

Chapter 3
 ELEMENTS OF GROUP 3

George Davidson

3.1	BORON	75
3.1.1	Boranes	75
3.1.2	Borane Anions and Metallo-derivatives	78
3.1.3	Carba- and other Non-metal Heteroboranes	86
3.1.4	Metallo-heteroboranes	88
3.1.5	Compounds containing B-C Bonds	92
3.1.6	Aminoboranes and other Compounds containing B-N Bonds	94
3.1.7	Compounds containing B-P Bonds	96
3.1.8	Compounds containing B-O Bonds	97
3.1.9	Boron Halides	99
3.1.10	Boron-containing heterocycles	101
3.1.11	Boron Nitride, Metal Borides	109
3.2	ALUMINIUM	109
3.2.1	Aluminium Hydrides	109
3.2.2	Compounds containing Al-C or Al-Ge Bonds	110
3.2.3	Compounds containing Al-N or Al-P Bonds	111
3.2.4	Compounds containing Al-O or Al-Se Bonds	113
3.2.5	Aluminium hydrides	116
3.3	GALLIUM	118
3.3.1	Compounds containing Ga-C Bonds	118
3.3.2	Compounds containing Ga-N or Ga-P Bonds	118
3.3.3	Compounds containing Ga-O, Ga-S or Ga-Se Bonds	119
3.3.4	Gallium halides	120
3.4	INDIUM	121
3.4.1	General	121
3.4.2	Compounds containing bonds between Indium and Atoms of Group 6 Elements	122
3.4.3	Indium Halides	123
3.5	THALLIUM	124
3.5.1	Thallium (III) Compounds	124
3.5.2	Thallium (I) Compounds	125

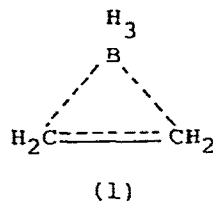
3.1 BORON

3.1.1 Boranes

Ab initio LCAO-MO-SCF Hartree-Fock-Roothaan calculations were carried out on B^{3+} , E^+ , BH , BH_2^- , BH_2^+ , EH_3 and BH_4^- . Proton and hydride affinities were calculated, together with energies of reaction between various pairs of these species.¹

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

Ab initio m.o. calculations on the reaction of BH_3 with ethylene suggest that the reaction is exothermic, via an intermediate π -complex (1), and with no overall activation barrier. The mechanism



in the gas-phase consists of two facile stages: (i) formation of the π -complex, and (ii) rearrangement to the ethyl borane product.³

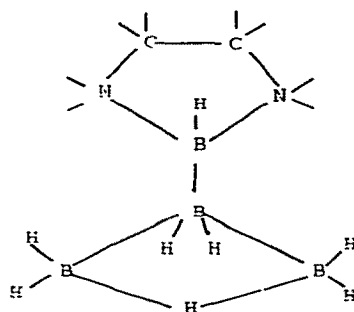
Irradiation of B_2H_6 with the 973 cm^{-1} line of a CW CO_2 laser produced $B_{10}H_{14}$, B_5H_9 , B_5H_{11} , $(BH)_n$ and H_2 . The number of photons needed to produce one molecule of $B_{10}H_{14}$, $(B_5H_9 + B_5H_{11})$, H_2 , and to transform one molecule of B_2H_6 were: 22000, 287, 156 and 156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

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

The low-temperature ^{19}F n.m.r. spectra of $E_4H_8PF_2NMe_2$ reveal the presence of two geometrical isomers. One form has slow rotation about the P-B bond at low temperatures, to give resolvable resonances due to the non-equivalent fluorines in that isomer (believed to be the one in which the PF_2NMe_2 group is endo- with respect to the ring).⁷

Variable-temperature ^{11}E and 1H n.m.r. spectra have been reported for the fluxional hypho-borane $(Me_2NCH_2CH_2NMe_2)B_4H_8$. The low-

temperature, limiting structure has two equivalent and two unique boron atoms. All of the observations are accounted for by the structure (2). The mechanism of the fluxional behaviour was not



(2)

settled however.⁸

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

Extended-Hückel m.o. calculations have been performed on $(\text{BH})_n$ systems, where $n = 1$ to 9. The energies of alternative structures were calculated for 6-, 7- and 8-vertex structures with differing overall charges. Thus, for $\text{B}_6\text{H}_6^{n-}$, ($n = 0, 2, 4$ or 6), the most stable structures are predicted to be bicapped tetrahedral (C_{4v}), octahedral (O_h), pentagonal pyramidal (C_{5v}) and trigonal prismatic (D_{3h}) respectively. All stable forms have their bonding orbitals filled, and therefore their structures are anticipated by the 'capping' principle.¹⁰

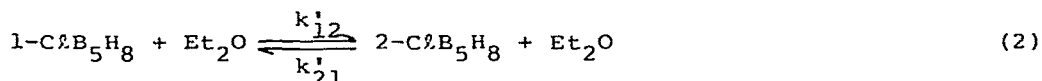
The effects on the electronic structures of $\text{B}_5\text{H}_5^{2-}$ or $\text{B}_6\text{H}_6^{2-}$ of adding one or two extra terminal or bridging protons have been calculated. Trigonal bipyramidal and square pyramidal B_5H_6^- and B_5H_7 were the five-vertex species considered. The six-vertex systems examined were octahedral, trigonal prismatic and capped square pyramidal B_6H_7^- and B_6H_8 . If the polyhedron consists of triangular faces only, then there is little preference for bridging ligands. If square faces are present there is a marked preference for bridging ligands at the edge of such faces.¹¹

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



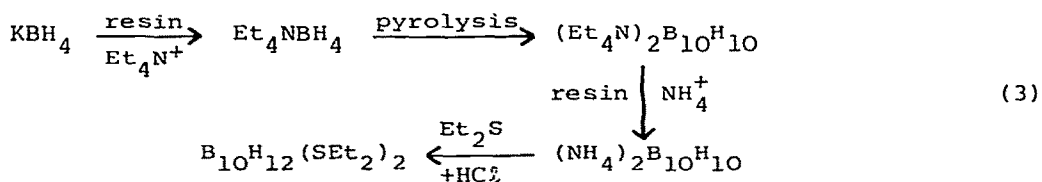
molecule of known proton affinity. The value of the $(B_5H_8)-H$ dissociation energy was found to be $98.4 \pm 2 \text{ kcal.mol}^{-1}$, i.e. close to the value of the energy of dissociation of a proton from HBF_2 , but less than the value from borazine.¹²

1-C₂- and 2-C₂-B₅H₈ isomerise under the influence of diethyl ether as catalyst. The reaction is first-order in borane and in ether. The rate constants for equation (2) are $k'_{12} = 2.72 \times 10^{-6}$



$M^{-1}s^{-1}$ and $k_{21}' = 0.48 \times 10^{-6} M^{-1}s^{-1}$ (at $24.5^\circ C$, with $0.174 M$ $1-C_2-B_5H_8$, $3.65 M$ Et_2O). The activation energy for the forward reaction is $14.6 \text{ kcal.mol}^{-1}$. The isomerisation probably proceeds via a boron cage rearrangement involving an $Et_2O.C_2B_5H_8$ complex, and not via B-Cl bond breaking.¹³

An improved route, equation (3), has been devised for the conversion of KBH_4 to $\text{B}_{10}\text{H}_{12}(\text{SEt}_2)_2$. This avoids the hazardous pyrolysis



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

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

Reaction of X_2 ($X = Br$ or I) with $Me_2SnB_{10}H_{12}$ gives Me_2SnX_2 and $B_{10}H_{12}X_2$. The crystal structure of 5,10- $B_{10}H_{12}Br_2$ was determined, showing that the B-Br distance is 1.94 Å, and that the B_{10} cage is only very slightly distorted compared to that in $B_{10}H_{14}$. When $Me_2SnB_{10}H_{12}$ reacts with a deficiency of Br_2 , traces of Me_2SnBrB_{10}

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

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

3.1.2 Borane Anions and Metallo-derivatives

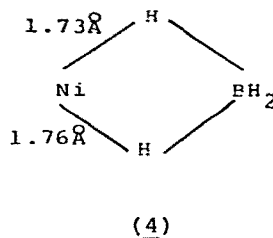
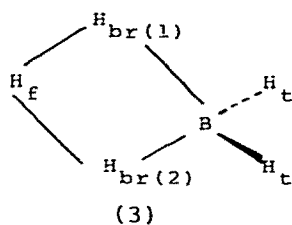
Gas-phase ^{11}B and 1H n.m.r. spectra of $Be(BH_4)_2$ show that only one, monomeric, species is present, with a linear B-Be-B framework. The hydrogens of each BH_4 unit undergo rapid intragroup internal exchange. $Be(B_3H_8)_2$, $cpBe(B_3H_8)$ and $(MeBeB_3H_8)_2$ were also prepared and characterised.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

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

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

The vibrational spectrum of $(MeC_5H_4)_2Hf(BH_4)_2$ shows that the perturbation of the BH_4^- ion is less than in most transition metal tetrahydroborate complexes. N.m.r. spectra show that the exchange

of bridge and terminal H atoms of the BH_4^- groups is rapid down to -155°C on the n.m.r. time scale (thus ΔG^\ddagger is less than about $4.9 \text{ kcal. mol}^{-1}$). The crystal structure shows that the coordination of BH_4^- is unsymmetrical, (3). Thus $\text{Hf}-\text{H}_{\text{br}(1)} = 2.069\text{\AA}$, $\text{Hf}-\text{H}_{\text{br}(2)} = 2.120\text{\AA}$, with $\text{H}_{\text{br}(1)}-\text{B} = 1.255\text{\AA}$, $\text{H}_{\text{br}(2)}-\text{B} = 1.208\text{\AA}$.²²

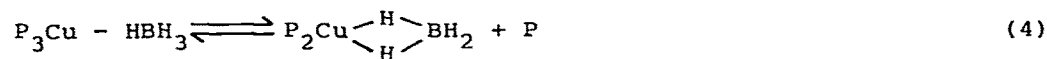


From reactions of NaBH_4 with Co(II) salts in the presence of PPh_3 , it has been possible to isolate two Co(I) complexes, $\text{Co}(\text{BH}_4)(\text{PPh}_3)_n$ (where $n = 2$ or 3).²³ Similar reactions with Ni(II) salts give Ni(I) complexes; thus $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}, \text{PPh}_3$ and NaBH_4 give $[\text{Ni}(\text{BH}_4)(\text{PPh}_3)_3]_2$, while $\text{NiX}_2(\text{PPh}_3)_2$ (where $\text{X} = \text{Cl}, \text{Br}$ or I) and NaBH_4 give $\text{Ni}(\text{BH}_4)(\text{PPh}_3)_{1.5}$.²⁴

The crystal structure of $\text{Ni(H)(BH}_4)(\text{PCy}_3)_2$ shows that the tetrahydroborate is bonded in a bidentate fashion, (4); note that the bonding is almost symmetrical, unlike the Co analogue which is much more distorted. The difference is related to the different electron configurations, the Ni(II) (d^8) prefers trigonal bipyramidal, the Co(II) (d^7) square pyramidal, coordination.²⁵

A new diamagnetic Cu(I)-BH_4 complex has been prepared: $[(\text{MeO})_3\text{P}]_2\text{CuBH}_4$. This is soluble enough to enable low-temperature n.m.r. spectra to be obtained. and these show a slowing-down of the fluxional process.²⁶

The crystal structure of $\text{Cu}(\text{PPh}_2\text{Me})_3\text{BH}_4$ has been determined, and this showed that the BH_4^- is attached to the Cu via a single hydrogen bridge, with $\text{Cu}-\text{H}_{\text{br}} = 1.47\text{\AA}$, $\text{H}_{\text{br}}-\text{B} = 1.19\text{\AA}$. The solid-phase i.r. data are consistent with this, but in benzene solution there was evidence for the presence of bidentate BH_4 , presumably



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

$Y(BH_4)_3(THF)_3$ contains one bidentate BH_4 and two tridentate BH_4 groups. In the $Y \begin{array}{c} H \\ \diagup \quad \diagdown \\ H \end{array} B-H$ unit the ligand is tilted slightly from C_{3v} symmetry, with unequal Y-H bond lengths.²⁸

$Er(BH_4)_3 \cdot 2THF$ is formed from $NaBH_4$ and $ErCl_3$ in THF. It is not possible to remove the solvate without decomposition.²⁹ A preliminary report has appeared of the i.r. spectrum of $U(BH_4)_4$.³⁰

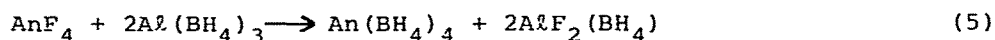
The adducts $U(BH_4)_4 \cdot L$ (where $L = Me_2O$ or Et_2O) were studied by X-ray diffraction. Each complex contains infinite linear chains of alternating U and B atoms, joined by double hydrogen-bridge bonds. The remaining BH_4 units were joined to U by triple hydrogen-bridge bonds.³¹

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

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

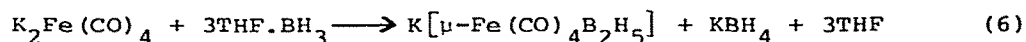
Tris(indenyl)thorium tetrahydroborate, $(\eta^5-C_9H_7)_3ThBH_4$ has been prepared from the chloro-analogue and $NaBH_4$. Its i.r. spectrum is consistent with tridentate BH_4 coordination.³⁴

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

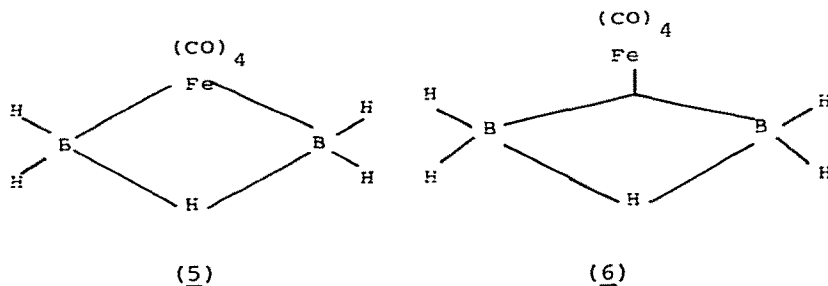


diffraction patterns show that the Pu and Np compounds are isomorphous, with a tetragonal crystal structure. I.r. spectra show that all of the BH_4 units are equivalent (in a tetrahedral array) and tridentate, thus the metals are formally 12 coordinate.³⁵

