO_3)_3$-$Al(NO_3)_3$-H_2O. The double compound $2Al(IO_3)_3{:}Al(NO_3)_3.18H_2O$ is formed.[303] Thermogravimetric and infrared data were reported for hydroxo-fluoro complexes of aluminium, e.g. $Al(OH)_p(H_2O)_qF_{6-(p+q)}$.[304] MgO and aluminium sulphate solution can give a crystalline double sulphate of variable composition, $Mg_mAl_n(OH)_p(SO_4)_q.\ell H_2O$, where $m = 2.42 - 1.31$; $n = 1$; $p = 6.90 - 4.55$; $q = 0.60 - 0.66$; $\ell \simeq 3.0$.[305]

Barium tetrakis(1,2-ethanediolato)dialuminate(III), $Ba[Al_2(C_2H_4O_2)_4]$ forms orthorhombic crystals (space group Ccc2). The aluminium coordination is very unusual, a distorted trigonal bipyramid. Two polyhedra share an edge to form the dimer. Apical Al-O distances are 192 and 188pm, equatorial Al-O at 172, 180 and 186pm.[306] The compound "$BaO.Al_2O_3.7H_2O$" was shown by infrared, ^{27}Al and ^1H n.m.r. and by thermoanalytical methods to be $Ba_n[Al_2(OH)_8]_n.3nH_2O$. This contains condensed, edge-sharing AlO_6 groups.[307]

The twenty-first member of a new group of synthetic aluminophosphates ("$AlPO_4$-21") was shown to have the formula

$4Al_3P_3O_{12}(OH).1{\cdot}33N_2C_7H_{21}$. The framework contains two types of trigonal bipyramidal, and one type of tetrahedral aluminium atoms, in 3- and 5-membered rings. The organic molecule N,N,N',N'-tetramethyl-1,3-propanediamine (used as an attempted template during synthesis) split into 3 units, encapsulated in the aluminophosphate framework.[308]

Two isostructural framework structures, $M_3(PO_4)_3.H_2O.en$, where M = Al or Ga, have been synthesised as single crystals. The structure contains sheets of alternating corner-linked MO_4 and PO_4 tetrahedra interlinked with slabs containing tetramers of M-centred trigonal bipyramids cross-linked by PO_4 tetrahedra.[309]

$[Al_2Me_6(OPh)]^-$ and $[AlMe_2(OPh)_2]^-$ have been prepared and characterised by X-ray diffraction. The former has a Y-shaped structure, with Al-O-Al 128.3(7)°, and Al-O 186(1)pm. The latter has a short Al-O distances(180pm).[310] The zeolite, brewsterite, $(Sr_{0.95}Ba_{0.05})Al_2Si_6O_{16}.5H_2O$, forms monoclinic crystals, space group $P2_1/m$. The aluminium-contents of the TO_4 tetrahedra are estimated as T(1), 0; T(2), 25; T(3), T(4), 37%.[311]

Ion-exchange ($2OH^- \rightleftharpoons SO_4^{2-}$) on $Li_2O.2Al_2O_3.11H_2O$ gives $Li_2SO_4.2Al_2O_3.nH_2O$, with a layer structure (unit depth 8.8Å).[312] Lithium phosphatohydroxoaluminate has been prepared, with the empirical formula $(0.88-0.98)Li_2O.2Al_2O_3.(0.50-0.54)P_2O_5.(8.9-9.6)H_2O$. The structure is based on bayerite, $[Al_2(OH)_6]_{2n}$ layers.[313] Conditions of formation and properties were described for aluminium, gallium and indium vanadates.[314]

$H_3O^+Al_4SiP_3O_{16}^-.nH_2O$ forms trigonal crystals, space group R3. The structure is formed by joining together 4-, 6- and 8-membered rings of AlO_4 and $(P,Si)O_4$ tetrahedra.[315] $BaAl_5HO_9$ (from the hydrothermal reaction of $Ba(OH)_2$ and hydrated alumina) forms hexagonal crystals (space group $P6_3/mmc$), and its structure is related to that of β-alumina, $Na_2O.11Al_2O_3$.[316] Lazurite, with the idealised formula $Na_6Ca_2(Al_6Si_6O_{24})S_{21}$ forms cubic crystals (space group $P\bar{4}3n$). Two different specimens were formulated as $Na_{8.56}(Al_6Si_6O_{24})(SO_4)_{1.56}S_{0.44}$ and $Na_{8.16}(Al_6Si_6O_{24})(SO_4)_{1.14}S_{0.86}$ respectively, with complete ordering of Al and Si in each case.[317] $GdAl_{11}O_{18}$ forms hexagonal crystals. Some assignments of infrared bands were proposed.[318] Infrared and Raman spectra of $CdAl_{12}O_{19}$, $CdAl_4O_7$, $CdAl_2O_4$ and $CdGa_2O_4$ were interpreted using $^{106,116}Cd$ isotopic substitution.[319]

