Coordination Chemistry Reviews, 49 (1983) 117–192
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

Chapter 3

ELEMENTS OF GROUP 3

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0010-8545/83/$22.80

3.1 BORON

3.1.1 Boranes

A new method has been proposed, by which it is possible to describe uniquely all closed, fully-triangulated boron polyhedra with 4 to 24 vertices. The system is based on currently accepted procedures for numbering coordination and boron polyhedra, with minor extensions and midifications.[1]

The system for describing closed, fully-triangulated boron polyhedra having at least one rotational symmetry axis and one symmetry plane has been applied to boron polyhedra belonging to D_n, T and C_s point groups, which have only one of these elements. Extensions to the numbering procedure were suggested to accommodate these polyhedral structures.[2]

Potential energy curves have been determined, by *ab initio* calculations, for low-lying states of BH^+ dissociating to $B^+(^1S)+H$, $B^+(^3P)+H$ and $B(^2P)+H^+$. Agreement between the experimental and calculated values of spectroscopic constants for $X^2\Sigma^+$ and $A^2\Pi$ states supports the theoretical predictions about the bound $B'^2\Sigma^+$ state. The $3^2\Sigma^+$ and $2^2\Pi$ states are predicted to be repulsive.[3]

Ab initio MRD-CI calculations have been carried out to near full-configuration interaction accuracy for several large AO basis sets for the potential curves of the BH_2 molecule in its X^2A_1 and A^2B_1 electronic states. The resulting structural data agree within 0.002Å and 2° of measured bond distances and angles respectively.[4]

The geometrical structure and vibrational wavenumbers were calculated by *ab initio* m.o. methods for the so-far unknown diborane(4), B_2H_4. The equilibrium geometry was calculated to have r_e(B-B) = 1.669Å, r_e(B-H) = 1.195Å, $\angle$HBH = 116.6°, with D_{2d} symmetry. This fits into the known series of B_2X_4 (X = F,Cl or Br) geometries, allowing for the changed electronegativity of X. The barrier to internal rotation about the B-B bond was calculated to be 11.9 kcal.mol^{-1}.[5]

A quadratic vibrational force-field has been calculated for B_2H_6 using an STO4-31G orbital basis.[6]

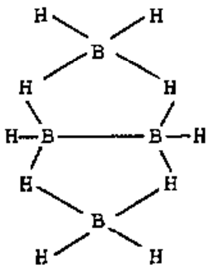
Triborane(7) adducts of PH_3, PH_2Me and $PHMe_2$ have been prepared from B_4H_{10} and the appropriate phosphine. The adduct $PH_3.B_3H_7$ can also be prepared from a displacement reaction of $THF.B_3H_7$.

All were characterised by ^{31}P and ^{11}B n.m.r. spectra.[7]

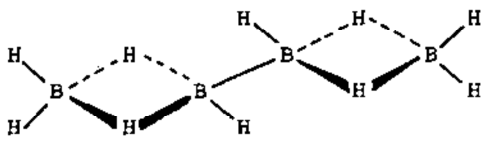
A theoretical study has been made of the isomerisation of the hypothetical B_4H_4. The tetrahedral structure is calculated to be the most stable. The D_{2d} structure lies at a shallow minimum,with a barrier of about 34 kJ mol^{-1} on the pathway to the T_d structure. The D_{4h} structure is not at a local minimum, and can therefore be regarded as a transition state between two symmetry-equivalent D_{2d} structures. The effects of electron correlation are important. The T_d structure is 137 kJ.mol^{-1} more stable than the D_{4h} form at the 6-31G level, and by 310 kJ. mol^{-1} when a correlation correction is included.[8]

New difluorophosphine complexes of B_4H_8 have been prepared, e.g. $B_4H_8.L$, where L = $PF_2(OMe)$, $PF_2(SMe)$, PF_2CF_3 or $PF_2(\underline{t}-C_4H_9)$. Multinuclear ($^{11}B$, ^{13}C, ^{19}F, ^{31}P) n.m.r. demonstrated that all the $B_4H_8PF_2X$ exist as two geometrical isomers (except for X = CF_3). The ^{19}F spectra are the most sensitive indicators for the presence of isomers. Rotational isomers were observed in some complexes (from low-temperature ^{19}F n.m.r.), although only for $B_4H_8.PF_2CF_3$ was a limiting low-temperature spectrum obtained.[9]