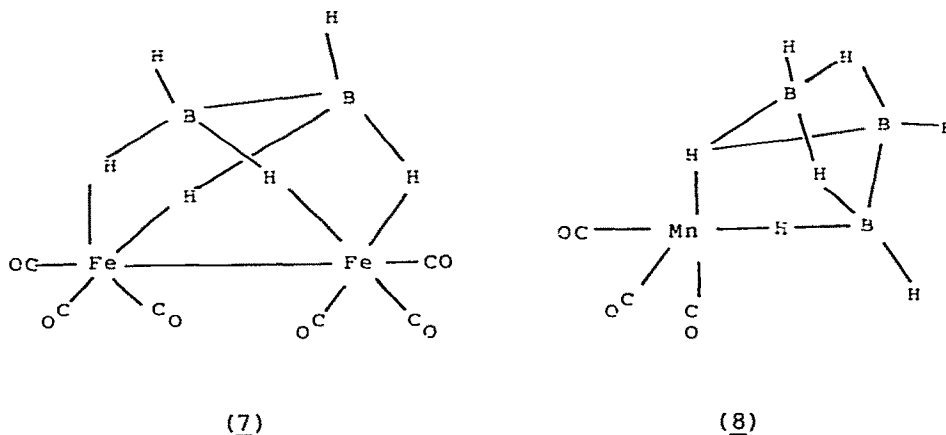
The first example of a substituted diborane(6) with a transition metal at a bridge site has been reported. It is $K[\mu-Fe(CO)_4B_2H_5]$, prepared as in equation (6). There is insufficient experimental



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



The reaction of $\text{Fe}(\text{CO})_5$ and B_5H_9 gives as one product $\text{B}_2\text{H}_6\text{Fe}_2(\text{CO})_6$ (yield 1-10%). I.r., n.m.r. and mass spectra are consistent with the formulation (7). This framework is nido- according to electron-counting rules - a derivative of the unstable B_4H_8 . It could alternatively be viewed as $\text{B}_2\text{H}_6^{2-}$ acting as an eight-electron donor to $\text{Fe}_2(\text{CO})_6^{2+}$, in agreement with the eighteen-electron rule.³⁷



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

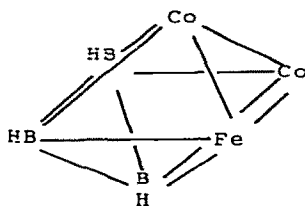
$(\text{OC})_3\text{Mn}(\text{B}_3\text{H}_8)$ contains a tridentate B_3H_8^- ligand attached to Mn

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

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

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

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

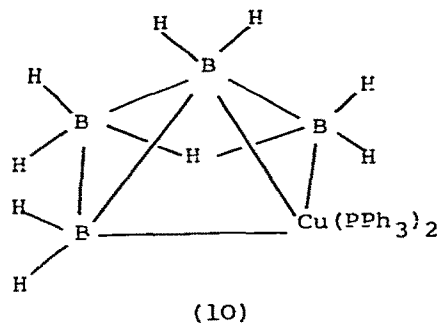


(9)

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

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

$(\text{Ph}_3\text{P})_2\text{CuB}_4\text{H}_9$ is the first metallo-derivative containing the B_4H_9 unit to be reported. It has a unique structure in that the copper atom is at the vertex of a cluster skeleton, and there is no evidence for Cu-H-B bridge bonding, (10).⁴⁵



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

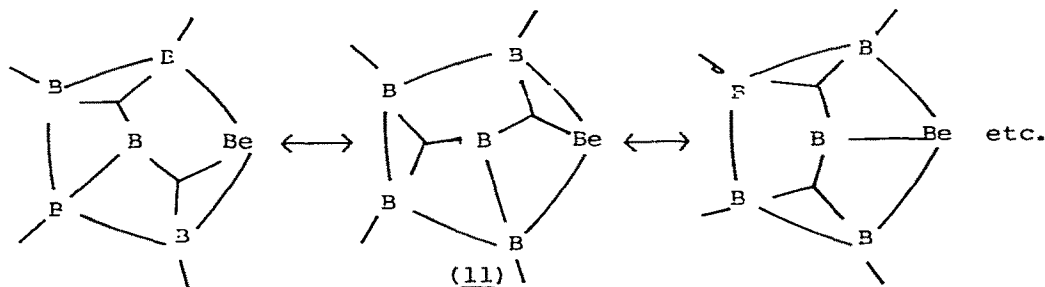
B_5H_8^- reacts with $[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\text{I}]$ to form $[\text{Fe}(2\text{-B}_5\text{H}_8)(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{I}]$. KH deprotonates this to give the anionic complex $[\text{Fe}(2\text{-B}_5\text{H}_7)(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]^-$. The latter can react with a further 1 mole of $[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\text{I}]$, forming $[\{\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\}_2(2,4\text{-B}_5\text{H}_7)]$. The structures of the complexes are consistent with the idea that the nido-pentaborane anions act as 2-3- η ligands in the 16-electron compounds, and as 2- σ ligands in the 18-electron compounds.⁴⁷

Potassium nido-octahydropentaborate, KB_5H_8 , reacts with cis-bis(phosphine) complexes of $\text{Pd}(\text{II})$ or $\text{Pt}(\text{II})$ to give cis- $[\text{M}(\text{B}_5\text{H}_8)(\text{PR}_3)_2\text{X}]$, where $\text{M} = \text{Pd}$ or Pt ; $\text{X} = \text{Cl}, \text{Br}, \text{I}$ or Me ; $\text{PR}_3 = \text{PPh}_3, \text{PMe}_2\text{Ph}, \text{PMe}_3$ or $\frac{1}{2}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$. The Pt complexes are more stable than those of Pd . Analogous reactions produce AsPh_3 derivatives, cis- $[\{\text{Pt}(\text{B}_5\text{H}_8)\text{X}(\text{PMe}_2\text{Ph})(\mu\text{-SMe})\}_2]$ and the less stable trans- $[\text{Pt}(\text{B}_5\text{H}_8)\text{X}(\text{PMe}_2\text{Ph})_2]$, where $\text{X} = \text{I}$ or Me . The B_5H_8 is always η^2 -bonded.⁴⁸

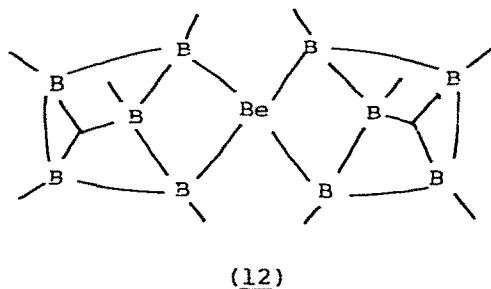
16-electron $\text{Cu}(\text{I})$ complexes, $[\text{Cu}(\mu\text{-1-BrB}_5\text{H}_7)(\text{PPh}_3)_2]$ and $[\text{Cu}(\mu\text{-B}_5\text{H}_8)\text{dppe}]$, where $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, have been prepared. They are very similar to $[\text{Cu}(\mu\text{-B}_5\text{H}_8)(\text{PPh}_3)_2]$. The silver analogue, $[\text{Ag}(\mu\text{-B}_5\text{H}_8)(\text{PPh}_3)_2]$, decomposes in solution even in the absence of light, although ^{11}B n.m.r. spectra show that it is not fluxional. The species " $\text{Au}(\text{B}_5\text{H}_8)(\text{PPh}_3)$ " is possibly formed at -78°C , but it could not be isolated.⁴⁹

Trans-IrCl(CO)(PMe₃)₂ reacts with 1- or 2-halopentaboranes with insertion into a basal B-H bond at the site predicted to be the most susceptible to nucleophilic substitution by S.C.F. calculations. The relative order of reactivity is: 2-BrB₅H₈ ~ 2-ClB₅H₈ > 1-BrB₅H₈ > 1-ClB₅H₈ ~ B₅H₉ >> 1-MeB₅H₈.⁵⁰

Several beryllaboranes have been prepared in which the Be atom occupies a basal position in a pentagonal-pyramidal borane cage, B₅H₁₀BeX (where X = BH₄, B₅H₁₀, Cl, Br, Me or C₅H₅). The beryllium atom has unusual flexibility in coordination, and the bonding in several compounds cannot be interpreted using conventional bond concepts. The styx bonding description classifies these B₅H₁₀BeX species as 5210 forms, with several resonance forms, probably not all of equal weight, (11).⁵¹



The crystal structure of B₅H₁₀BeBH₄ has been elucidated. The molecule consists of a pentagonal-pyramidal cage with Be in a basal position. The BH₄ is attached to the beryllium by two bridging hydrogens. For 2,2'-commo-bis[2-berylla-nido-hexaborane-(11)], B₅H₁₀BeB₅H₁₀, there are two pentagonal-pyramidal cages linked by a common Be atom. The topological structure is shown in (12).⁵²

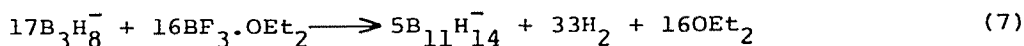


Various 10- or 12-vertex, closo- or nido-metalloboranes are formed by nido-cage closure or polyhedral expansion of closo-borane anions, with metallocenes being used as sources of the metal vertex. Thus $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}$ reacts with nido- $\text{B}_{11}\text{H}_{13}^{2-}$, $\text{B}_{10}\text{H}_{13}^-$ or $\text{B}_9\text{H}_{12}^-$ in the presence of a catalytic amount of Na/Hg to produce, respectively, closo- $[(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{11}\text{H}_{11}]^-$, nido- $[(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{12}]^-$ and the isomeric closo- $[1-$ and $-[2-(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]^-$. The polyhedral expansion of borane anions involves the first recorded oxidative addition of a B-B bond unit of a borane to a metal complex.⁵³

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

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

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



$\text{BF}_3\cdot\text{OEt}_2$ and NaBH_4 , giving the overall stoichiometry shown in (8).⁵⁶



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

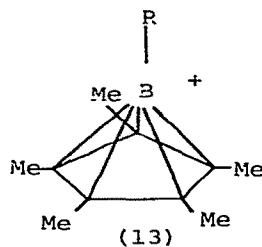
Theoretical calculations have been carried out on hypothetical large closo-borane anions, using the PRDDO technique. They sugg-

ested that (a) some structures can have full polyhedral symmetry only if they are neutral, that is $2n$ framework electrons for n vertices; (b) there is no difference, on average, in the stabilities of even and odd numbered polyhedra; and (c) 22 vertices probably represents the upper limit for truly stable structures.⁵⁸

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

3.1.3 Carba- and other Non-metal Heteroboranes

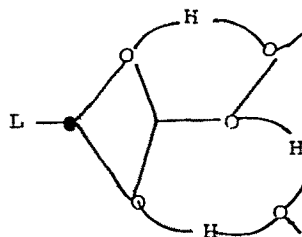
$(Me_5C_5)BCl_2$ reacts with $(Me_5C_5)Li$ to form $(Me_5C_5)_2BCl$ and $LiCl$. The former reacts with further BCl_3 to give (13), as the BCl salt, where $R = C_5Me_5$.⁶⁰



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

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

Alkaline methanolysis of 6-NMe₂-6-CB₉H₁₁ produces a 75% yield of hypho-3,4-μ-(trimethylaminecarba)hexaborane(11), Me₃N.CB₅H₁₁ (14) where ● is CH, o is BH, σ is BH₂ and L = NMe₃. Thus the



(14)

3,4-H-bridge of B₅H₁₁ has been replaced by a CHNMe₃ bridge.⁶³

A discussion has been given of the appropriate descriptions for a number of heteroboranes containing hetero-atoms which could contribute different numbers of electrons to the cage structure, e.g. S in 6,8-S₂B₇H₉ etc. It appears that the majority of nine-atom arachno- and nido-frameworks differ only in electron count, and not in both electron count and framework structure.⁶⁴

Aqueous K[B₉C₂^{7,8}H₁₂] reacts with aqueous FeCl₃ to produce 33% of B₈C₂^{5,6}H₁₂, with small amounts of B₈C₂^{5,6}H₁₁(OH), 1.6%, B₈C₂^{5,6}ClH₁₁, 0.9%, and B₇C₂^{4,5}H₁₁, 4.2%. Decreasing the reactant concentrations leads to an increase in the percentage yield of the last, giving a simple route to an otherwise inaccessible carbaborane.⁶⁵

B₁₀H₁₂CNMe₃ reacts successively with trimethylamine and then RPhCl₂, R = Me, Et or Ph, to form nido-Me₃NCB₁₀H₁₀PR. When R = Ph, an X-ray structure determination showed that the PPh group bridges two boron atoms at the open face of the B₁₀H₁₀CNMe₃ icosahedral fragment, i.e. B(9) and B(10).⁶⁶

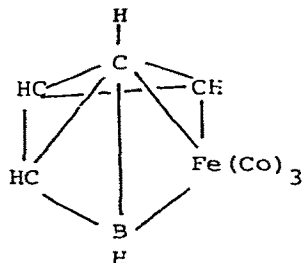
Dicarbadoodecarborate(14) dianions react with ArMgX or ArLi to form B-aryldianions. Oxidation of these by CuCl₂ produces 3-, 4-, 8- and 9-aryl-o-carbaboranes. The 4-o- and 9-o-carbaboranyl groups were established as electron-releasing substituents.⁶⁷

A report has been given of the formation of 1,2-dicarbadoodecaborane(12) attached to polystyrene, and its conversion to a polymer-bound Rh complex, written as P-CH₂C₂B₉H₁₀Rh(H)(PPh₃)₂, where P represents the rigid polystyrene framework, which is a potentially useful hydrogenation catalyst.⁶⁸

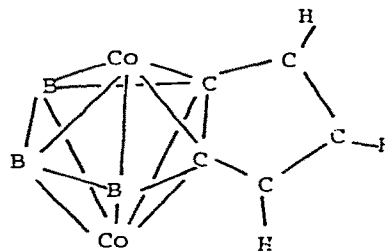
3.1.4 Metallo-heteroboranes

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

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



(15)



(16)

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

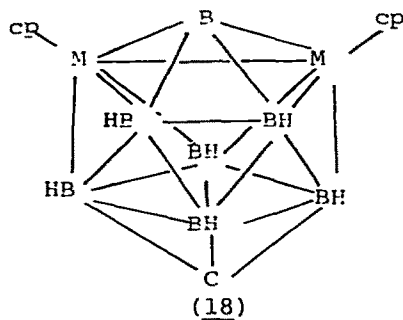
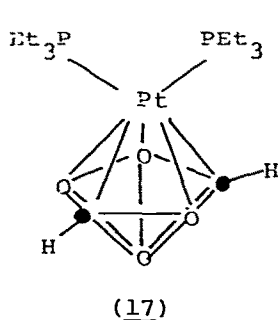
The complexes $5-[(\eta^5-C_5H_5)Co(\eta^5-C_5H_4)]-[2,3-Me_2C_2B_4H_3]Co-[2,3-Me_2C_2B_3H_5]$ and $\sigma-(CH_2)_4O-[2,3-Me_2C_2B_4H_3]Co[2,3-Me_2C_2B_3H_5]$ have been prepared by the action of $(\eta^5-C_5H_5)Co(CO)_2$ in THF on $[2,3-Me_2C_2B_3H_5]CoH[2,3-Me_2C_2B_4H_4]$ under u.v. irradiation. A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