Raman bands were assigned which were characteristic of the motion of the oxygen atoms in different environments in the $Al_{12}Si_{12}O_{48}^{2-}$ framework.[320] In very concentrated basic aluminium chloride solutions ($C_{Al} \sim 7.7$ molar; OH/Al = 2.48) polymeric aluminium cations predominate. Dilution produces some monomeric cations, but on ageing the solutions these react with polymeric species to give $Al_{13}O_{40}$ cations.[321] The charges on such species were determined by paper electrophoresis. The average charge was 6.3±0.4 i.e. the 6+ and 7+ species are chiefly present.[322]

High-resolution solid-state ^{27}Al and ^{29}Si n.m.r. spectra of pillared clays show that in uncalcined specimens the pillaring agent is the Al_{13} polymer, made up of 12 aluminium octahedra surrounding one aluminium tetrahedron.[323]

Aluminium and gallium trihalides and RSH form adducts $MX_3.RSH$, where M = Al, Ga; X = Cl, Br or I; R = Me, Et, Pr, ^iPr, Ph. Indium analogues cannot be isolated, however, although there is n.m.r. evidence for their existence in solution.[324]

3.2.5 Aluminium Halides

pF-potentiometric titrations establish the formation of monofluoride complexes of aluminium on aluminium oxide surfaces.[325]

The crystal structure of $(NH_4)_2[AlF_5(H_2O)]$ shows the presence of isolated octahedral anions and NH_4^+. The former are linked by F---H-O-H---F bonds to form zigzag chains parallel to <u>c</u>.[326] In the structure of thomsenolite, $NaCaAlF_6.H_2O$, hydrogen bonds link AlF_6 octahedra into infinite chains, which are in turn cross-linked to give infinite double sheets, $\{[AlF_6]+Ca\}-(H_2O)-\{[AlF_6]+Ca\}$.[327] Thermodynamic data were tabulated for the molten mixtures $Na_3AlF_6-Al_2O_3$ and $NaF-AlF_3$. In the latter, the Gibbs free energy changes associated with the formation of $Na_3AlF_6(\ell)$, $Na_5Al_3F_{14}(\ell)$, $NaAlF_4(\ell)$ and $NaAlF_4(g)$ were calculated.[328]

Methods for the preparation of 2/3 basic aluminium chloride were described.[329] The nature of the ionic species formed by dissolving $AlCl_3$ or $Al(ClO_4)_3$ in anhydrous alcohols, and diluted by $CDCl_3$, were studied by ^{27}Al n.m.r. Except in EtOH, $AlCl_3$ gives chloro-complexes, but the anomalous behaviour of EtOH was not explicable.[330]

The systems $AlCl_3-NiCl_2$ and $AlCl_3-PdCl_2$ were studied by various physicochemical methods. The $NiCl_2$ system is eutectic, but for $PdCl_2$ the compound $2AlCl_3.PdCl_2$ is formed.[331] High-precision measurements have been made of the $KCl-AlCl_3$ phase diagram near the equimolar composition. The freezing point and enthalpy of freezing of $KAlCl_4$ were found to be 257.3±0.1°C, 18.0±1.2 $kJ.mol^{-1}$ respectively. Great care was taken to eliminate oxide impurities.[332] The Raman spectra of molten mixtures of $NaAlCl_4$ and $NaAlBr_4$ show that equilibration to a random mixture of all $[AlCl_{4-n}Br_n]^-$ species occurs very rapidly.[333]

The tetrachloroaluminate dissociation constant in aluminium chloride/1-methyl-3-ethylimidazolium chloride melt was measured (log K = −17.1±0.5).[334] MNDO calculations were carried out on anions in molten chloroaluminate salts. The calculated geometries generally agree with available data for $AlCl_4^-$ and $Al_2Cl_7^-$. C_2 symmetry was assigned for the latter.[335] Fusion diagrams were established for the systems $AlCl_3-SOCl_2$ and $AlCl_3-NdCl_3$ in the absence of air.[336] Solvent acid/base properties were reported for acidic ($AlCl_3$-rich) $AlCl_3$-*n*-butylpyridinium chloride melts. The ionic species can be fully

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \qquad ...(20)$$

$$2Al_2Cl_7^- \rightleftharpoons Al_3Cl_{10}^- + AlCl_4^- \qquad ...(21)$$

described by the equilibria (20) and (21).[337] ^{27}Al n.m.r. for butylpyridinium chloride-$AlCl_3$ melts gave the following results for the dominant species: 55±2 mol% $AlCl_3$, $AlCl_4^-$ and $Al_2Cl_7^-$; 71±1 mol% $AlCl_3$, $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$; 80 mol% $AlCl_3$, $Al_3Cl_{10}^-$ only.[338] $CoCl_2$ reacts with Al_2Cl_6(gaseous), at a pressure of *ca*. 3 atmos., to form $CoAl_2Cl_8$ and a small amount of $CoAl_3Cl_{11}$.[339]