Calculations of the electronic arrangements in B_4H_{10} in which polarisation and configuration interaction are included reveal that the observed structure (1) is more stable than the gauche-bis(borane) structure (2) by only about 5.8 kJ.mol^{-1}. Addition of electron correlation would probably increase the stability of the observed structure, however.[10]



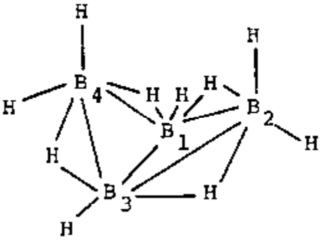
(1)



(2)

Restricted Hartree-Fock-level calculations on B_4H_{10}, indeed, suggest that at that level the form (2) is predicted to be more stable. Generalised-molecular-orbital, configuration-interaction calculations show that electron correlation is responsible for the reversal.[11]

There have been two reports of microwave spectroscopic investigations on B_4H_{10}. These are not entirely consistent with one another. In the first report, the spectrum was assigned between 26.5 and 40GHz. This was consistent with a nearly prolate rotor of C_{2v} symmetry, with the molecular dipole oriented along the c-axis. If the atoms are numbered as in (3), 1.845±0.002Å;



(3)

$r(B_1-B_3) = 1.718\pm0.002$Å; $r(B_2-B_4) = 2.806\pm0.001$Å; $r(B_1-H_\mu) = 1.428\pm0.02$Å; $r(B_2-H_\mu) = 1.425\pm0.02$Å. The dipole moment was calculated to be 0.486±0.002 D from Stark shift measurements.[12]

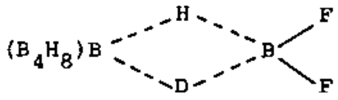
The second report used a joint analysis of electron diffraction and microwave spectral data. The basic structure, (3) was confirmed, but it was suggested that (i) the B-H-B bridges are unsymmetrical, the H_2B-H_μ distances being 17 pm. longer than $HB-H_\mu$, and that (ii) the bridging hydrogens are 5.6pm. above the plane defined by the three boron atoms of each $H_2B(HB)_2$ moiety, i.e. they fall within the fold of the tetraboron framework.[13]

The bonding and structures of B_5H_9, B_6H_{10} and $B_6H_6^{2-}$, together with the protonated species $B_5H_{10}^+$, $B_6H_{11}^+$, $B_6H_7^-$ and B_6H_8, have been analysed by MNDO, Gaussian-80 and self-consistent charge calculations. For B_6H_{10}, the known structure is more stable than other isomers for which metalloborane analogues are known. The bonding in $B_5H_{10}^+$ could be described as a $B_5H_8^+$---H_2 complex, but $B_6H_{11}^+$ prefers a structure with 6 $B-H_t$ and 5 $B-H_b-B$ bonds. The protonation of $B_6H_6^{2-}$ gives face-capped $B_6H_7^-$. In B_6H_8 the B_6 octahedral skeleton is entirely disrupted, and the molecule is predicted to be highly unstable.[14]

The action of difluoroborane, HBF_2, as an H/D exchange catalyst has been studied for pentaborane(9). The suggested intermediate is (4) - similar to that proposed for the difluoroborane-borazine exchange reaction.[15]

A theoretical study of the probable fluxional behaviour of pentaborane(11) supports C_1 symmetry for the molecular structure, with a low barrier for the C_1-C_s-C_1 process.[16]

Proton competition reactions show that the relative Brønsted acidities of substituted hexaborane(10) derivatives are in the sequence $2\text{-}BrB_6H_9 > B_6H_{10} > 2\text{-}CH_3B_6H_9$. KH reacts with the 2-substituted compounds to form the conjugate bases $2\text{-}XB_6H_8^-$ (where X = Br or Me). Diethylmagnesium reacts with $2\text{-}MeB_6H_9$ (at a 1:2 molar ratio in THF) to produce $(THF)_2Mg(2\text{-}MeB_6H_8)_2$.[17]



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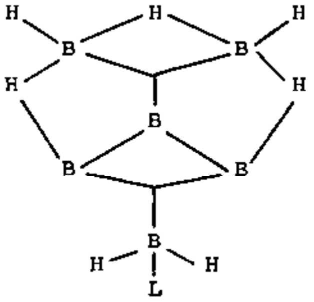


(5)