Treatment of dicarbon cobaltaboranes closo-1,2,3- $(\eta^5-C_5H_5)-CoC_2-B_4H_6$, nido-1,2,3- $(\eta^5-C_5H_5)CoC_2B_3H_7$ and their C,C'-dimethyl derivatives with a 10% solution of KOH in ethanol, open to the atmosphere, led to oxidative fusion of the dicarbon species. This gave tetra-

carbon 12-vertex cage systems with $\text{Co}_2\text{C}_4\text{B}_6$ and CoC_4B_7 frameworks respectively e.g. $(\eta^5\text{-C}_5\text{H}_5)\text{CoC}_4\text{B}_7\text{H}_{11}$ and three isomers of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_4\text{B}_6\text{H}_{10}$, the first parent tetracarbon metallocarbaboranes. The crystal structure of one of the latter showed the presence of an open 12-vertex cage system, with cobalt atoms at five- and six-coordinate vertices, and all four carbon atoms at the open face.⁷³

Metallocarbaboranes can be prepared using metal atoms or organo-metallic reagents without prior synthesis of the carbaborane system. Thus, cyclopentadiene, B_5H_9 and 2-butyne react with Co atoms to give $\text{cpCo}(\text{C}_2\text{Me}_2\text{B}_4\text{H}_4)$, the "triple-decker sandwich" $\text{cpCo}(\text{C}_2\text{Me}_2\text{B}_3\text{H}_3)\text{-Cocp}$, and $\text{cpCo}_2(\text{C}_2\text{Me}_2\text{B}_5\text{H}_5)$. Yields are low, but further experiments have suggested possible improvements.⁷⁴

$\text{Pt}(\text{PEt}_3)_2$ reacts with nido-2,3- $\text{C}_2\text{B}_4\text{H}_8$ or nido-2,3- $\text{Me}_2\text{-2,3-C}_2\text{B}_4\text{H}_6$ to give [nido- $\mu_4,5$ -[trans-(Et_3P) $_2\text{Pt}(\text{H})$]- $\mu_{5,6}$ -H-2,3- $\text{C}_2\text{B}_4\text{H}_6$], and its 2,3-dimethyl derivative. Pyrolysis of these gave closo-platinacarboranes with adjacent, non-adjacent carbon atoms respectively, e.g. (17) where O is BH, ● C.⁷⁵



The crystal and molecular structures of 2,3- $(\eta\text{-C}_5\text{H}_5)_2\text{-(2,3)-NiCo-10-CB}_7\text{H}_8$ have been determined. The structure has the bicapped square antiprismatic geometry expected for a closo ten-vertex polyhedron. The two metal atoms are indistinguishable, and occupy adjacent sites in the same equatorial belt; the carbon atom is not adjacent to the two metal atoms, (18).⁷⁶

The molecular structure of 1,8- $(\eta\text{-C}_5\text{H}_5)_2\text{-1-Fe-8-Co-2,3-C}_2\text{B}_7\text{H}_9$, shows that although the complex is one electron short of the $2n+2$ electrons required for closo-polyhedral bonding, the molecule has the closo-11-vertex, octadecahedral geometry. The iron atom is at a six coordinate vertex, the two carbon atoms at four-coordinate vertices, and the Co atom at a five-coordinate position, adjacent

to carbon, not iron.⁷⁷

Transition metal complexes of arsaboranes have been reported. Thus, CoCl_2 or NiCl_2 react with $\text{B}_{10}\text{H}_{12}\text{As}^-$ to form $\text{M}(\text{B}_{10}\text{H}_{10}\text{As})_2^{n-}$ (where $\text{M} = \text{Co}$, $n = 3$; $\text{M} = \text{Ni}$, $n = 2$). Related complexes are also formed which contain $\text{B}_9\text{H}_9\text{As}_2^-$ as ligand. It is found that the number of transition metal complexes formed by arsaboranes is very much less than for other heteroborane systems.⁷⁸

Polyhedral expansion of $3,1,2\text{-C}_5\text{H}_5\text{FeC}_2\text{B}_9\text{H}_{11}$ leads to the formation of three new electron-deficient biferracarboranes: $(\text{cpFe})_2\text{C}_2\text{B}_9\text{H}_{11}$, $(\text{cpFe})_2\text{C}_2\text{B}_8\text{H}_9(\text{OH})$ and $(\text{cpFeC}_2\text{B}_9\text{H}_{11}\text{FeC}_2\text{B}_9\text{H}_{11})^-$. All contained formally Fe(III) atoms, and were diamagnetic. They are the first recorded complexes in which there is long-range electron-spin coupling through a carbaborane polyhedron.⁷⁹

SCCC m.o. calculations on cp_2Fe and $\text{cpFe}(\text{C}_2\text{B}_9\text{H}_{11})^-$ show that in the former the cyclopentadienyl π -orbitals are mainly involved in bonding, whereas the dicarbollide ligand bonding gives the σ -orbitals an important role. Thus the view that the frontier orbitals of the dicarbollide ligand are directly comparable to the cyclopentadienyl π -orbitals is in need of qualification. In $\text{cpFe}(\text{C}_2\text{B}_9\text{H}_{11})^-$ the cyclopentadienyl ligand donates 0.164 of an electronic charge to Fe(II), the dicarbollide ligand 1.037 of an electronic charge.⁸⁰

Oxidative addition of 7,9- or 7,8- $\text{C}_2\text{B}_9\text{H}_{12}^-$ to $(\text{PPh}_3)_2\text{Ru}(\text{H})\text{Cl}$ gives respectively 2,2- $(\text{PPh}_3)_2\text{-2,2-H}_2\text{-2,1,7-RuC}_2\text{B}_9\text{H}_{11}$ and 3,3- $(\text{PPh}_3)_2\text{-3,3-H}_2\text{-3,1,2-RuC}_2\text{B}_9\text{H}_{11}$. Heating the 2,1,7-isomer in vacuo led to reversible elimination of one molecule of H_2 , giving a five-coordinate, d^6 , formal Ru(II) complex.⁸¹

The crystal structure of $[(\text{PPh}_3)_2\text{RhC}_2\text{B}_9\text{H}_{11}]_2$ shows that each Rh atom is symmetrically bound to the pentagonal face of a $\text{C}_2\text{B}_9\text{H}_{11}$ ligand, and that it interacts with the other ligand by a Rh-H-B bridge.⁸²

The crystal structures of $3\text{-}[\text{C}_2\text{H}_4(\text{NMe}_2)_2]\text{-3,1,2-PdC}_2\text{B}_9\text{H}_{11}$ and of $3,3\text{-(PMe}_3)_2\text{-3,1,2-PdC}_2\text{B}_9\text{H}_{11}$ show a considerable structural influence of the ligands trans to the $\text{C}_2\text{B}_9\text{H}_{11}$ cage. The amino-compound adopts a "slipped" configuration, while replacement by $(\text{PMe}_3)_2$ leads to more symmetrical metal-cage bonding.⁸³

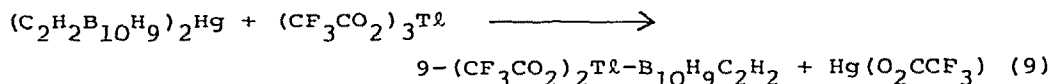
$\text{AuBr}_2(\text{S}_2\text{CNEt}_2)$ reacts with $\text{Te}(\text{B}_9\text{C}_2^{1,2}\text{H}_{11})$ to produce, in addition to the known ion $[3,3^1\text{-Au}(\text{B}_9\text{C}_2^{1,2}\text{H}_{11})_2]^-$, the novel carba-auraborane $\text{B}_9\text{C}_2^{1,2}[\text{Au}(\text{S}_2\text{CNEt}_2)]^3\text{H}_{11}$. Single-crystal X-ray diffraction shows that the molecular structure is definitely distorted.

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

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

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

Carbaboranes with B-Tl bonds are prepared by the reaction of $Tl(O_2CCF_3)_3$ with carbaboranyl derivatives mercurated at B(9), equation (9). The mercury compound is therefore a possible conven-

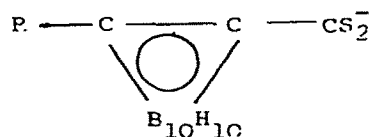


ient starting material for the formation of other B-M bonded species.⁸⁷

This was borne out by further reactions with $SnCl_2$, MCl_3 (M = As or Sb) and S, giving B-Sn, B-M or B-S carbaboranes.⁸⁸

Raman spectra of bis(dicarba-closo-dodecarboran(12)yl)mercury and its $TlCl$ analogue show ν_{Hg-C} or ν_{Tl-C} bands in the region $130-180\text{ cm}^{-1}$. The low values suggest that the vibrations involve motion of the whole carbaborane fragments.⁸⁹

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



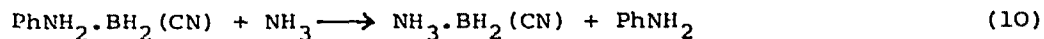
(19)

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

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

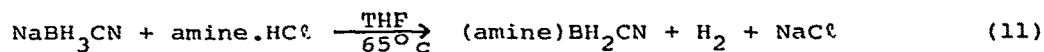
3.1.5 Compounds containing B-C Bonds

Ammonia-cyanoborane, $\text{NH}_3\cdot\text{BH}_2(\text{CN})$, has been prepared by the amine displacement reaction (10). This is the first definite report of



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

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



NH_2 . ν_{CN} values were as expected for B-CN, not B-NC bonding.⁹³

Addition of an equivalent of X_2 ($\text{X} = \text{Cl}, \text{Br}$ or I) to $\text{Na}[\text{H}_3\text{BCN}]$ in 1,2-dimethoxyethane leads to formation of cyclic cyanoborane oligomers. In the presence of excess Lewis base, the oligomer forms cyanoborane adducts $\text{L}\cdot\text{BH}_2\text{CN}$. If $\text{L} = \text{py}$, chlorination of $\text{L}\cdot\text{BH}_2\text{CN}$ in moist C_6H_6 produces $\text{L}\cdot\text{BCl}_2\text{CN}$.⁹⁴

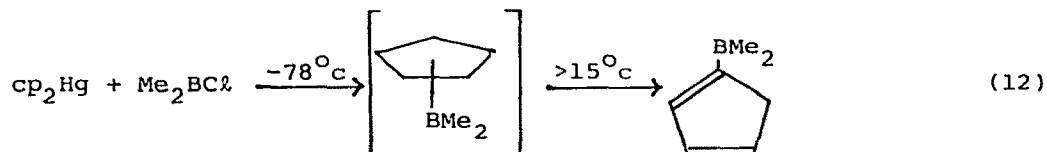
A complete assignment of all vibrational fundamentals of CH_3BF_2 has been proposed, using i.r. and Raman spectra of the normal compound, together with ^{11}B - and ^{10}B -enriched CH_3BF_2 and CD_3BF_2 .⁹⁵

SiMe_4 and BY_3 ($\text{Y} = \text{Br}$ or I) react in 1:1 molar ratio at $120\text{--}150^\circ\text{C}$

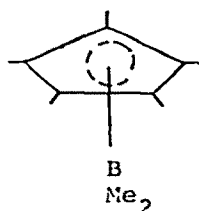
(Br), 80-90°C (I), to give Me_3SiY and MeBY_2 . In a 2:1 ratio, the products are Me_3SiY (2 moles) and Me_2BY . Except for MeBI_2 these are convenient routes for the preparation of these compounds.⁹⁶

A microwave examination of the $\text{Me}_3\text{N.BMe}_3$ structure led to the following bond lengths being obtained: $d(\text{BN})$ 1.698 Å; $d(\text{NC})$ 1.470 Å; $d(\text{BC})$ 1.69 Å. The NBC and BNC angles were 108.0°, 111.6° respectively.⁹⁷

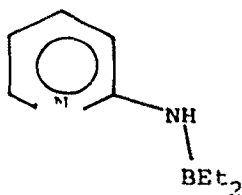
Cyclopentadienyldimethylborane is formed by the reaction (12). N.m.r. results reveal fluxional behaviour, described as [1,5]-



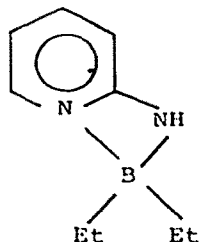
sigmatropic migration of BMe_2 . The pentamethyl analogue is stable as the form (20) to room temperature.