3.2.6 Other Aluminium-containing Species

A study of phase equilibria in the Tb-Al-Si system revealed a compound Tb_6Al_3Si. This forms tetragonal crystals, space group I4/mcm. Isostructural Ln_6Al_3Si compounds were also obtained for Ln = Sm-Tm and Y.[340]

The reactions of H_2 with intermetallic compounds of Ln (= Ce, Pr, Ho or Er), Se or Y, and Al were studied. Various hydride phases were identified.[341]

3.3 GALLIUM

3.3.1 Compounds containing Ga-C Bonds

Statistical thermodynamics were used to determine thermodynamic functions for $Me_3Ga.OEt_2$. Part of the P-T-x diagram of the Me_3Ga-Et_2O system was constructed.[342] Halo(methyl)(organylthio)-gallanes, Me(RS)GaX, where X = Br or I; R = Me, Et, ^nPr, ^iPr, Ph or CH_2Ph, are formed by the reaction of dibromo- or di-iodo-(methyl)gallane with $Me_3Si(SR)$.[343] Various routes were studied as routes to halogeno(phenyl)(organylthio)gallanes, Ph(RS)GaX, e.g. dihalogenophenylgallanes + silyl sulphides, heterogeneous reactions of dihalogenophenylgallanes + lead bis(dithiolates), and halogenophenylgallanes + free thiols.[344]

The crystal structure of bis[(trimethylcitrato)dimethylgallium(III)] reveals the presence of centrosymmetric dimers in which each citrate ligand is coordinated via the hydroxyl oxygen (bridging) and the C=O oxygen atom of the central ester group, to give five-membered chelate rings. Each gallium has irregular trigonal-bipyramidal geometry (Ga-O(eq) 195.0(3); Ga-O(ax) 210.3(3), 239.5(3); Ga-C(eq) 195.3(5); 194.7(5)pm).[345] $Ga(CH_2SiMe_3)_3.Me_2NC_2H_4NMe_2.Ga(CH_2SiMe_3)_3$ has been fully characterised by a range of physical measurements. The crystal structure shows distorted tetrahedral geometry about Ga, with Ga-C(av) 199pm; Ga-N 224pm.[346]

The first pentamethylcyclopentadienyl compounds of gallium have been reported: $Ga(C_5Me_5)_2Cl$ and $Ga(C_5Me_5)Cl_2$. These were fully characterised by various physicochemical measurements. The crystal structures of both show that they are dimeric, with chlorine-bridges and η^1-C_5Me_5 rings.[347] $Ga(C_5H_5)_3$ has also been prepared (from $GaCl_3$ and $Li^+C_5H_5^-$) and characterised for the first time. The crystals are monoclinic (space group $P2_1/n$), with all Cp rings η^1-coordinated to Ga (Ga-C(av) = 205(3)pm). $Ga(C_5H_5)_3$ is a weak Lewis acid.[348] A review has been published on the syntheses and structures of arene complexes of Ga^I, In^I and Tl^I.[349]

3.3.2 Compounds containing bonds between Gallium and Elements of Group 5

The kinetics and equilibria of Ga^{III}/NCS^- complex formation were studied in aqueous solution. The complexation equilibrium quotient, $[GaNCS^{2+}]/([Ga^{3+}][NCS^-])$ was found to be 20.8±0.3 M^{-1} at

25°C, and an ionic strength of 0.5M.[350]

Me_2NGaH_2 was characterised by electron diffraction and vibrational spectroscopy. The predominant species in the gas-phase is the dimer, $[Me_2NGaH_2]_2$, with a cyclic Ga_2N_2 skeleton and effective D_{2h} symmetry. The Ga-N distance is 202.7(4)pm, with Ga-H 148.7(3.6)pm. The vibrational spectrum (also for the GaD_2 analogue) shows that the dimeric form is retained in benzene solution, and in the crystalline state.[351] $GaCl_3$ and $(Me_3Si)_2NR$ (where R = H or Me) form $[Cl_2GaN(R)SiMe_3]_2$. The trans-isomer of each dimer was identified in the solid state by X-ray crystallography. N.m.r. data show the existence of an equilibrium mixture of $[Cl_2GaN(H)SiMe_3]_3$, trans- and cis-$[Cl_2GaN(H)SiMe_3]_2$ in solution. For R = Me, only the trans- and cis-dimers are present in solution.[352]