The formation of $B_6H_{10}.PMe_3$ has been confirmed; it is stable below -20°C in THF or dichloromethane solutions. It reacts with further trimethylphosphine to give $B_6H_{10}.2PMe_3$. Triphenylphosphine also gives a 1:1 adduct. ^{11}B and ^1H n.m.r. spectra suggest that the 1:1 adducts possess a structure derived from that of $B_5H_8^-$. The structure of $B_6H_{10}.PMe_3$ is (5), with L = PMe_3.[18]

Hexaborane(10) forms complexes with the following Lewis acids: BCl_3, B_2Cl_4, BBr_3, BI_3, $AlMe_3$, $AlEt_3$, $A(\underline{i}\text{-Bu})_3$. With BMe_3, BEt_3 and BF_3 no complex formation occurs. The BX_3 adducts (where X = Br or I) undergo halogen exchange with the B_6H_{10} to produce XB_6H_9 and $I_2B_6H_8$. Excess B_6H_{10} with BI_3 gives up to 40% yields of $B_{13}H_{19}$. Finally, gaseous chlorine and KB_6H_9 react to form ClB_6H_9.[19]

Several groups of workers have reported new synthetic routes to decaborane(14). In one, the first step is to treat BH_4^- with acids such as $BF_3.OEt_2$, BCl_3, $SiCl_4$, or alkyl halides. This produces $B_{11}H_{14}^-$, which is then oxidised by $Na_2Cr_2O_7$, $KMnO_4$, H_2O_2 or $H_2O_2/FeSO_4$ to give $B_{10}H_{14}$. The optimum procedure is to treat $NaBH_4$ with $BF_3.OEt_2$ in diglyme at 105°C (step 1). In step 2, water is added to the cooled reaction mixture, and the diglyme removed by distillation of the H_2O/diglyme azeotrope. The final step is to treat the resulting aqueous solution of $B_{11}H_{14}^-$ with H_2O_2 in the presence of $FeSO_4$, H_2SO_4 and hexane or cyclohexane. The organic phase is separated, dried and the solvent distilled off. Crystalline $B_{10}H_{14}$ separates on cooling the concentrated solution.[20]

A practical scheme has been devised for converting B_5H_9 into $B_{10}H_{14}$. This first involves the formation of $B_9H_{14}^-$ from B_5H_9, NaH and $NMe_4^+Cl^-$ in THF at room temperature. This can then be converted to $B_{10}H_{14}$ according to equation (1). Syntheses giving good yields of B_4H_{10} or B_5H_{11} were reported, analogous to (1).[21]

$$[NMe_4][B_9H_{14}] + BCl_3 \xrightarrow[\text{then sublime at } 90^\circ C.]{R.T.;6h} B_{10}H_{14} + [NMe_4][HBCl_3] + H_2 + \text{solid BH residue} \quad ...(1)$$

Decaborane(14) can also be prepared by opening the $B_{10}H_{10}^{2-}$ cage in a strongly acidic medium, such as pure H_2SO_4. The reaction is carried out in the presence of an inert solvent which dissolves $B_{10}H_{14}$. The best yields (28%) were achieved when zinc dust was also added.[22]

Boron-11/proton two-dimensional n.m.r., with heteronuclear decoupling in both frequency dimensions, has been used to study $B_{10}H_{14}$. The chemical shift correlation map shows clearly how resonances from the various boron and hydrogen sites are related. It shows, in particular, the association of bridging protons with $B^{5,7,8,10}$ and $B^{6,9}$.[23]

Tetradecaborane(20) can be obtained, although in poor yield (<2%) by the route shown in (2). The product is crystalline, yellow

$$K\,B_6H_3 + B_8H_{12} \xrightarrow{Et_2O} KB_{14}H_{21} \xrightarrow{HCl} B_{14}H_{20} + H_2 + KCl \quad ...(2)$$

and thermochromic. The crystals belong to the space group $P2_12_12_1$. The molecule consists of two B_8H_{12}-like fragments. These are fused together in cis-fashion, and the resulting molecular symmetry is close to C_{2v}.[24]

Irradiation of crystalline $B_{10}H_{14}$ in the beam of a 3MeV van der

Graaf generator, followed by chromatographic separation, produced several isomers of the *conjuncto*-borane, $(B_{10}H_{13})_2$. The ^{11}B n.m.r. data on the known 2,2'-, 2,6'-, 6,6'- and 1,5'-isomers of $(B_{10}H_{13})_2$ were assigned. The three new isomers were 1,2'-, 2,5'-$(B_{10}H_{13})_2$, together with 5,5'- or its *meso*-diastereoisomer 5,7'-$(B_{10}H_{13})_2$.[25]