(20)



(21)



(22)

The microwave, i.r. and Raman spectra of $\text{Et}^{10}\text{BF}_2$ and $\text{Et}^{11}\text{BF}_2$ have been reported. The BF_2 internal torsional mode is at 44cm^{-1} , corresponding to a two-fold barrier of $1.17\text{ kcal.mol}^{-1}$. The B-C bond distance was calculated to be 1.572 Å.⁹⁹

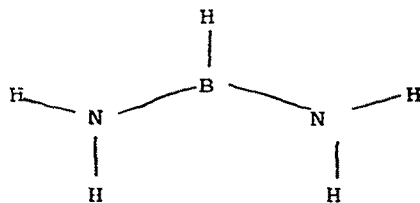
Triethylborane and 2-aminopyridine react in a molar ratio of 2:1, in the absence of a solvent to give a good yield of pure (2-pyridylamino)diethylborane. ^{13}C n.m.r. data suggest that there is an equilibrium between two different forms - one containing three-coordinate boron, (21), the other four-coordinate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

3.1.6 Aminoboranes and other Compounds containing B-N Bonds

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



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



(23)

Methyl lithium reacts with $\text{Me}_2\text{B-NH-X}$, where $\text{X} = \text{NMe}_2$ or SiMe_3 , to form $[\text{Me}_3\text{BNHX}]^-\text{Li}^+$. These lose CH_4 to give the N-lithio derivatives, $\text{Me}_2\text{B-NLi-X}$. The B-N bond order in the latter is greater than one (from n.m.r. data), and it seems from mass spectrometry that when $\text{X} = \text{SiMe}_3$ the compound is hexameric, but when $\text{X} = \text{NMe}_2$ it is polymeric.¹⁰²

The mean amplitudes of vibration were calculated for $\text{Me}_3\text{N.BX}_3$, where $\text{X} = \text{Cl}$ or F , from force field calculations.¹⁰³

Microwave spectra have been obtained for several isotopic variants of $\text{Me}_3\text{N.BFH}_2$, ($^{11}\text{B}/^{14}\text{N}$; $^{11}\text{B}/^{15}\text{N}$; $^{10}\text{B}/^{14}\text{N}$; $^{10}\text{B}/^{15}\text{N}$). Assuming the geometry of the Me_3N fragment, a value of $1.63 \pm 0.01 \text{ \AA}$ was obtained for the B-N distance, which is close to the values for the BH_3 and BF_3 analogues.¹⁰⁴

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

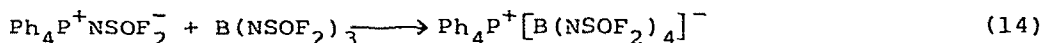
1:1 Adduct formation was established in the following systems: $\text{L/BBr}_n\text{Me}_{3-n}$, where $\text{L} = \text{py}$, 4-Mepy, Me_3N or Me_3P , $n = 1$ or 2 , except for py and 4-Mepy, which only form 2:1 adducts with BBrMe_2 .¹⁰⁶

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

Monoalkylboranes, BH_2R , react with N,N,N',N' -tetramethylethylenediamine (TMED), to form adducts $\text{TMED} \cdot \text{BH}_2\text{R}$ and $\text{TMED} \cdot (\text{BH}_2\text{R})_2$. BF_3 reacts with these, liberating the borane - and so these adducts are very convenient for the storage of BH_2R .¹⁰⁸

Spectroscopic data, especially the observation of only one resonance in the ^{19}F n.m.r. spectra, on $(\text{CF}_3)_2\text{C}:\text{NB}(\text{NMe}_2)_2$ and other $(\text{CF}_3)_2\text{C}:\text{NBR}_2$ systems are consistent with linearity of the $\text{C}:\text{NB}$ unit.¹⁰⁹

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

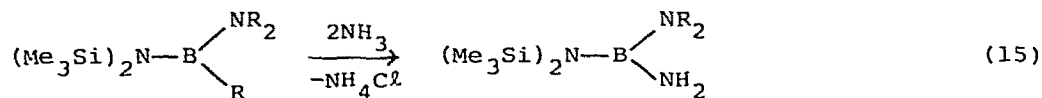


formulation shown.¹¹⁰

3,3'-Diaminodipropylamine reacts with $\text{Et}_2\text{B}(\text{NMe}_2)$ to produce the new compounds $\text{Et}_2\text{BN}[(\text{CH}_2)_3\text{NHBET}_2]_2$ and $\text{HN}[(\text{CH}_2)_3\text{NHBET}_2]_2$.¹¹¹

Lithiated silylamides, $t\text{-BuMe}_2\text{SiN}(\text{R})\text{Li}$, where $\text{R} = \text{H}$, Me or SiMe_3 , react with chloroboranes to form t -butyldimethylsilyl-substituted aminoboranes, e.g. $[t\text{-BuMe}_2\text{SiN}(\text{H})]_3\text{B}$. These decompose at or above room temperature to form borazines. When R is SiMe_3 the decomposition is most difficult, presumably because the bulk of the SiMe_3 group gives steric protection against nucleophilic attack.¹¹²

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



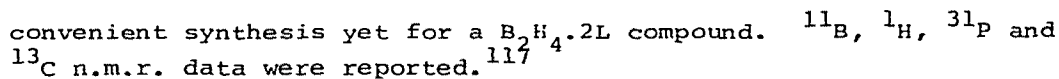
show considerable thermal stability - which can be explained by the high barriers to rotation about the $\text{B}-\text{NR}_2$ bond.¹¹³

Bis(di-isopropylamino)alkylaminoboranes, $\text{RR}'\text{NB}[\text{N}(i\text{-Pr})_2]_2$, possess

$$\begin{array}{c}
 \text{X}_2 \\
 \diagup \quad \diagdown \\
 \text{N} \quad \text{B} \quad \text{N} \\
 \diagdown \quad \diagup \\
 \text{B} \\
 \text{X}_2
 \end{array}
 \begin{array}{l}
 \text{Ph}_3\text{P}=\text{N} \\
 \\
 \\
 \text{N}=\text{PPh}_3
 \end{array}
 \quad (24)$$

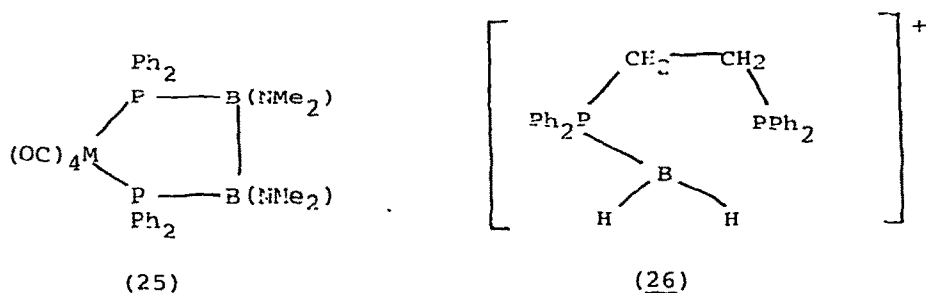
3.1.7 Compounds containing B-P Bonds

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



A series of borylphosphine complexes of group 6 metal carbonyls have been prepared: $(OC)_5M.PR_2B(NR'_2)_2$, cis- $(OC)_4M.(PR_2)_2B(NR'_2)_2$,

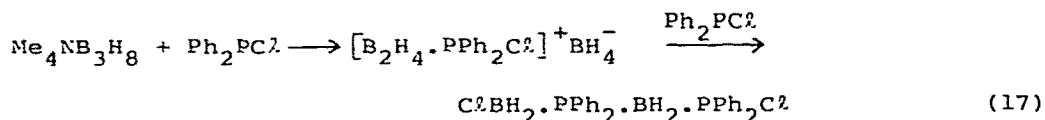
and (25), where M = Cr, Mo or W; R = Ph, R = Me or Et. No evidence was found for significant M-B interaction.¹¹⁸



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

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

Comparison between the very stable cyclic phosphinoboranes, $(BH_2PR_2)_n$, and an acyclic analogue is now possible with the synthesis of 1,4-dichloro-1,1,3,3-tetraphenyl-catena-borophosphane from $Me_4N^+B_3H_8^-$ and Ph_2PCl_2 , equation (17). N.m.r. and X-ray data confirm the expected butane-like structure, with distorted tetra-



hedral angles about B and P.¹²¹

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

3.1.8 Compounds containing B-O Bonds

An electron-diffraction study of the gaseous MBO_2 molecules, M = Cs, Rb or Tl, has been reported. All have linear O-B-O groups

but bent M-O-B units. The M-O distances were found to be 2.57 \AA (Rb), 2.62 \AA (Cs), 2.42 \AA (Tl).¹²³

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

The compound $\text{K}[\text{B}(\text{SO}_3\text{Cl})_4]$ forms triclinic crystals, space group $\text{P}1$. The $\text{B}(\text{SO}_3\text{Cl})_4^-$ anions are present as a racemic mixture. Crystal forces lead to positional inversion of some Cl and O atoms. The SO_3Cl^- ligands are unidentate, with an average $\text{B}-\text{O}_{\text{br}}$ distance of 1.465 Å.¹²⁹

Perhydrolysis (using an $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixture, 85:15 by weight) of $\text{B}(\text{OR})_3$ in the presence of LiOR' or RbOn-Bu (where $\text{R} = \text{Me}, i\text{-Pr}, t\text{-Bu}, n\text{-C}_8\text{H}_{17}$; $\text{R}' = \text{Me}, \text{Et}, n\text{-Bu}, t\text{-Bu}$) gives a variety of peroxo-borates, such as $\text{LiBO}_3 \cdot 7/2 \text{H}_2\text{O}$, $\text{RbBO}_4 \cdot 0.5 \text{H}_2\text{O}$ etc. All contain active oxygen as $\text{B}-\text{O}-\text{O}$ groups.¹³⁰

Single crystals of LiB_3O_5 have been prepared for the first time. They are orthorhombic, and belong to the space group $\text{Pna}2_1$. B_3O_5 units are present, similar in geometry to those found in CsBr_3O_5 , but the two compounds are not isotypic.¹³¹

$\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ forms orthorhombic crystals, belonging to the space group Pbca . The structure contains $\text{B}-\text{O}$ chains, with the repeating unit $[\text{B}_4\text{O}_6(\text{OH})_2]^{2-}$. Connection between the $\text{B}-\text{O}$ chains is provided by sodium polyhedra and by hydrogen-bonding.¹³²

"Ester hydrolysis" or evaporation of solutions of base and boric acid under reduced pressure, with the very strong bases $\text{BzNR}_3^+\text{OH}^-$, $\text{Bz} = \text{benzoyl}$, $\text{R} = \text{Me}$ or Et , give corresponding salts of $[\text{B}_5\text{O}_6(\text{OH})_4]^-$. The more bulky, but less basic, $n\text{-Bu}_3\text{N}$ produces $[n\text{-Bu}_3\text{NH}][\text{B}_7\text{O}_6(\text{OH})_{10}]$. The less bulky but more basic R_3N , ($\text{R} = \text{Et}$ or $n\text{-Pr}$), again give pentaborate salts. Benzylamine and tri- n -octylamine cannot form cations for polyborates.¹³³

$\text{NaB}_5\text{O}_6(\text{OH})_4$ forms monoclinic crystals, belonging to the space group $\text{P}2_1/\text{c}$. The isolated polyanion $\text{B}_5\text{O}_6(\text{OH})_4^-$ is present, built up from a tetrahedron and three triangles, giving a double hexagonal ring.¹³⁴

3.1.9 Boron Halides

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

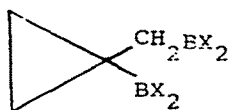
BF_3 forms complexes formulated as $[\text{BF}_3(\text{anion})]^-$ when anion =

ClO_4^- , NO_3^- , NO_2^- , CH_3OO^- , HCOO^- , N_3^- , CN^- , CNO^- , NCS^- or SPh^- .

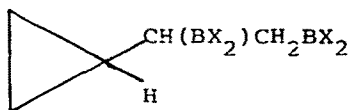
Anions of strong acids do not disproportionate to $[\text{BF}_2(\text{anion})_2]^-$. Complexes of anions of weaker acids may disproportionate or complex a second molecule of BF_3 .¹³⁶

The new compound $\text{Mg}(\text{BF}_3\text{OH})_2(\text{THF})$ has been prepared from $\text{BF}_3 \cdot \text{THF}$ and a Grignard reagent RMgBr (where R is a very bulky group). The magnesium is octahedrally coordinated. B-F distances fall in the range 1.30 to 1.38 Å, while the B-O distance is 1.42 Å.¹³⁷

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



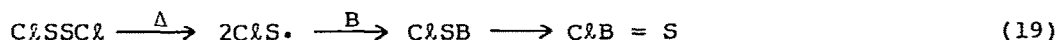
(29)



(30)

Anilinebis(difluoroborondimethylglyoximate)nickel(II) forms monoclinic crystals, space group $\text{P2}_1/\text{c}$. The nickel atom is surrounded by four nitrogen atoms of the planar macrocycle, plus a nitrogen atom of the aniline. The boron-fluorine distances are 1.364 Å and 1.380 Å.¹³⁹

Passage of S_2Cl_2 over crystalline boron at 800-1000°C produces the new unstable species ClBS . Its identity was confirmed by photoelectron and microwave spectroscopic results. A possible



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

MCl_3X^- , where M = B or Al, X = N_3 or NCO, are prepared from MCl_3 and X^- in liquid SO_2 as solvent. Excess halide must be avoided. Infrared spectra show that the NCO^- ligand is N-bonded.¹⁴¹

Nitrosyl chloride and BCl_3 react directly to form $\text{NO}^+\text{BCl}_4^-$. A Raman spectrum of the solid confirmed the ionic formulation. On melting, two layers are formed, one a mixture $\text{NOCl} + \text{BCl}_3$, the other a compound $(\text{NO} \cdot n\text{NOCl})^+\text{BCl}_4^-$.¹⁴²

The reactions of $\text{B}_{10}\text{Cl}_{10}/\text{B}_{11}\text{Cl}_{11}$ mixtures with H_2 , Cl_2 , Br_2 or I_2 have been examined. At 135°C, Cl_2 reacts to produce B_9Cl_9 in

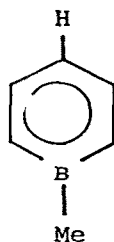
high yield, giving the best preparative route for this compound so far recorded.¹⁴³

Nine equivalents of SO_2Cl_2 react with a solution of $[\text{Bu}_4\text{N}]_2[\text{B}_9\text{H}_9]^-$ at -78°C , and on warming to room temperature a good yield of $[\text{Bu}_4\text{N}]_2[\text{B}_9\text{Cl}_9]$ is obtained. If a large excess of SO_2Cl_2 (20 equivalents) is used, some B_9Cl_9 is also formed, which can easily be separated from the ionic compound.¹⁴⁴

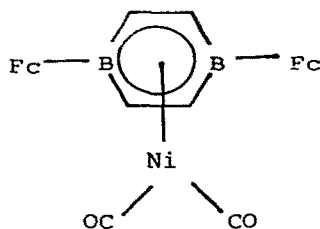
The preparation of BBr_3 from KBF_4 and AlBr_3 has been improved, giving yields greater than 80%. The process is therefore now suitable for the conversion of K^{10}BF_4 into $^{10}\text{BBr}_3$.¹⁴⁵

3.1.10 Boron-containing Heterocycles

Ion-cyclotron resonance techniques were used to determine the gas-phase Brønsted and Lewis acidities, and the Brønsted basicity of 1-methyl-1,4-dihydroborabenzene, MeBC_5H_6 . The ring proton is highly acidic, because of the formation of the six π -electron aromatic anion $\text{MeBC}_5\text{H}_5^-$, (31).¹⁴⁶

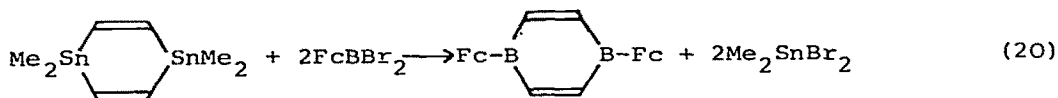


(31)



(32)

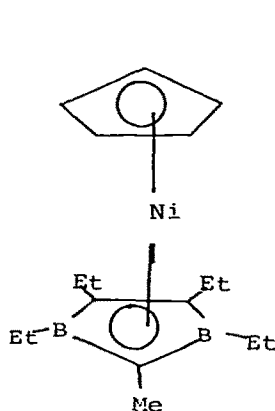
A new synthesis, equation (20) (where $\text{Fc} = \text{cpFe}(\text{C}_5\text{H}_4)$), has been