The crystal structure of $[Me_2Ga(N_2C_3H_3)_2](PPh_3)Re(CO)_3$ shows that the $ReGaN_4$ chelate ring has a twisted-boat conformation, with an Re---Ga separation of ca. 390pm.[353] Direct reaction of Pt(Me)Cl(COD) and $Na[Me_2Gapz_2]$, followed by addition of L (= CO, PPh_3 or PhC≡CPh), gives $[Me_2Gapz_2]Pt(Me)L$. Variable-temperature ^1H n.m.r. shows them to be fluxional in solution.[354] The crystal structure of $[Me_2Ga(3,5\text{-}Me_2pz)_2]Rh(CO)(PPh_3)$, where pz = pyrazolyl, $N_2C_3H_3$, shows that the central $RhGaN_4$ six-membered ring is in a steep boat conformation, with Rh---Ga 338.19(4)pm.[355] Several rhodium(I) monocarbonyl complexes have been prepared, with unsymmetrical, tridentate pyrazolylgallate ligands. Oxidative addition produces a Rh(III) acetyl complex. Crystal structures were determined for $[Me_2Gapz(OCH_2CH_2NH_2)]Rh(CO)$ and $[Me_2Gapz(OCH_2CH_2NMe_2)]Rh(COMe)I$.[356] The crystal structure of $[Me_2Gapz_2]Ir(COD)$ shows a boat conformation for the $Ga(NN)_2Ir$ ring. This, and related species, often show non-rigid behaviour in solution (probed by variable-temperature ^1H n.m.r.).[357]

Electrochemistry, n.m.r. and u.v./visible spectra were reported for 18 different Ga(III) porphyrins with ionic Cl^- or σ-bonded axial ligands. The first step in oxidation or reduction is always to $[(P)Ga(R)]^+$, $[(P)Ga(R)]^-$ respectively. The singly- and doubly-reduced species are always stable.[358]

$CH_2(PPh_2)_2$ forms 1:1 complexes with $AlMe_3$, $GaMe_3$, $GaEt_3$, $GaClMe_2$, and a 1:2 complex with $AlMe_3$. X-ray diffraction of the Me_2GaCl complex shows that in the solid the gallium is coordinated to only one phosphorus (Ga-P) 253.5(2)pm).[359]

Ca_3GaAs_3 and Ca_3InP_3 crystallise in the orthorhombic system (space group Pnma), with $GaAs_4$ or InP_4 tetrahedra corner-linked to form chains. Ba_3GaSb_3 belongs to the same space group, but contains isolated Ga_2Sb_6 units.[360] The new compounds $Ca_5Ga_2Sb_6$, $Ca_5In_2Sb_6$ and $Sr_5In_2Sb_6$ all crystallise in the orthorhombic system (space group Pbam). The anionic structure consists of $M_2^{III}Sb_6$ units linked into chains.[361] The phase diagram of the Ga-Sb-Bi system gave no evidence for the formation of ternary compounds.[362]

3.3.3 Compounds containing bonds between Gallium and Elements of Group 6

The thermal decomposition of β-(Fe,Ga)O(OH) was followed by DTA and TG.[363] $GaCl_3$ and $Li^+C_5^5H_5^-$ in Et_2O at ambient temperature give an ethoxy-bridged dimer, $[(\eta^1-C_5H_5)GaOEt]_2$. The Ga_2O_2 rhombus is planar, with Ga-O(av) 192.3(3)pm.[364]

Several galliophosphate framework systems have been synthesised. Some have structures related to the $AlPO_4$-family of molecular sieves, e.g. the structure of $\{(^iPrNH_3)[Ga_4(PO_4)_4OH]\}H_2O$ is related to $AlPO_4$-12, -15 and -21.[365] Stability constants were determined for Ga^{3+} and In^{3+} complexes with anions of various carboxylic, hydroxycarboxylic and aminopolyacetic acids, glycine and quinolinol.[366] Kinetics and mechanisms were studied for complex formation by Ga^{III} and In^{III} with 4-(2-pyridylazo)-resorcinol in H_2O, aqueous MeOH, MeCN etc.[367]

Phase relationships were examined in the isohydrate isothermal section of the $Li_2O-Ga_2O_3-SiO_2-H_2O$ system at 200°C, 1.6MPa and 90 mass % H_2O,[368] and for $K_2O-Ga_2O_3-SiO_2-H_2O$ system at 200°C and 80 or 90 mass % H_2O.[369] Reactions in the $Li_2O-Ga_2O_3-TiO_2$ system lead to the formation of $LiGaTiO_4$, with the spinel structure.[370] Solubility in the systems $Ga(IO_3)_3-Mg(IO_3)_2-H_2O$ and $Ga(IO_3)_3-Al(IO_3)_3-H_2O$ was studied isothermally at 25°C. Limited solid solutions were found in the former; the latter is eutonic.[371]

New synthetic routes have been established for sulphur-bridged Ga^{III} and In^{III} halide complexes, e.g. (22), where R = Et, ^nBu or

$$Ga_2X_4 + 2RSH \rightarrow Ga_2X_4(SR)_2 + H_2 \qquad \ldots(22)$$

cyclohexyl; X = Cl, Br or I. These are all dimeric, as shown; this was confirmed by the crystal structure of $Ga_2I_4(SMe)_2$.[372]