It has proved to be possible to isolate and identify triacontaborane(38), $B_{30}H_{38}$ - formed as a minor component in syntheses of $B_{10}H_{14}$. It can be formulated as $B_{10}H_{13}$-$B_{10}H_{12}$-$B_{10}H_{13}$, the first bis-*conjuncto*-borane. Mass spectral data were discussed.[26]

3.1.2 Borane anions and Metallo-derivatives

A survey has been published of the bonding modes established for metal-borohydride complexes. It was suggested that an ionic radius of 1.6 0.1Å can be assigned to BH_4^- when it forms a bidentate bridge to the metal atom, but 1.36 0.06Å when forming a tridentate bridge.[27]

Previously unreported bands in the infrared spectrum of BH_4^- isolated in RbI can be explained in terms of summation bands of internal and external vibrational modes.[28]

T-Butoxyl radicals abstract hydrogen rapidly from BH_4^- or BH_3CN^-, to give $\cdot BH_3^-$ or $\cdot BH_2CN^-$ respectively. These were characterised by e.s.r. spectroscopy.[29]

Ab initio calculations have been performed on $NaBH_4$ and H_2AlBH_4 to try to understand the peculiarities of M-BH_4 bonding. The results suggest that the preferred coordination to sodium is tridentate, to aluminium bidentate. In the hydrogen exchange mechanism the presence of a Berry pseudorotation step can be excluded, as the associated activation energy is too high.[30]

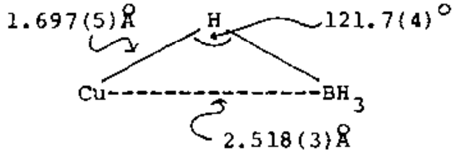
Sodium borohydride can be converted efficiently to $LiBH_4$ either by stirring with LiBr in diethyl ether at 25°C for 48 hours, or by refluxing with LiBr in THF for 16 hours.[31]

Ligand exchange has been studied for the Bu_4NBH_4-Bu_4NBBr_4 system in benzene. It was possible to isolate salts of ions $[BH_{4-n}Br_n]^-$, where n = 1, 2 or 3, although the compound with n = 1 is unstable, and decomposes at 20°C. The others are stable to 140°C (n = 2) or 160°C (n = 3). These bromo-compounds are much more stable towards disproportionation than their chloro-analogues.[32]

Molecular orbital calculations have been performed on $(BeB_2H_8)_n$, for n = 1 to 6, as models for the electronic structure of polymeric beryllium borohydride. They show that the systems can best be described in terms of an ionic array of $BeBH_4^+$ and BH_4^-.[33]

Non-solvated $Mg(BH_4)_2$ can be prepared in yields of greater than 80% (for purity of >99%) by the reaction of sodium borohydride with anhydrous $MgCl_2$ in diethyl ether. An excess of $NaBH_4$ is required, and refluxing for 20 to 25 hours.[34]

A single-crystal neutron diffraction study has been performed on $Cu(PPh_2Me)_3(BH_4)$, which belongs to the space group $Pna2_1$. Only one hydrogen of the BH_4^- bonds to Cu, (6); this is the first accurate determination of an unsupported metal-hydrogen-boron bridge bond.[35]



(6)

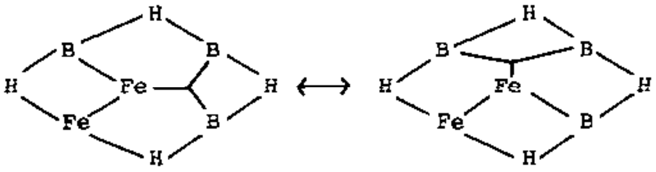
^1H, ^{11}B and ^{91}Zr n.m.r. spectra were recorded for $Zr(BH_4)_4$. The ^{11}B-decoupled ^{91}Zr spectrum gave a 17-line spectrum, with the coupling constant $J_{^{91}Zr-^{11}B}$ = 18Hz. The data can be interpreted in terms of a rapid intramolecular exchange of bridging and terminal hydrogen atoms.[36]