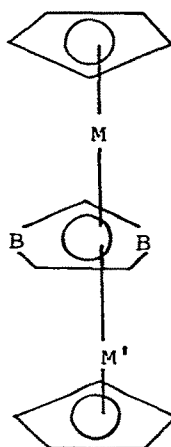
reported for 1,4-dibora-2,5-cyclohexadiene. This in turn reacts with $\text{Ni}(\text{CO})_4$ to give the nickel complex (32).¹⁴⁷

1,3,4,5-Tetraethyl-2-methyl-1,3-diborolene reacts with dicyclopentadienylnickel or $[(\text{C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ to form (33). The sandwich formulation was confirmed by X-ray diffraction.¹⁴⁸

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



(33)

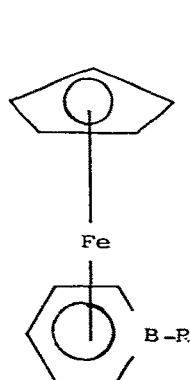


(34)

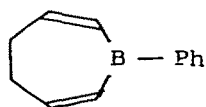
Thallium borinates, $Tl(C_5H_5BR)$, where $R = Me$ or Ph , can be made from alkali metal borinates and $TlCl$ in acetonitrile solution. Mass, 1H , ^{11}B - and ^{13}C n.m.r. spectroscopic data were reported.¹⁵⁰

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

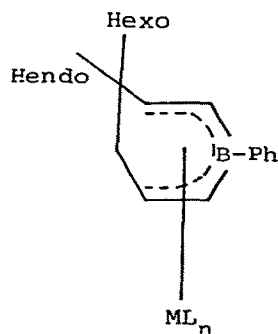
The complexes (35), $R = Me$ or Ph , can be prepared from the reaction of $[cpFe(CO)_2]_2$ with $Co(C_5H_5BR)_2$.¹⁵²



(35)



(36)

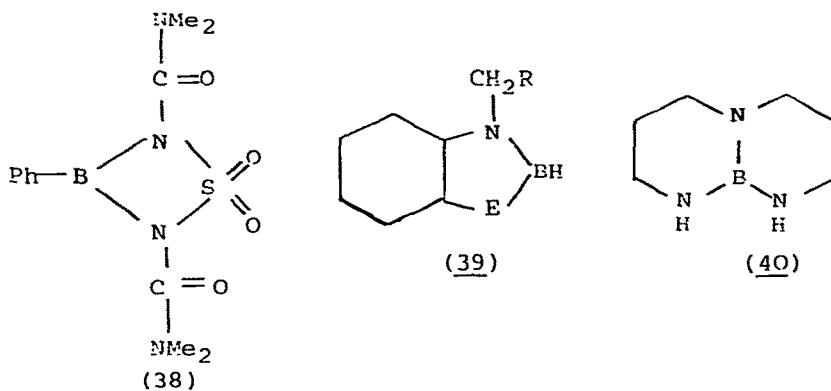


(37)

Bis(borinato)cobalt complexes, $\text{Co}(\text{C}_5\text{H}_5\text{BR})_2$, where $\text{M} = \text{Me}$ or Ph , are reduced by sodium amalgam to form the twenty-electron anions $\text{Na}^+[\text{Co}(\text{C}_5\text{H}_5\text{BR})_2]^-$ in solution. They can be isolated as stable crystalline salts with the cation PPh_4^+ .¹⁵³

1-Phenyl-4,5-dihydroborepin, (36), reacts with substituted carbonyls of Cr , Mo , W or Mn to give the stable complexes (37), where $\text{ML}_n = \text{M}(\text{CO})_4$, ($\text{M} = \text{Cr}$, Mo or W) or $\text{Mn}(\text{CO})\text{Cp}$.¹⁵⁴

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

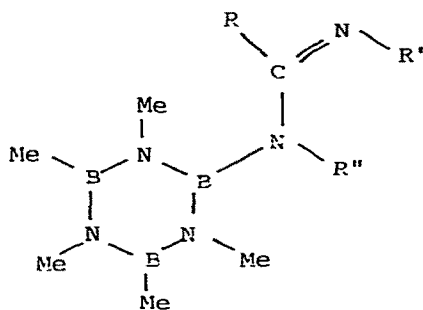


Diborane reacts with benzo-fused heteroaromatic compounds to produce (39), where $\text{R} = \text{H}$, $\text{E} = \text{O}$ or S ; $\text{R} = \text{Me}$, $\text{E} = \text{S}$ or Se .¹⁵⁶

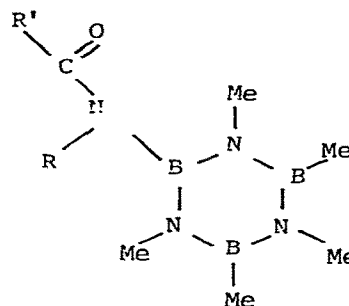
BH_3 , generated in situ from $\text{Me}_3\text{N} \cdot \text{BH}_3$, reacts with 3,3'-diaminodipropylamine to form the BH_2B -bridge-associated [3,3'-bis(dihydroborylamino)dipropylamino]dihydroborane, 1-aminopropyl-1,3,2-diazaboracyclohexane or 1,8,10,9-triazaboradecalin, (40), depending upon the conditions.¹⁵⁷

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

Trimethylsilylamidines react with 2-chloro-1,3,4,5,6-pentamethylborazine to form the amidinoborazines (41), where $\text{R} = \text{CF}_3$; $\text{R}' = \text{Ph}$ or $3\text{-CF}_3\text{-C}_6\text{H}_4$; $\text{R}'' = 2\text{-F-C}_6\text{H}_4$ etc.¹⁵⁹ The same borazine will react with silylated carbonic acid amides and thioamides to give amido borazines, e.g. (42).¹⁶⁰

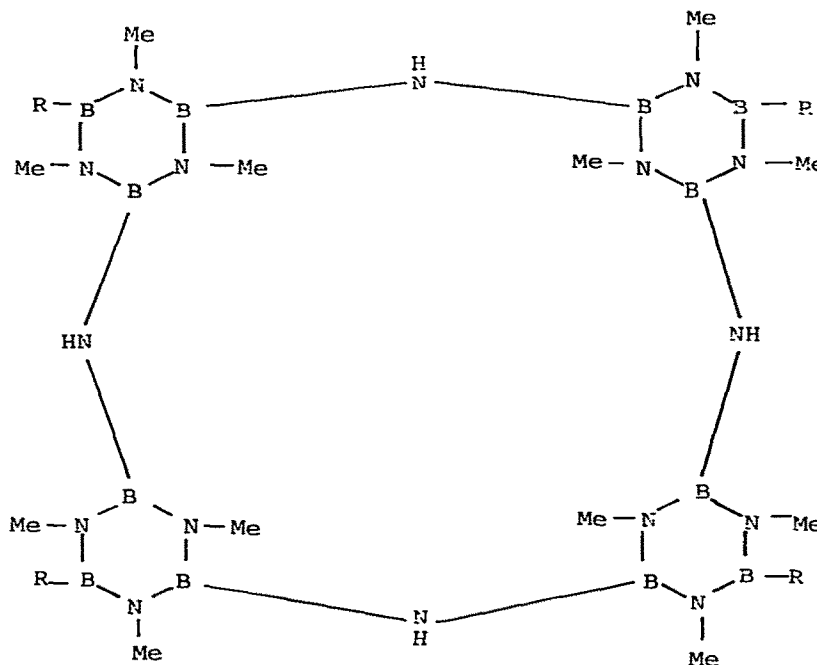


(41)



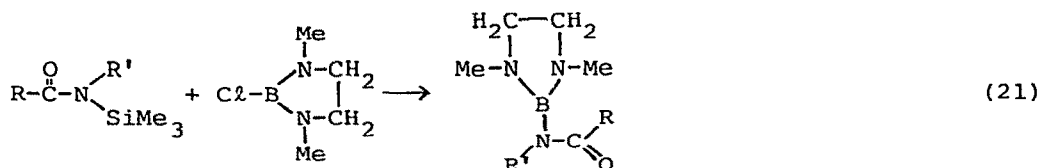
(42)

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

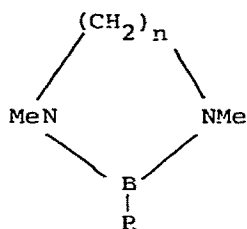


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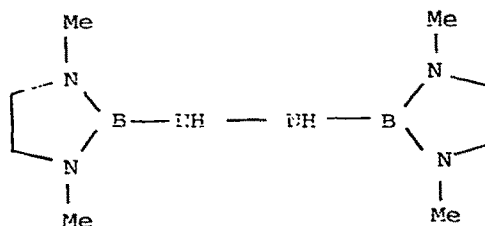
$\text{RC}(=\text{O})\text{N}(\text{R}')\text{SiMe}_3$, where $\text{R}, \text{R}' = \text{Me}$ or Ph , react with several boron compounds to give monomeric amido(amino)boranes, e.g. equation (21).¹⁶³



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



(44)

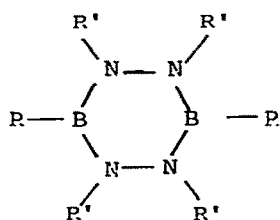


(45)

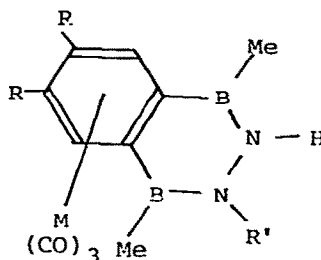
Several mixed amino-hydrazinoboranes have been prepared and characterised, from the reaction of 1,3-dimethyl-2-chloro-1,3,2-diazaboracycloalkanes with substituted hydrazines, and by condensation of the corresponding 2-methylthio-derivatives with hydrazine. A typical example is (45). N.m.r. and i.r. data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

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

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

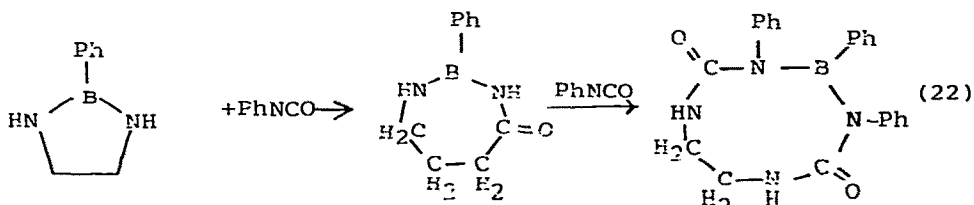


(46)



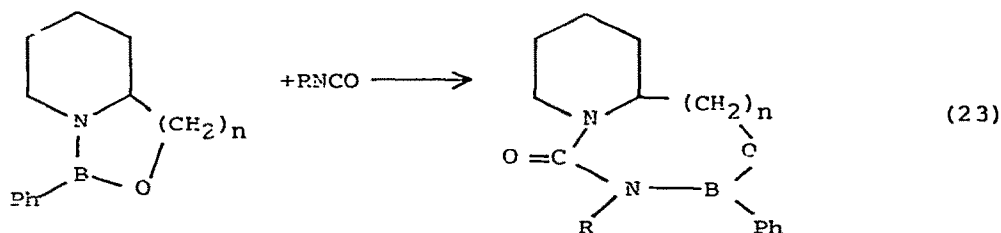
(47)

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



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

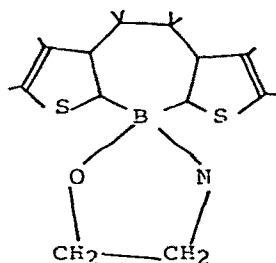
Organic isocyanates react with heterocyclic aminoboranes, giving some novel heterocyclic organoboranes. A typical example is shown



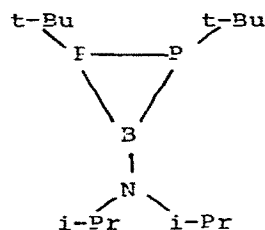
in equation (23) where $n = 1$ or 2 , $R = \text{Ph}$ or $p\text{-MeC}_6\text{H}_4\text{SO}_2$.¹⁷¹

$\text{C}_{12}\text{H}_{14}\text{BNOS}_2$, (48), gives monoclinic crystals, space group $\text{P2}_1/\text{n}$. The seven-membered ring is in a boat conformation, while the oxazaborolidine ring is in the "half-chair" conformation. The two rings are approximately perpendicular to one another.¹⁷²

$\text{K}(\text{t-Bu})\text{P}-\text{P}(\text{t-Bu})\text{K}$ reacts with $(i\text{-Pr})_2\text{NBCl}_2$ in $n\text{-hexane}$ at -40°C to form the first three-membered P_2B heterocycle, (49). There was no evidence for dimerisation in the range -50°C to $+140^\circ\text{C}$.¹⁷³

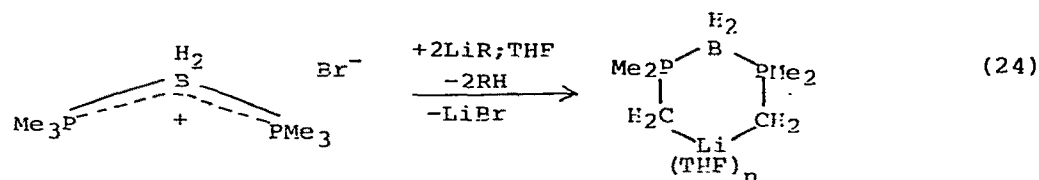


(48)

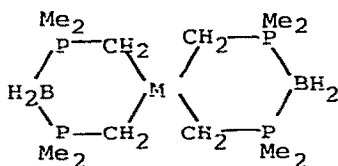


(49)

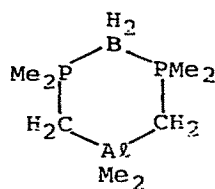
The boratobis(dimethylphosphinomethylide) anion can be prepared as in equation (24), where R = t-Bu or n-Bu. It reacts with MX_2 ,



where M = Zn, Cd or Hg, X = halide, to form the chelate complexes (50). The aluminium compound (51) can be prepared from the original starting material by the action of $LiAlMe_4$.¹⁷⁴

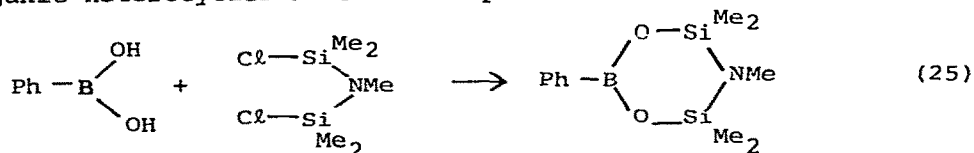


(50)