Gallium(III) tri-dialkyldithiophosphates, Ga[S$_2$P(OR)$_2$], where R = Et, ^{n}Pr, ^{i}Pr, ^{n}Bu or ^{i}Bu, and related species, have been reported for the first time. They are monomers in solution, and spectral data are consistent with chelated octahedral structures.[373]

The oxide-sulphides CaLaGa$_3$S$_6$O, SrLaGa$_3$S$_6$O and La$_2$ZnGa$_2$S$_6$O have been prepared for the first time.[374] The Ga$_2$S$_3$–Eu$_2$O$_3$ phase diagram has been studied by D.T.A., microstructural analysis etc. Two incongruently-melting compounds were found: 2Ga$_2$S$_3$.Eu$_2$O$_3$ and Ga$_2$S$_3$.Eu$_2$O$_3$.[375]

Phase equilibria were studied for the following systems: Tl–Ga–S;[376] CdGa$_2$S$_4$–CdGa$_2$Se$_4$;[377] TlGaSe$_2$–TlInSe$_2$;[378] and TlGaSe$_2$–Nd$_2$Se$_3$.[379] Crystals of InGaSe$_2$ and InGaTe$_2$ possess the TlSe structure type (space group I4/mcm).[380]

The binary liquid systems Ga–Te, In–Te were studied by ultrasound.[381] Phase transformations were studied in the system SmTe–Ga$_2$Te$_3$. There was evidence for an incongruently-melting compound Sm$_2$Ga$_2$Te$_5$.[382]

3.3.4 Gallium Halides

BaCaGaF$_7$ forms monoclinic crystals, space group P2$_1$/n. The structure contains GaF$_6$ octahedra linked to CaF$_{8/2}^{2-}$ polyhedra. The average Ga–F distance is 187.8pm.[383]

GaCl$_3$ reacts with lead dithiolates, Pb(SR)$_2$, where R = Me, Et, Pr, ^{i}Pr, Ph, CH$_2$H, in benzene to give moisture-sensitive GaCl$_{3-n}$(SR)$_n$, where n = 1, 2 or 3.[384] Taking into account corrections for small amounts of water present, the dissociation enthalpy for Ga$_2$Cl$_6$(g) $\rightarrow$ 2GaCl$_3$(g) was found to be ($\Delta H°(298)$) 22.49 kcal.mol^{-1}, with $\Delta S°(298)$ 35.95 cal.K^{-1}.[385]

Gallium and trithiazyl chloride form S$_5$N$_5$[GaCl$_4$]. This reacts in turn with GaCl$_3$ to form S$_5$N$_5$[Ga$_2$Cl$_7$]. Infrared spectra and crystal structures were reported.[386] Raman spectroscopy and potentiometric measurements were used to follow complex formation by Ga(III) in KCl/AlCl$_3$ melts at 300°C. GaCl$_4^-$ is formed at 0.26<pCl<3.01. For pCl>3.01 there was evidence for the mixed species GaAlCl$_7^-$, and Ga$_2$Cl$_7^-$.[387] Ga$_2$X$_4$.2L, where X = Cl or Br; L = py, 3-Me-, 4-Me-pyridine, morpholine, 1,4-thioxane, 1,4-dithiane, tetrahydropyran, thf, tetrahydrothiophen or dimethylsulphoxide, have been prepared. The vibrational spectra show that all contain Ga–Ga bonds, which was confirmed by X-ray structure determination for Ga$_2$Cl$_4$.2py.[388]

Phase relationships were established for the systems MX_3-M_2S_3, where M = Ga, In; X = Cl, Br, I. All are quasi-binary, and contain incongruently-melting MSX species.[389] GaX_3, where X = Br or I, and lead bis(thiolates), $Pb(SR)_2$ (R = Me, Et, Pr, ${}^iPr$, Ph or CH_2Ph) form moisture-sensitive mono-, bis- and tris(alkyl and phenylthio)gallanes, $X_nGa(SR)_{3-n}$, n = 2, 1 or 0.[390]

Some synthetic routes were reported for $I_2Ga(SMe)$, and several of its reactions.[391]

3.4 INDIUM

3.4.1 Compounds containing bonds between Indium and Elements of Group 5

$In(DAPSC)(H_2O)_2{}^{3+}$, where DAPSC = 2,6-diacetylpyridinesemicarbazone, has been shown to have seven-coordinate geometry (pentagonal bipyramidal), with In-N(av) 228pm, In-O(ax), 213, 215 pm.[392] $Me_2In(Ph_2pz).\frac{1}{2}CH_2Cl_2$ is produced from Me_2InCl and $Ag(Ph_2pz)$ in non-aqueous solvents (pzH = pyrazole). The analogous $Me_2Tl(R_2pz)$, where R = Me or Ph, were prepared from Me_2TlCl.[393]