The kinetics of thermal decomposition of $U(BH_4)_4$ have been studied in the gas-phase. The process was monitored by changes in the infrared spectrum with temperature. The decomposition was first order in the range 130-170°C, but second order between 100°C and 120°C.[37]

The electronic structures of the ferraboranes $Fe_2(CO)_6B_2H_6$ and 1,2-$[Fe(CO)_3]_2B_3H_7$ have been studied by U.V.-photoelectron spectroscopy and U.V.-visible absorption spectroscopy. The results were analysed with the help of quantum-mechanical calculations using extended Hückel and Fenske-Hall methods. The experiments showed significantly different charges in the iron atoms in the B_3H_7 complex, which the calculations suggested are required by the cage geometry. Thus, in close analogy with B_5H_9, it seems that the square-pyramidal cage geometry requires greater valence-orbital participation in bonding for iron in an apical position compared to a basal position.[38]

Non-solvated NaB_3H_8 can be made by the interaction of $Bu_4NB_3H_8$ with $NaBPh_4$ in isopropyl alcohol , extracting the product with diethyl ether. The NaB_3H_8 decomposes to $NaBH_4$ and a mixture of B_5H_9, B_2H_6 and H_2 at about 100°C.[39]

The crystal structure has been determined for $(OC)_6Fe_2B_3H_7$; the crystals are monoclinic and belong to the space group $P2_1/c$. The molecular structure is a di-iron analogue of pentaborane(9). The B_3H_7 fragment is bonded to $Fe_2(CO)_6$ via 2 Fe-H-B bridges (to one iron) and through multicentre Fe-B bonding (to the other iron). The overall symmetry is close to C_s, and each boron has a single terminal hydrogen. It is thus derived from B_5H_9 by the replacement of one apical and one basal BH groups by $Fe(CO)_3$ units. The valence-bond description of the bonding is shown in (7).[40]



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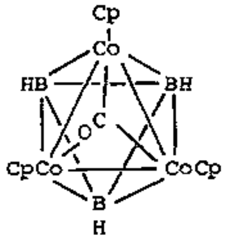


(8)

Crystals of 1,2,3-μ_3-carbonyl-1,2,3-tri-(η-cyclopentadienylcobalta)hexaborane(6), μ_3-CO-1,2,3-$(\eta^5\text{-}C_5H_5)_3Co_3B_3H_3$, are monoclinic, belonging to the space group C2/c (C^6_{2h}). The molecular structure, (8), confirms that proposed from spectroscopic results.[41]

Extended-Hückel m.o. calculation on the model complexes $[B_4H_4(CoL_3)_4]^{4+}$ and $B_4H_4(CoL_3)_4$, where L is a two-electron σ-donor ligand, have established the electronic factors responsible for the breakdown of the polyhedral skeletal electronic pair theory when applied to $B_4H_4[Co(\eta\text{-}C_5H_5)]_4$ and $B_4H_4[Ni(\eta\text{-}C_5H_5)]_4$. In addition, the observation that these last two complexes possess D_{2d} structures based on the dodecahedron can be rationalised in terms of the different electronic needs for stabilising the flattened metal tetrahedral structure in $B_4H_4[Co(\eta\text{-}C_5H_5)]_4$ and the elongated metal tetrahedral structure in $B_4H_4[Ni(\eta C_5H_5)_4]$.[42]

It has been shown that solid KOH can be used, below -40°C, to abstract a proton from B_5H_9, equation (3). The resultant

$$B_5H_9 \; + \; 2KOH(s) \xrightarrow[THF]{< -40^{o}C} KB_5H_8 \; + \; KOH.H_2O(s) \qquad \ldots(3)$$

KB_5H_8 is stable in the presence of KOH, and undergoes all the typical reactions of this compound.[43]

Self-consistent charge calculations on $Fe(CO)_3$ derivatives of hexaborane(10) rationalise the observed formation of only 4-$[B_5H_9Fe(CO)_3]$. The HOMO of this is directly comparable to that of B_6H_{10}. Calculations on $[C_2B_3H_7Fe(CO)_3]$ and observations on $(C_5H_5)Co$ complexes were used to suggest possible reasons for the stability of known compounds. The predicted most likely structure for $[C_4BH_5Fe(CO)_3]$ had the Fe atom and the BH unit adjacent on the basal plane.[44]

^9Be n.m.r. data have been presented for a series of beryllaboranes, $B_5H_{10}BeX$, where $X=BH_4$,Br,Cl or BeB_5H_{10}.[45]