(51)

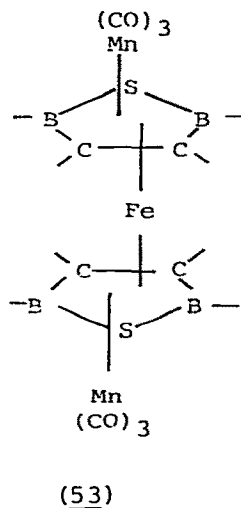
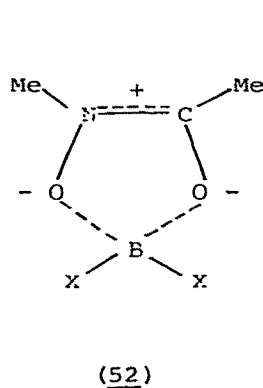
A group of new 6-membered, BNO_2Si_2 , and 8-membered, BO_3Si_4 , inorganic heterocycles have been reported for the first time. The



(25)

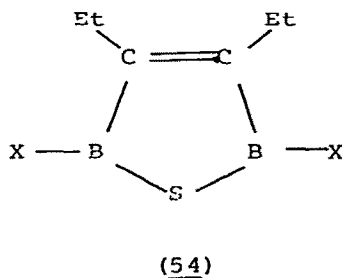
former are given by the coupling reaction (25). The latter result from the action of PhB(OH)_2 on $\text{SiMe}_2\text{ClSiMe}_2\text{Cl}$, via an unisolable 5-membered ring intermediate, BO_2Si_2 .¹⁷⁵

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



The first reported 'four-decker' sandwich complex contains two $\text{C}_2\text{B}_2\text{S}$ rings, which act as six π -electron donors, (53).¹⁷⁷

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



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

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

3.1.11 Boron Nitride, Metal Borides

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

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

The phase $ZrIr_3B_{\sim 4}$ forms hexagonal crystals, space group $P6_3/m$. Two different types of boron atom are present: (i) isolated atoms, in distorted trigonal prisms, and (ii) linear chains (B-B distance 1.756 Å) at the centres of Ir octahedra. The crystal structure is related to that of Fe_2P .¹⁸²

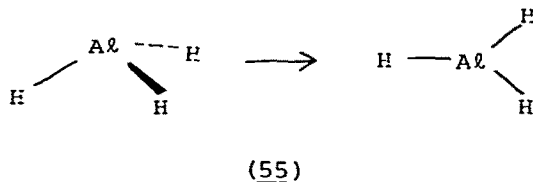
3.2 ALUMINIUM

3.2.1 Aluminium Hydrides

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

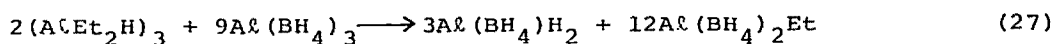
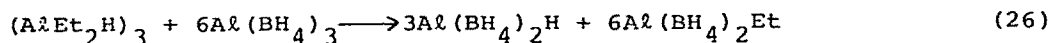
$AlCl$ and HCl react in an argon matrix under mercury lamp irradiation to form $HAAlCl_2$. The vibrational bands observed were consistent with a planar model: $\nu Al-H$, 1967.6 cm^{-1} ; $\nu Al-D$, 1430.1 cm^{-1} ; $\nu Al-Cl$ 481.3 cm^{-1} ($HAAl^{35}Cl_2$) 477.6 cm^{-1} ($HAAl^{35}Cl^{37}Cl$), 477.5 cm^{-1} ($DAAl^{35}Cl_2$), 473.6 cm^{-1} ($DAAl^{35}Cl^{37}Cl$).¹⁸⁴

The reorganisation energy of AlH_3 , (55), ΔE_r , has been calculated as $9.8\text{ kcal. mol}^{-1}$. This enables the strength of the $Al-H-Al$ bridge bond in Al_2H_6 to be calculated, i.e. $27.7\text{ kcal. mol}^{-1}$.¹⁸⁵



Vibrational assignments have been given for $\text{Al}(\text{BH}_4)_3 \cdot \text{L}$, where $\text{L} = \text{NH}_3$, NH_2Me , NHMe_2 or NMe_3 . The results suggest that $\text{Al}(\text{BH}_4)_3 \cdot \text{NHMe}_2$ possesses a plane of symmetry, passing through the Al, B, N and H atoms. The vibrations of the $\text{Al}(\text{BH}_4)_3$ fragments were only slightly affected by changes in L.¹⁸⁶

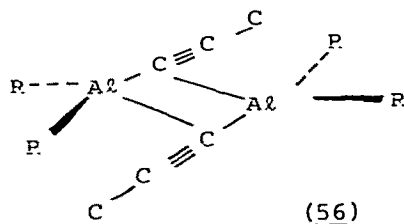
$\text{Al}(\text{BH}_4)_3$ reacts with $(\text{AlEt}_2\text{H})_3$ in appropriate molar ratios to form liquid hydridoaluminium tetrahydroborates, equations (26) and (27). The ethyl compound can be removed easily. The $\text{Al}(\text{BH}_4)_2\text{H}$ is



the more stable compound, but in vacuo both disproportionate. This produces $\text{Al}(\text{BH}_4)_3$ and a residue increasingly rich in Al-H bonds. The latter solidifies when the concentration of AlH_3 units exceeds 78 mole%.¹⁸⁷

3.2.2 Compounds containing Al-C or Al-Ge Bonds

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



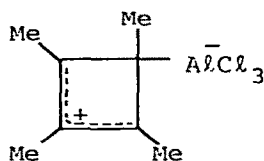
Trimethylaluminium reacts with the caesium salts of SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$ or $\text{S}_2\text{O}_6^{2-}$ to form $\text{Cs}_2\text{SO}_4 \cdot 4\text{AlMe}_3$; $\text{Cs}_2\text{S}_2\text{O}_3 \cdot 4\text{AlMe}_3$ and $\text{Cs}_2\text{S}_2\text{O}_6 \cdot 4\text{AlMe}_3$. Some vibrational assignments were given.¹⁸⁹

The crystal structure of $[(\eta\text{-C}_5\text{H}_5)_2\text{YMe}_2\text{AlMe}_2]$ shows the presence of a dimethyl bridge - the average bridging bond distances being $2.58(3)\text{\AA}$ for Y-C and $2.10(2)\text{\AA}$ for Al-C. The Y-Al separation is $3.056(6)\text{\AA}$.¹⁹⁰

The mass spectra of $(\text{Me}_2\text{AlOPh})_n$, where $n = 2$ or 3 , have been recorded. Skeletal fragmentation was observed at low temperatures.

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

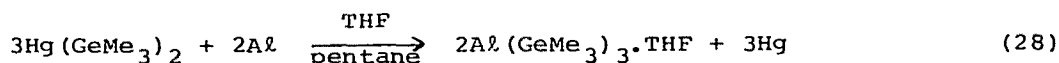
N.m.r. studies on the σ -complex of AlCl_3 with a substituted cyclobutadiene, (57) show that the molecule is fluxional, with the main process being a 1,2-shift of the AlCl_3 group.¹⁹²



$\text{Al}(\text{i-Bu})_3$ reacts with potassium metal in hexane at 20°C to form a novel dialuminium compound, $\text{K}_2[\text{i-Bu}_3\text{Al}-\text{Ali-Bu}_3]$. The ^1H and ^{13}C n.m.r. spectra, together with its chemical properties, are consistent with the presence of an $\text{Al}-\text{Al}$ σ -bond.¹⁹³

Triphenylaluminium dissolves in $\text{Al}(\text{BH}_4)_3$ giving the dimeric solid " Ph_2AlBH_4 ". The monophenyl form could not be isolated. The alkyl derivatives show the reverse trend in stabilities.¹⁹⁴

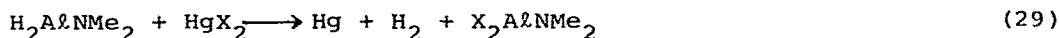
The first alkylgermyl aluminium compound has been prepared, equation (28). The THF adduct has considerable thermal stability;



it melts at 81°C .¹⁹⁵

3.2.3 Compounds containing $\text{Al}-\text{N}$ or $\text{Al}-\text{P}$ Bonds

The compounds X_2AlNMe_2 , where $\text{X} = \text{Br}$ or I , can be prepared by reactions (29), in benzene solution. Both are structurally anal-

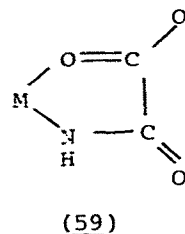
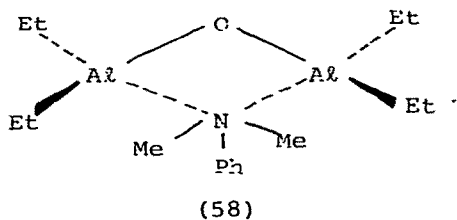


ogous to the chloro-compound. Crystal structure determinations show that they are dimers, with a planar, four-membered, Al_2N_2 , ring, all of the atoms being four-coordinate. The $\text{Al}-\text{N}$ bond distance is 1.94\AA ; for the $\text{Al}-\text{Br}$, $\text{Al}-\text{I}$ and $\text{N}-\text{C}$ bonds the distances

are 2.26Å, 2.49Å, 1.50-1.55Å.¹⁹⁶

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

Tetra-alkylalumoxanes, $\text{R}_4\text{Al}_2\text{O}$, where $\text{R} = \text{Et}$ or $i\text{-Bu}$, react with nitrogen-containing donor molecules, e.g. NMe_2Ph , PhHC=N-n-Bu or PhCN , to give adducts. They are generally 1:1, and monomeric. Their structures, based on ^1H n.m.r. evidence, are thought to be (58).

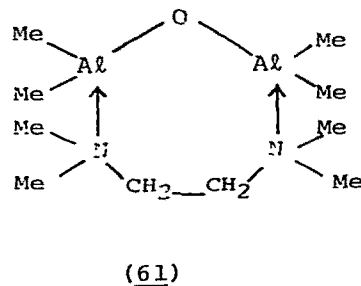
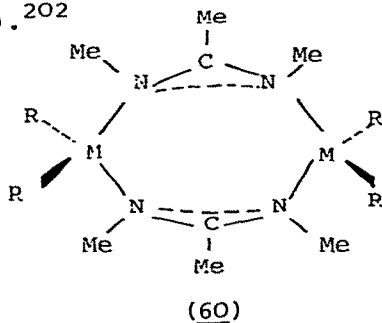


The ^1H n.m.r. spectrum of $(\text{HALNCHMePh})_6$ is consistent with the presence of a closed hexameric cage structure.¹⁹⁹

Complex anions of Al , Ga , In or Tl with oxamic acid, $[\text{M}(\text{C}_2\text{HO}_3\text{N})_3]^{3-}$, have been prepared. Their infrared spectra suggest that coordination has taken place via the carboxyl oxygen and the amidic nitrogen, after ionisation of one of the amidic hydrogens as shown in (59).²⁰⁰

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

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



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

Gas-phase electron diffraction results were used to obtain the molecular structure of $\text{Me}_3\text{AlPMe}_3$. The following bond lengths were found: $\text{Al}-\text{C}$, $1.973(3)\text{\AA}$; $\text{Al}-\text{P}$, $2.53(4)\text{\AA}$; $\text{P}-\text{C}$, $1.822(3)\text{\AA}$. The PAAlC and AlPC angles were $100.0(1.3)^\circ$ and $115.0(0.7)^\circ$ respectively.²⁰⁴

3.2.4 Compounds containing $\text{Al}-\text{O}$ or $\text{Al}-\text{Se}$ Bonds

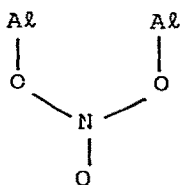
Lattice vibrations of boehmite, $\gamma\text{-AlOOH}$, show that the true space group must be $\text{Cmc}2$, (C_{2v}^{12}), rather than the Cmcm (D_{2h}^{17}) indicated as statistical symmetry by diffraction.²⁰⁵

Ranges in which sodium aluminate solution exists mainly as (a) NaOH , with monomeric $\text{Al}(\text{OH})_4^-$ or (b) NaOH , with dimeric $\text{Al}_2\text{O}(\text{OH})_6^{2-}$ have been estimated from water-activity measurements. The former condition applies at aluminium concentrations of $1\text{--}4\text{ M dm}^{-3}$, the latter at $2\text{--}7\text{ M dm}^{-3}$.²⁰⁶

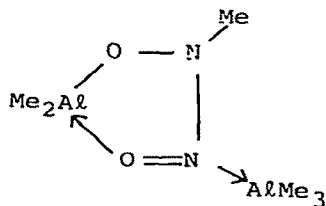
Single-crystal Raman spectra have been obtained for $[\text{Al}(\text{OH}_2)_6]\text{Cl}_3$ and its deuteriate. All of the Raman bands predicted by factor group analysis are seen. The symmetric stretch, ν_1 , of AlO_6 is at 524 cm^{-1} (the alternative assignment at 701 cm^{-1} gives less satisfactory force constants). ν_3 of AlO_6 is probably at about 670 cm^{-1} .²⁰⁷

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

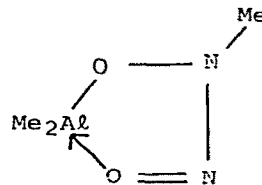
Addition of Al_2Me_6 to MNO_3 , where $\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{NMe}_4$ or NEt_4 , in benzene produces $\text{M}[\text{Al}_2\text{Me}_6(\text{NO}_3)]$. The crystal structure of the potassium salt shows that the nitrato-group is bridging, (62). If dibenzo-18-crown-6 is added to this species $\text{K}[\text{AlMe}_3(\text{NO}_3)] \cdot 7\text{C}_6\text{H}_6$ is obtained, in which the NO_3 is unidentate ($\text{Al}-\text{O}$ distance of $1.930(7)\text{\AA}$).²⁰⁹



(62)



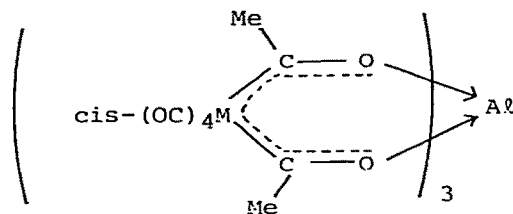
(63)



(64)

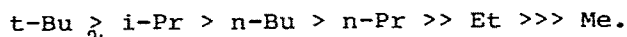
Nitric oxide reacts with trimethylaluminium to form " Me_3AlNO " and " $\text{Me}_3\text{Al}(\text{NO})_2$ ". Infrared and n.m.r. spectra, and the results of hydrolysis experiments suggest that they are, in fact, (63) and (64) respectively.²¹⁰

^{13}C n.m.r. spectral data were tabulated for (65), where $\text{M} = \text{Mn}$ or Re , $\text{R} = \text{Me}$; $\text{M} = \text{Re}$, $\text{R} = \text{PhCH}_2$ or Me_2CH , as well as for some related boron complexes.