X-ray diffraction show $Et_2InX(tmen)$, where X = Br or I; tmen = N,N,N',N'-tetramethylethylenediamine, to have five-coordinate indium, i.e. InC_2N_2X. $[Ph_4P][EtInI_3]$ contains isolated anions, with C_{3v} symmetry.[394] The crystal structure of $MeIn\{[Me\overline{N(CH_2)_2NMe]Me_2In[MeN(CH_2)_2NMe]Me_2In}\}$ shows the presence of a central five-coordinate, square pyramidal indium (apical methyl), with 2 peripheral, tetrahedral indium atoms. $MeIn[Me\overline{NC(CH)_4N}]_2$ also contains square pyramidal indium.[395]

Electrochemistry and spectroelectrochemistry were reported for In(III)tetraphenyl- and octaethylporphyrins. E.s.r. spectra were obtained for each of the cation and anion radicals generated.[396] N.m.r. and u.v./visible spectroscopy and electrochemistry were used to study 16 In(III) porphyrins in non-aqueous media. The In is σ-bonded to alkyl or aryl groups etc. Oxidation or reduction takes place by multiple single-electron steps, with the first steps to $[(P)In(R)]^+$ or $[(P)In(R)]^-$. The singly-reduced species was stable in all cases.[397]

The temperature dependance of the dissociation pressure of the alkyls of the quasibinary InAs-InP section was measured by direct manometry.[398] $Ca_{11}InSb_9$ crystallises in the orthorhombic system, space group Iba2. There are isolated Sb^{3-} anions, $Sb_2{}^{4-}$ units and isolated $InSb_4^{9-}$ tetrahedra in the structure.[399]

The liquidus of the In-Sb-Se system comprises 8 primary crystallisation fields.[400] Interaction of components in the In-Sb-Tl system was examined; no ternary compounds are formed.[401]

3.4.2 Compounds containing bonds between Indium and Elements of Group 6

Phase equilibria were studied in the CdO-In_2O_3-CaO system in the subsolidus region.[402] Solid state reactions were used to prepare single crystals of $BaInO_{2.5}$. This possesses the perovskite structure, space group O_h^1-Pm3m. It is a rare example of a defect perovskite compound with a pure M^{3+} ion and an alkaline earth element.[403] The existence of the cubic pyrochlore $Pb_2^{II}[In_{0.5}Sb_{1.5}]O_{6.5}$ has been established. The In and Sb are randomly distributed, with an apparent interatomic distance, [(In,Sb)-O], of 201.9pm.[404] The new triple molybdates $KAIn(MoO_4)_3$, where A = Mg or Mn, are formed in K_2MoO_4-$AMoO_4$-$In_2(MoO_4)_3$ systems. They were investigated by X-ray diffraction and DTA.[405]

Raman spectra were reported for $In(NO_3)_3$ in aqueous solutions containing $NaNO_3$, HNO_3 or NaOH. The following assignments were proposed: (i) 485cm^{-1} : totally symmetric In-O stretch of $In(H_2O)_6^{3+}$; (ii) 465, 425cm^{-1} : In-O(H_2) vibrations of aquo-complexes with one or more inner-sphere nitrato-groups.[406] Infrared and Raman spectra of $InVO_4$ and $TlVO_4$ phases structurally related to $CrVO_4$ were assigned in terms of site symmetry changes.[407] The crystal symmetry was studied for mixed crystals in the orthorhombic $InPO_4$-$InVO_4$ system. Infrared spectra were assigned using site- and factor-group symmetries.[408]

Cl_2O_6 and $InCl_3$ or $TlCl_3$ form $ClO_2M(ClO_4)_4$, where M = In or Tl. These decompose on heating (80°C) to $M(ClO_4)_3$. The thermal stability is In>Tl. Infrared and Raman spectra were assigned on the basis of a polymeric structure (AsI_3 type) with bridging bidentate perchlorato groups. $M(ClO_4)_4^-$ has both uni- and bidentate ClO_4 groups.[409] Solubility in $In(IO_3)_3$-HIO_3-H_2O was studied by an isothermal method at 25°C. It is a simple eutonic system.[410]

CO_2 inserts into the In-C σ-bond of methylindium(III) porphyrins on irradiation by visible light in dry benzene/pyridine media to form acetato complexes. The same products occur from the reaction of acetic acid with alkyl- or arylindium(III) porphyrins or the aquohydroxoindium(III) porphyrins. The crystal structure shows that in (OEP)$InCO_2Me.2CHCl_3$, where OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato, the acetato group is unsymmetrically bidentate (In-O 214,260pm).[411]

Equilibrium constants were determined for complexes of In(III) with the indicator 1-(2-pyridylazo)-2-naphthol, and the mechanism of formation of InL^{2+} proposed.[412] Six-coordinate mono-, bis- and tris(monothio-β-diketonates) of In(III) have been synthesised and characterised. The crystal structure of tris[benzyl(thiobenzyl)methanato-O,S]indium(III) shows In to have a distorted octahedral geometry, with a facial arrangement of the S and O ligand atoms.[413]