(65)

Alkoxyaluminium compounds, $(\text{RO})\text{AlCl}_2$, where $\text{R} = \text{Me}$, Et , $n\text{-Pr}$, $i\text{-Pr}$, $n\text{-Bu}$ or $t\text{-Bu}$, react with MeAlCl_2 with evolution of gases (RMe , PCl_3), producing alumoxane systems, $\text{Al}-\text{O}-\text{Al}$. The sequence of reactivities is as follows:

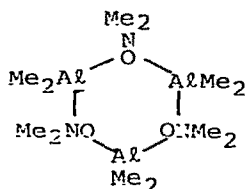


This suggests that the formation of a carbocation from the RO- group must play a significant part in the mechanism.²¹²

The complex $[\text{Ta}(\text{H}_2\text{Al}(\text{OC}_2\text{H}_4\text{OMe})_2)(\text{Me}_2\text{PC}_2\text{H}_4\text{PMe}_2)_2]_2$ contains an approximately square pyramidal $\text{P}_4\text{Ta}-\mu\text{-H}_2-\text{Al}$ group; Al_2O_2 bridge units are also present.²¹³

The compound $[\text{Me}_2\text{AlONMe}_2]_3$ contains a six-membered ring, (66). The crystal structure shows that this is in the skew-boat conformation. The following average bond lengths were determined: $\text{Al}-\text{O}$, 1.867 Å; $\text{Al}-\text{C}$, 1.961 Å; $\text{N}-\text{O}$, 1.477 Å; $\text{N}-\text{C}$, 1.459 Å.²¹⁴

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



(66)

New salts $M_2[Al(ClO_4)_5]$, where $M = Na$ or K , have been reported - formed by the interaction of MA_2Cl_4 with $HClO_4$ or $MClO_4/HClO_4$ mixtures. The infrared spectra show shifts and splitting of the ClO_4^- modes characteristic of $Al-ClO_4$ covalent bonding.²¹⁶

The electron density distribution in crystals of $CoAl_2O_4$ shows that the net charges on the atoms are: Co , $+1.5e$; Al , $+2.8e$; O , $1.8e$. Thus the bonding is very largely ionic.²¹⁷

Aluminite, $Al_2(OH)_4(SO_4) \cdot 7H_2O$, forms monoclinic crystals, space group $P2_1/c$. The complex ion $[Al_4(OH)_8(H_2O)_6]^{4+}$ is present, built up from four edge-sharing aluminium octahedra polymerised in chains. These are connected to SO_4^{2-} ions by a three-dimensional, hydrogen-bonded system. The formula of this substance should therefore be written as $[Al_2(OH)_4(H_2O)_3]SO_4 \cdot 4H_2O$.²¹⁸

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

The crystal structure of aluminium tris(dihydrogen phosphate), on the other hand, shows the presence of isolated AlO_6 octahedra stacked, by corner-sharing with $O_2P(OH)_2$ tetrahedra, to give columns parallel to the c axis. The columns are linked by hydrogen-bonding. The heavy atoms have an almost centrosymmetric arrangement, but the symmetry is lowered by the positions of the protons.²²⁰

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

The crystal structure of the metastable phase of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ shows that the crystals are orthorhombic, but that the space group is $\text{Cmc}2_1$, not $\text{C}222_1$ as previously reported. The structure consists of alternating twisted sheets of AlO_4 tetrahedra and calcium atoms lying perpendicular to $[001]$. The tetrahedra are linked via corners to give a network of five-membered rings.²²²

A solid-state reaction occurs at 1700°C in the $\text{BaO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3$ system to yield single crystals of $\text{Ba}_2\text{Fe}_{11}\text{Al}_{11}\text{O}_{34}$, space group $\text{P}6_3/\text{mmc}$. It is isotypic with $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ (structure of β -alumina).²²³

CaAl_2Se_4 and SrAl_2Se_4 can be prepared by heating stoichiometric mixtures of the elements. Both are orthorhombic, space group Cccm . They are isostructural, with a structure closely related to that of TlSe .²²⁴

3.2.5 Aluminium Halides

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

Aluminium chloride reacts with the perchlorates MClO_4 , $\text{M} = \text{Na}$, Li or NBu_4 , in 1,2-dimethoxyethane (DME), to form MAlCl_4 and an insoluble species formulated as $\text{AlCl}_2(\text{ClO}_4) \cdot 2\text{DME}$.²²⁶

Fourier-transform infrared spectroscopy was used to obtain infrared data for the first time on AlCl_4^- in chloroaluminate melts MAlCl_4 where $\text{M} = \text{Li}$, Na or K .²²⁷

Potassium tetrachloroaluminate forms monoclinic crystals, space group $\text{P}2_1$. Discrete K^+ and AlCl_4^- ions are present, although the latter are slightly distorted from tetrahedral geometry. The structure is a slightly deformed version of that of $(\text{NO})\text{AlCl}_4$, i.e. BaSO_4 type.²²⁸

The analogous ammonium salt forms orthorhombic crystals, space group Pnma , isostructural with NH_4ClO_4 . The $\text{Al}-\text{Cl}$ bond lengths are very close to those in other chloroaluminates. Spectroscopic results (i.r., Raman, ^1H n.m.r.) suggest that the NH_4^+ is rotating freely.²²⁹

Quartz glass is attacked by Al_2Cl_6 vapour at temperatures above 300°C to give gaseous SiCl_4 . At lower temperatures oxygen is incorporated as the gaseous oxide chloride $\text{Al}_4\text{OCl}_{10}$, about 300°C

as crystalline AlOCl , and at even higher temperatures as Al_2O_3 .²³⁰

Raman spectra of liquid mixtures of AlCl_3 and 1-butylpyridinium chloride, at room temperatures and molar ratios between 0.75:1.0 and 2.0:1.0, show that the association equilibrium constant for Al_2Cl_7^- ion formation, equation (30), is significantly larger than in $\text{AlCl}_3\text{-MCl}$ melts, where M = alkali metal cation.²³¹



²³Na, ²⁷Al and ³⁵Cl n.m.r. studies on fused (Na K) Al_2Cl_7 at 170°C show that the structure is essentially ionic $\text{M}^+\text{Al}_2\text{Cl}_7^-$.²³² TiCl_4 in the presence of gaseous Al_2Cl_6 forms the species TiAlCl_6 and $\text{TiAl}_3\text{Cl}_{11}$ in the gaseous phase. In condensed phases the stable species is TiAl_2Cl_8 .²³³

Spectrophotometric and potentiometric measurements on the $\text{KCl-FeCl}_3\text{-AlCl}_3$ system at 300°C suggest that the two most likely melt

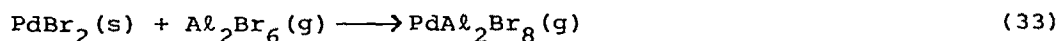


reactions are (31) and (32), with pK values of 6.75 ± 0.03 and 6.53 ± 0.06 respectively.²³⁴

The electronic spectra of Pd(II) dissolved in Al_2Cl_6 , $\text{Al}_2\text{Cl}_6\text{-KCl}$ eutectic or in KAlCl_4 are all similar, suggesting square-planar four-fold coordination in all cases. The temperature dependence of the spectra is consistent with the presence of centrosymmetric species.²³⁵

Mass-spectrometric measurements on the vapour over $\text{CuCl(solid)/Al}_2\text{Cl}_6$ showed that Cu_3AlCl_6 and $\text{Cu}_2\text{Al}_2\text{Cl}_8$ are the principal components. Enthalpy and Entropy changes associated with their formation were estimated. The molecules probably have a cubic structure, based upon that on Cu_4Cl_4 .²³⁶

Spectrophotometric measurements on the $\text{PdBr}_2\text{(s)/Al}_2\text{Br}_6\text{(g)}$ system suggest that one predominant species is present, equation (33), for



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

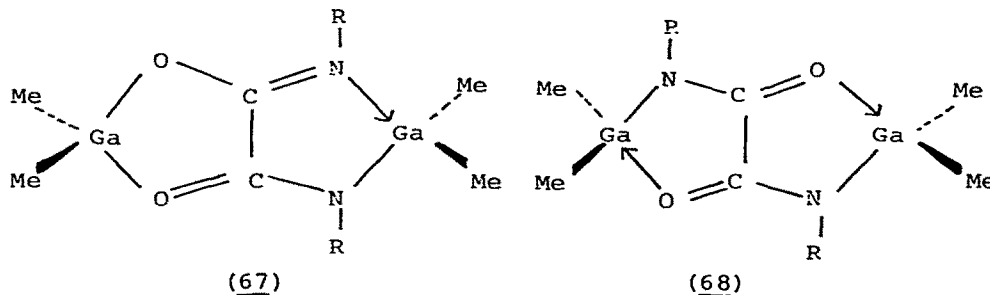
3.3 GALLIUM

3.3.1 Compounds containing Ga-C Bonds

$\text{GaMe}_2(\text{BH}_4)$ can be prepared from trimethylgallium and diborane, but a better reaction is between GaMe_2Cl and LiBH_4 in the absence of solvent at -15°C . Characterisation of the product was based on molecular weight determination, mass-, vibrational- and ^1H n.m.r.-spectra. The infrared spectrum of the gas was consistent with the formulation $\text{Me}_2\text{Ga}(\mu\text{-H})_2\text{BH}_2$, of C_{2v} symmetry, i.e. four-coordinate gallium linked to bidentate BH_4 . This appears to persist in the condensed phases, although the vibrational spectra of the solid suggest increased polarisation in the sense $\text{GaMe}_2^+\text{BH}_4^-$.²³⁸

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

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

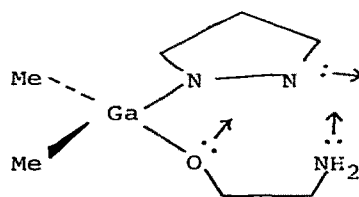


3.3.2 Compounds containing Ga-N or Ga-P Bonds

The anionic tridentate ligand $[\text{MeGa}(\text{N}_2\text{C}_3\text{H}_3)_3]^-$ has been prepared. It acts as a six-electron chelating ligand to transition metal

cations, M^{2+} , forming ML_2 complexes with an octahedral MN_6 skeleton. The tridentate bonding was confirmed by a determination of the crystal structure of $[MeGa(N_2C_3H_3)_3]Mo(CO)_2(\eta^3-C_3H_5)$.²⁴¹

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



(69)

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

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

The adducts $L.GaBr_3$ have been reported, where $L =$ pyridine-N-oxide, 2- 3- or 4-picoline-N-oxide, 4-chloropyridine-N-oxide or 4-nitropyridine-N-oxide. All show decreases in ν_{NO} on coordination, showing that the ligands are bound to the gallium via the oxygen atom. Tentative assignments to ν_{GaO} were made in the $400-450\text{ cm}^{-1}$ range.²⁴⁴

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

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

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

$M_6[Ga_2O_6]$, where $M = K$ or Rb , can be prepared from the constituent oxides. Both are isotypic with $K_6Fe_2O_6$, and belong to the

space group C2/m. The hitherto unknown Na_3GaO_3 , space group Imcm or I2cm, and $\text{Cs}_6[\text{Ga}_2\text{O}_6]$, $\text{P2}_1/\text{a}$, were also prepared.²⁴⁸

Single crystals of $\text{Bi}_2\text{Ga}_4\text{O}_9$ and $\text{Bi}_2\text{Ga}_2\text{Fe}_2\text{O}_9$ have been prepared from appropriate oxide mixtures under the influence of a CO_2 laser. The former is one of the few Ga^{3+} compounds in which the gallium is octahedrally, as well as tetrahedrally coordinated. In the latter the Ga^{3+} is only tetrahedrally coordinated, showing the preferential occupation of tetrahedral holes by the gallium.²⁴⁹

The three ordered synthetic feldspars $\text{SrGa}_2\text{Si}_2\text{O}_8$, $\text{BaGa}_2\text{Si}_2\text{O}_8$ and $\text{BaGa}_2\text{Ge}_2\text{O}_8$ all belong to the space group I2/c.²⁵⁰

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

Infrared and Raman spectroscopic data have been obtained for single crystals of $\alpha\text{-Ga}_2\text{S}_3$. The spectra were consistent with approximate C_{2h}^6 crystal symmetry. Frequencies were assignable to both external and internal modes of the GaS_4 groups.²⁵²

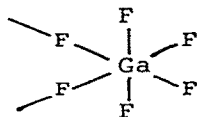
It was found that $\beta\text{-Ag}_9\text{GaSe}_6$ formed cubic crystals, space group P2_13 . GaSe_4 tetrahedra were present, of C_3 symmetry; three GaSe distances were $2.367(6)\text{\AA}$, the fourth $2.363(9)\text{\AA}$.²⁵³

The crystal structure of TlGaSe shows that large $\text{Ge}_4\text{Se}_{10}$ tetrahedra are present, composed of four corner-linked GeSe_4 tetrahedra. The Tl^+ ions are situated in straight lines, parallel to the edges of the $\text{Ga}_4\text{Se}_{10}$ groups. The Tl is six-coordinated by the selenium, giving trigonal prismatic TlSe_6 units.²⁵⁴

3.3.4 Gallium Halides

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

BaGaF_5 has been isolated from the $\text{BaF}_2\text{-GaF}_3$ system. It crystallises in the space group $\text{P2}_12_12_1$, and contains chains based on the unit (70).²⁵⁶



(70)

All of the compounds $\text{GaX}_3 \cdot \text{SbX}_3$ (where $\text{X} = \text{Cl}, \text{Br}$ or I) are formed in the solid state, but $\text{GaX}_3 \cdot \text{SbX}'_3$ (where $\text{X} \neq \text{X}'$) do not exist. The GaCl_3 - SbI_3 system is a simple eutectic, whereas in GaI_3 - SbCl_3 complete halogen exchange occurs.²⁵⁷

The crystal structure of $\text{Me}_4\text{Sb}^+\text{GaCl}_4^-$ shows that the ions are isolated from one another, and only very slightly distorted. The average Ga-Cl bond length is 2.172\AA .²⁵⁸

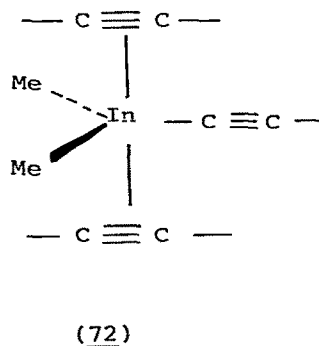
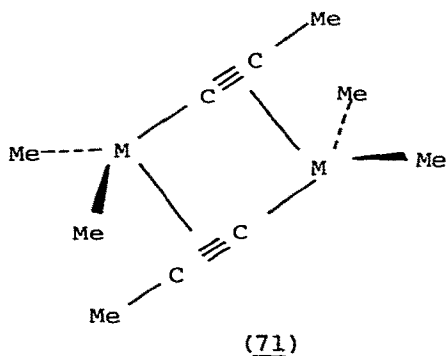
The rates of phenyl ring rotation in gallium chloro-complexes of p-tetraphenylporphyrins have been measured by variable-temperature ^1H n.m.r. spectroscopy. The rates of rotation found were the fastest to date for any metallotetraphenylporphyrin complexes.²⁵⁹

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

3.4 INDIUM

3.4.1 General

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



Li_2In has been found to be isotypic with Li_2Ga , belonging to the space group Cmcm . The indium atoms form zig-zag chains. $\text{Li}_{13}\text{In}_3$, on the other hand, belongs to a new structure type. It is face-centred cubic, space group $\text{Fd}3\text{m}$. It can best be described as an ordered variant of a body-centred cubic form, containing isolated indium atoms.²⁶²

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

E.m.f. measurements on liquid In/Hg amalgams, in the cell $\text{In/InCl}_3/\text{amalgam}$, were used to deduce values of ΔG , ΔH and ΔS for the process In+Hg amalgam at various indium concentrations.²⁶⁴

3.4.2 Compounds containing Bonds between Indium and Elements of Group 4

The vapour pressures of pure indium, and of $\text{In+In}_2\text{O}$ mixtures over the mixture $\text{In+MgIn}_2\text{O}_4\text{+MgO}$ have been measured by the Knudsen effusion technique in the temperature range 1095–1300K. The results were used to determine the free energy of formation of the inverse spinel MgIn_2O_4 from its component oxides, i.e. $-6190+0.6T(\pm 400)$ cal., at T_K .²⁶⁵

The mixed oxide $\text{In}_2\text{Te}_3\text{O}_9$ forms orthorhombic crystals, space group Pbnm . The structure is built up from sheets of TeO_3^{2-} anions, with InO_6 octahedra linked in parallel chains.²⁶⁶

$\text{K}_{0.72}(\text{In}_{0.72}\text{Sn}_{0.28})\text{O}_2$ exists as hexagonal crystals, belonging to the space group $\text{P}6\text{m}2$. The structure contains sheets of $(\text{MO}_2)_n$ stoichiometry, ($M = \text{In}$ or Sn), containing linked octahedral units, in which the indium and tin atoms are statistically distributed over two non-equivalent positions.²⁶⁷

A new quenchable high-pressure modification of In_2S_3 has been obtained at 35 kbar and 500°C. The new form has been named $\epsilon\text{-In}_2\text{S}_3$, its crystals belong to the space group $\text{R}\bar{3}\text{c}$, and it is isotypic with Lu_2S_3 (corundum-type structure).²⁶⁸

Orthorhombic crystals are formed by La_3InS_6 , which belong to the space group $\text{P}2_12_12_1$. The indium atoms are present in both four-coordinate ($\text{In-S} = 2.44\text{\AA}$) and six-coordinate ($\text{In-S} = 2.61\text{\AA}$) sites.²⁶⁹

Crystal structure determinations have been carried out on $\text{Pb}_4\text{In}_9\text{S}_{17}$ and $\text{Pb}_3\text{In}_{6.67}\text{S}_{13}$. The crystals belong to the space groups Pbam

and B2/m respectively. In both cases the indium atoms are approximately octahedrally coordinated by six sulphur atoms with In-S distances in the range 2.46 to 2.92 Å.²⁷⁰

Similar studies have also been carried out on indium phosphorus chalcogenides, yielding the following information: InPS₄, tetragonal, space group I $\bar{4}$; In₄(P₂S₆)₃, monoclinic, space group P2₁/c; In₄(P₂Se₆)₃, orthorhombic, space group Pba2.²⁷¹

Four different phases were identified in the intercalation substitution system Na_xIn_xSn_{1-x}S₂, where 1 > x > 0. They existed in the following ranges: (2) 1 > x > 0.63; (b) 0.60 > x > 0.43; (c) x ~ 0.40; (d) x ~ 0.20.²⁷²

X-ray diffraction was used to determine the crystal structure of the low-temperature form of In₂Se₃. The crystals belong to the space group P6₁, while the structure was a distorted form of the wurtzite structure, in which the indium atoms were either tetrahedrally- or five-coordinated.²⁷³

In₂Te₅ (II) forms monoclinic crystals; space group C2/c. The structure contains planar sheets, perpendicular to C*, which are similar to those found in In₂Te₅ (I), consisting of chains of four-membered In-Te rings, with each indium atom tetrahedrally coordinated. The average In-Te distance was found to be 2.849(5) Å.²⁷⁴

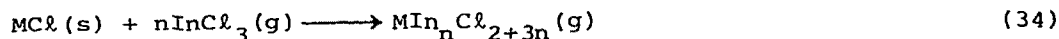
3.4.3 Indium Halides

Previous ambiguities in the interpretation of X-ray diffraction data on InF₃·3H₂O have been resolved. The coordination about the indium is octahedral, as previously thought, but the orientations of the octahedra were revised to account more satisfactorily with the observed results.²⁷⁵

Twenty-two fluoroindates, M_xIn_nF_{3n+x}, have been isolated and characterised by solid-state reactions in MF-InF₃ systems, where M = alkali metal, Tl or NH₄. The species found were as follows: MInF₄ (M = K, Rb, Cs or Tl); M₃InF₆ (M = Rb, Cs, Tl or NH₄); MIn₂F₇ (M = K, Rb or NH₄); MIn₃F₁₀ (M = Rb, Cs, Tl or NH₄); M₂In₃F₁₁ (M = Rb, Tl or NH₄); M₄In₃F₁₃ (M = Rb or Tl); M₅In₃F₁₄ (M = K or NH₄).²⁷⁶

Rb₂In₃F₁₁ forms monoclinic crystals, space group P2₁/m. The structure is built up from parallel sheets of edge- and corner-sharing pentagonal bipyramids (as in α-U₃O₈), joined together by infinite, parallel chains of corner-sharing octahedra.²⁷⁷

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

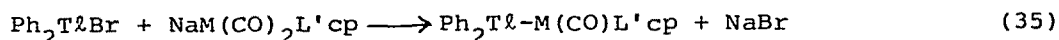


two complexes are formed ($n = 1$ or 2). When $M = \text{Cu}$, however, only CuInCl_5 is detected.²⁷⁸ $\text{M}_3\text{In}_2\text{Cl}_9$ (where $M = \text{Cs, Rb, Tl or In}$), and $\text{Cs}_3\text{In}_2\text{Br}_{9-x}\text{Cl}_x$ where $x = 7$ or 8 , all form crystals which are isotypic with $\text{Cs}_3\text{Tl}_2\text{Cl}_9$. $\text{Cs}_3\text{In}_2\text{Br}_{9-x}\text{Cl}_x$ (where $x = 3, 6$ or 7) belong to the $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ type of structure. Note that $\text{Cs}_3\text{In}_2\text{Br}_2\text{Cl}_7$ is dimorphic.²⁷⁹

3.5 THALLIUM

3.5.1 Thallium(III) Compounds

A number of R_2Tl -derivatives containing a thallium-transition metal bond have been prepared by various routes, e.g. $\text{R}_2\text{Tl-ML}_n$, where $\text{ML}_n = \text{M}'(\text{CO})_2\text{L}'\text{cp}$ ($\text{M}' = \text{Mo or W}$; $\text{L}' = \text{CO or PPh}_3$); $\text{Cr}(\text{CO})_3\text{cp}$; $\text{Fe}(\text{CO})_2\text{cp}$; $\text{Co}(\text{CO})_4$. A typical reaction is shown in (35), $\text{M}' = \text{Mo}$



or W ; $\text{L}' = \text{CO or PPh}_3$).²⁸⁰

Disproportionation of RTlX_2 (where $\text{R} = \text{alkyl or aryl}$; $\text{X} = \text{CH}_3\text{COO}^-$) does not occur at room temperature, i.e. the equilibrium concentrations of R_2TlX and TlX_3 are too small to detect. In the presence of $\text{P}(\text{OME})_3$, however, TlX_3 is removed from the equilibrium, leading to significant disproportionation.²⁸¹

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

TlOBr can be prepared by the reaction of Tl_2CO_3 with liquid bromine. It forms orthorhombic crystals, belonging to the space group Pmmn , isomorphous with InOBr (i.e. belonging to the FeOCl structure-type).²⁸³

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

The hydrated thallium(III) nitrate, $\text{Tl}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, forms rhombohedral crystals, space group $\text{R}\bar{3}$. The thallium atom is nine-coordinate, with three unsymmetrically-bidentate nitrate groups (Tl-O distances $2.299(8)\text{\AA}$, $2.637(10)\text{\AA}$), and three water molecules (Tl-O

distance 2.293(17)Å). The water molecules are ideally situated for transfer to an organic substrate when thallium(III) nitrate is used as an oxidant in solution.²⁸⁵

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

Heating a mixture of Na₂O and Tl₂O (Na:Tl ratio of 5.4:1) at 620°C for 7 days leads to the formation of Na₅Tl^(III)O₄. This forms orthorhombic single crystals, isotypic with Li₅GaO₄. Thermal decomposition of these produces, first, the previously unknown Na₃TlO₃, and, finally, NaTlO₂.²⁸⁷

The diarylthallium compounds R₂Tl(O₂CR), where R = C₆F₅, p-MeOC₆F₄, p-HC₆F₄, m-HC₆F₄ or o-HC₆F₄, all have associated structures, with bridging carboxylate groups. Except when R = o-HC₆HF₄ heating led to decarboxylation, and it was possible to isolate the dioxan adducts R₃Tl(dioxan)₂. The ease of decarboxylation was in the sequence R = C₆F₅ < p-MeOC₆F₄ < p-HC₆F₄ ~ m-HC₆F₄ >> o-HC₆F₄.²⁸⁸

Palladium(II) oxide reacts with TlNO₃ or Tl₂O₃ at 550°C to form TlPd₃O₄. The Pd/O skeleton forms a cage unit with cubic and rhombicuboctahedral spaces occupied by Tl³⁺, Tl⁺ respectively. Thus this is a thallium(III) thallium(I) oxopalladate(II). The analogous platinum(II) compound was also reported.²⁸⁹

Neutron powder-diffraction shows that TlPd₃O₄ is cubic, belonging to the space group Fm3m, and a = 9.5807Å.²⁹⁰

(DL-Tryptophanato)dimethylthallium(III) monohydrate forms monoclinic crystals, space group P2₁/c. Centrosymmetric dimers are present: (Me₂Tl)₂(D-tryptophan)(L-tryptophan). The coordination about the thallium atom is very irregular.²⁹¹

Another thallium(III) compound to form monoclinic crystals is Tl(S₂CNet₂)₃, space group A2/a. It is isostructural with the gallium and indium analogues. The average Tl-S distance is 2.66₅Å.²⁹²

3.5.2 Thallium(I) Compounds

Cyclopentadienylthallium(I)-d₅ can be prepared conveniently from C₅H₆, D₂O and Tl₂SO₄ at room temperature. It is a useful source material for a number of (C₅D₅)-metal compounds.²⁹³

S.C.F. molecular-orbital calculations on C_5H_5Tl , using the theory of effective potentials, shows that bonding is mainly due to the highest filled m.o. pair (of E_1 symmetry), based on pd^2 hybrids of Tl and p-orbitals of carbon atoms interacting in π -symmetry with respect to the C_5 axis of the molecule.²⁹⁴

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

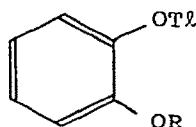
$MTlO$, where $M = K, Rb$ or Cs , are formed from mixtures of the appropriate oxides at $500-600^\circ C$. The oxothallates(I) crystallise in a monoclinic layer lattice (space group C_{2h}^3). The structures are closely related to that of Tl_2O .²⁹⁶

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

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

Thallium(I) sulphite can be prepared by passing SO_2 through a saturated solution of Tl_2CO_3 in inert solvents. The crystals are orthorhombic, space group $Pnam$. The structure is disordered, but related to those of Tl_2SO_4 and $Tl_2S_2O_3$. The thallium atoms statistically all have the same coordination number.²⁹⁹

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



(73)

The thallium(I) tetramolybdate, $Tl_2Mo_4O_{13}$, forms orthorhombic crystals, space group $Pbca$. The anions form a sheet structure, with $Mo_8O_{26}^{4-}$ units, containing the Tl^+ ions. There are two types of

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

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

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

The first mixed alkali metal-thallium(I) sulphides have been reported, e.g. $K_4Tl_2S_3$, $Rb_4Tl_2S_3$, K_7TlS_4 . All were isolated from the K_2S-Tl_2S or Rb_2S-Tl_2S systems. The first two are hexagonal, the third is monoclinic. The last structure is based on the CaF_2 type, i.e. they are derived from " K_8S_4 " by replacement of one K^+ by Tl^+ .³⁰⁴

The following phases were identified in the $Tl-V-S$ system: Tl_3VS_4 , TlV_5S_8 , $Tl_xV_6S_8$ and $Tl_2V_2S_5$.³⁰⁵

The chloroform adduct of thallium(I) diethylthiocarbamate, $[Tl(S_2CNET_2)]_2 \cdot CHCl_3$ forms monoclinic crystals, space group $P2_1/c$. The thallium atoms are four-coordinate, with the $Tl-S$ distances in the range 2.9-3.5 Å in the dimeric, centrosymmetric units $(TlS_2CNET_2)_2$. Each thallium atom also interacts with a further sulphur, in another unit (3.7-3.8 Å), and (weakly) with two chlorine atoms ($Tl-Cl$, 3.9-4.5 Å) of the chloroform molecules.³⁰⁶

$Tl_6Ag_2I_{10}$ is produced by heating a stoichiometric mixture of $TlI+AgI+I_2$ at 400°C in vacuo, or by refluxing a 3:1 mixture of TlI and AgI in 67% aqueous HI solution. The crystals belong to the space group $P\bar{6}2c$. The structure is built up from Tl_6I_6 units in chains parallel to the c axis, Ag_2 pairs and I_4^{2-} polyiodide ions are also present.³⁰⁷

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