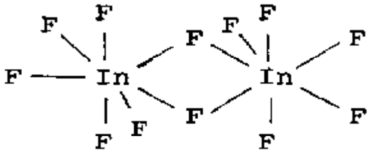
The systems In_2S_3-M_2O_3, where M = Eu or In, were studied by differential thermal, high-temperature differential, X-ray diffraction and microstructural analyses. Both systems are eutectic.[414] Phase equilibria have been studied for M_2X-In_2X_3, where M = Li, X = S; M = Na, X = S, Se or Te. The following compounds were identified: $LiInS_2$, $NaInS_2$, $NaIn_3S_5$, $NaInSe_2$, $NaIn_3Se_5$, $NaInTe_2$, $NaIn_3Te_5$.[415]

α-In_2S_3 can be prepared by the thermal decomposition of In(III) complexes, InL_3, where L is a sulphur-containing ligand.[416] Phase equilibria were established in the reciprocal system $Tl_2S + CuInS_2 \rightleftharpoons TlInS_2 + CuTlS$. The intermediate compound $CuTl_6In_5S_{11}$ was observed, and $Tl_4In_2S_5$ confirmed.[417]

$LiInTe_2$ is prepared by direct reaction of the elements, forming tetragonal crystals, with the chalcopyrite structure. Infrared studies show that the Li-Te bond is much weaker than the In-Te bond.[418] Solid solution formation was studied in the system In_2Te_3-HgTe : 3 different regions of solid solution formation were established.[419] The new high-pressure phase $MnIn_2Te_4$-II is orthorhombic, space group Pnma. Layers of $MnTe_6$ octahedra are bridged by chains of $InTe_4$ tetrahedra (In-Te 275-283pm).[420]

3.4.3 Indium Halides

α-$Ba_3In_2F_{12}$ is prepared by heating component fluorides in a gold tube under argon for 21d. at 650°C. It forms tetragonal crystals, space group P4/mbm. It is the first example of a structure containing isolated In_2F_{12} groups, (96) i.e. seven-coordinate In, with two bridging fluorines.[421]



(96)

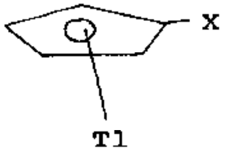
The reactions of powdered InX (X = halide) with water were studied at different temperatures. The presence of metallic indium has a significant effect on the kinetics of disproportionation.[422] Normal coordinate analyses were performed on InX_3Y^-, where X ≠ Y = Cl, Br or I.[423] A powder neutron-diffraction study has been made on $A_2M^{III}_{0.5}Sb^{V}_{0.5}X_6$, where A = Rb, Cs; M = In, Tl; X = Cl, Br. All were found to be disordered, except for A = Cs, M = Tl, X = Cl, where there was superlattice ordering of SbX_6^- and MX_6^{3-} (space group I4/nmd).[424]

Electroreduction of In(III) in acidic KBr solutions at gold electrodes proceeds by 2 successive charge transfer steps: In(III) + 2e → In(I); In(I) + e → In.[425] Sparingly soluble In(I) compounds are precipitated from aqueous solutions of InBr by addition of I^-, OH^-, CO_3^{2-} etc.[426] Indium(I) tetraiodoindate(III) forms orthorhombic crystals (space group Pnna), and In-I(av) in the anion is 271.4pm.[427]

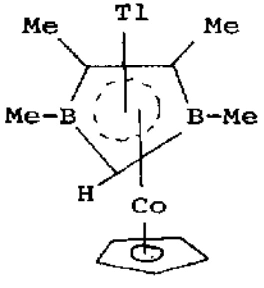
3.5 THALLIUM

3.5.1 Thallium(I) compounds

Preparations, in good yield, were reported for (97), where X = Cl, Br or I. They are useful reagents for preparing a range of halocyclopentadienyl complexes.[428] The first sandwich complex containing apical thallium has been prepared, (98). There are isolated molecules in the crystal, in which the Tl is not directly over the centroid of the C_3B_2 ring.[429]



(97)



(98)

$[\{1,3,5\text{-}(CH_3)_3H_3C_6\}_6Tl_4][GaBr_4]_4$ contains Tl^+ ions alternately coordinated by 1 or 2 mesitylene molecules. It is prepared from mesitylene and $Tl(GaBr_4)$.[430]

Several new ternary alkali metal oxides containing Tl_2O have been obtained, e.g. NaTlO, Na_3TlO_2, KTl_3O_2, $RbTl_3O_2$, $CsTl_3O_2$, in addition to the known KTlO, RbTlO and CsTlO.[431] TlOH reacts with liquid SO_2 to produce $Tl^I_2S_2O_5$, with a Raman spectrum like that of alkali metal disulphites. The product decomposes slowly at room temperature to Tl_2SO_3 and SO_2. Comparison of the Raman spectra of Tl_2SO_3 and of the matrix-isolated products of the $Tl_2O + SO_2$ reaction show that the latter are not Tl_2SO_3 and $Tl_2S_2O_5$, as previously suggested.[432]

Phase equilibria were studied by DTA and X-ray diffraction in the $Tl_2O\text{-}PbO\text{-}MoO_3$ system.[433] $TlLa(SO_4)_2.2H_2O$ forms monoclinic crystals, space group $P2_1/n$. The thallium is nine-coordinate by oxygen atoms, as an irregular polyhedron (Tl-O 274-346pm).[434] Three new oxosulphatovanadates of thallium(I) have been reported: $Tl[VO_2SO_4]$, $Tl[VO(SO_4)_2]$ and $Tl[VO_2(SO_4)(H_2O)_2]$.[435]

^{205}Tl and ^{13}C n.m.r. were used to determine the stabilities of Tl(I) complexes of macrocyclic ligands (such as 18-crown-6, dibenzo-18-crown-6, cis,syn,cis-dicyclohexano-18-crown-6 etc.) in non-aqueous solvents.[436] ^{205}Tl n.m.r. was also used to probe the interaction of Tl^+ with the antibiotics lasolacid$^-$ and gramicidin-A.[437]

The crystal structure of dimeric thallium(I) tri-tert-butoxysilane thiolate, $[(^tBuO)_3SiSTl]_2$, shows that there is a planar Tl_2S_2 ring, with the thallium atoms also weakly coordinated to an oxygen of the $(^tBuO)_3Si$ unit.[438] Tl_2TiS_4 is orthorhombic, space group Pbca. The structure contains puckered TlS_2 layers linking ∞-perthio anions.[439] Tl_3PSe_4 and Tl_3AsS_4 both crystallise in the space group Pcmn.[440]

Equilibrium diagrams of the $HgS\text{-}Tl_4S_3$ and HgS-TlS systems are similar in form except in the region adjacent to Tl_4S_3 or TlS.[441] Phase equilibria were studied in the ternary reciprocal systems $AgTlS + CuTlSe \rightleftharpoons AgTlSe + CuTlS$;[442] and $Tl_4GeS_4 + Tl_2SnS_3$ $Tl_2GeS_3 + Tl_4SnS_4$,[443] as well as in the systems $Tl\text{-}Tl_2S\text{-}Cu_2S\text{-}Cu$;[444] and $CuTlS\text{-}Tl_2S\text{-}S$.[445] Solid solutions with the composition $\alpha\text{-}Hg_3Tl_2Sn_{4-x}Se_x$, where $0 \le x \le 4$, show changes in conductivity at $x \sim 2$.[446] Phase equilibria measurements were also reported for: Tl-Cd-Se;[447] $Tl_2Se\text{-}SnSe_2$;[448] $Tl_4GeSe_4 + Tl_2SnSe_3 \rightleftharpoons Tl_4SnSe_4$ +

Tl_2GeSe;[449] Tl-Sb-Te;[450] $Tl_2Te-Bi_2Te_3-Te$.[451]

Relativistic configuration-interaction calculations (including spin-orbit interaction) have been reported for 9 low-lying excited states of TlF. These confirm the earlier assignment of experimentally observed spectra to these states.[452]

Tl_2PdCl_4 can be isolated from the TlCl-$PdCl_2$ system. It melts incongruently at 358°C.[453] The fusion diagram of AgCl-RbCl-TlCl shows 5 crystallisation fields.[454] The kinetics of solution of thallium(I) halides in water, and their solubilities, were studied, and thermodynamic parameters calculated.[455]

3.5.2 Thallium(III) compounds

A fuller normal coordinate analysis has been carried out on $PhTlF_2$, using new vibrational assignments, and assuming C_{2v} symmetry.[456] Quite detailed vibrational assignments were also proposed for $PhTlX_2$ (X = Cl or Br).[457] A comprehensive assignment of the high-field ^{13}C n.m.r. spectrum has been made for $Tl(CH_3COO)_3$.[458]

The solubility of Tl_2O_3 in HCl at 25°C was studied; several chloro-complexes are formed.[459] Complex formation in the $Tl^{III}-MoO_4{}^{2-}$ system has been followed spectrophotometrically. In the pH range 2-5, the final product is 12-molybdothallate-(III).[460] The mixed-valence thallium orthophosphate, $Tl_3[Tl_{0.5}(H_3O)_{0.5}]H_{14}(PO_4)_8.4H_2O$, forms triclinic crystals, space group $P\bar{1}$. The Tl^{3+} is octahedrally coordinated by oxygens (Tl-O 218-225pm), while Tl^+ is surrounded by eight oxygens (Tl-O 290-312pm).[461]

The kinetics of ligand exchange in aqueous thallium(III) halide solutions have been investigated by ^{205}Tl n.m.r.[462]

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