The stereochemical rigidity of $B_7H_7^{2-}$, compared by the fluxional behaviour of ML_7 molecules, can be explained by the non-accessibility of the capped octahedral geometry for the former.[46]

Cis-$[PtCl_2(PMe_2Ph)_2]$ reacts with excess of $[B_9H_{14}]^-$ to form 4,4-bis(dimethylphenylphosphine)-arachno-4-platinanonaborane, $[4,4\text{-}(PMe_2Ph)_2\text{-}4\text{-}PtB_8H_{12}]$. This forms monoclinic crystals (space group C2/c), and the molecular structure shows that the B_8 unit is bonded in trihapto-fashion to the platinum. The fourteen-vertex bis(dimethylphenylphosphine)bis-μ-(2-4-η-nido-hexaboranyl)diplatinum(Pt-Pt): $[Pt_2(B_6H_9)_2(PMe_2Ph)_2]$, was also formed in moderate yield from the $B_9H_{14}^-$ reaction. The $[4,4\text{-}(PMe_2Ph)_2\text{-}4\text{-}PtB_8H_{12}]$ reacts with further cis-$[PtCl_2(PMe_2Ph)_2]$ to produce the very stable diplatinum compound 6,6,9,9-tetakis(dimethylphenylphosphine)-arachno-6,9-diplatinadecaborane, $[6,6,9,9\text{-}(PMe_2Ph)_4\text{-}6,9\text{-}Pt_2B_8H_{10}]$. This is an arachno-diplatinadecaborane with a bis(trihapto) B_8 unit. It is topologically similar to, but not identical with, $B_{10}H_{14}^{2-}$.[47]

The crystal structure of 2-(η^5-cyclopentadienyl)-2-cobaltadecaborane(14), 2-(η^5-C_5H_5)-2-CoB_9H_{13}, has been determined. It is orthorhombic, space group Pbcn(D_{2h}^{14}). The molecule possesses an effective plane of symmetry passing through Co, B(4), B(6), B(9), C(2), and bisecting the line between C(1) and C(3). The average Co-B bond length to B(1), B(3), B(5) and B(7) is 2.051(10)Å, while Co-B(6) is significantly shorter, at 1.967(5)Å.[48]

K_2PtCl_4 reacts with PPh_3(=L) in the presence of $B_nX_n^{2-}$, where n=10 or 12, X=Cl or Br, to give $[L_3PtCl]_2B_nX_n$.[49]

Deprotonation of $B_{10}H_{14}$ by N,N,N',N'-tetramethylnaphthalene-1,8-diamine, followed by treatment with cis-[$PtCl_2(PMe_2Ph)_2$] gives a better synthesis of [$(PMe_2Ph)_2(PtB_{10}H_{12})$]. Analogous reactions applied to 2,2'-, 2,6'- and 1,5'-isomers of $(B_{10}H_{13})_2$ gave various isomeric platina-henicosaborane clusters: [$(PMe_2Ph)_2(PtB_{10}H_{11}$-$B_{10}H_{13})$]. Modification of the reaction stoichiometry for 2,2'-$(B_{10}H_{13})_2$ allowed the isolation of cisoid- and transoid-diplatinadocosaboranes, [$\{(PMe_2Ph)_2(PtB_{10}H_{11})\}_2$]. The crystal structure of [$(PMe_2Ph)_2(PtB_{10}H_{12})$] showed the presence of a PtB_{10} cluster in which the tetrahapto $B_{10}H_{12}$ is twisted by about 20° with respect to the PtP_2 plane. A similar twist is found in the (η^4-$B_{10}H_{11}$-$B_{10}H_{13}$) analogue, but only by about 8°. ^1H, ^{11}B, ^{31}P and ^{195}Pt n.m.r. data were also discussed.[50]

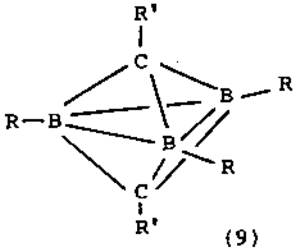
The fluoro-substituted borane derivatives $K_2B_{12}H_5F_7.2H_2O$, $K_2B_{12}H_4F_8.2H_2O$ and $K_2B_{12}H_2F_{10}.2H_2O$ are all prepared, for the first time, by direct fluorination of $K_2B_{12}H_{12}$ with HF. All were characterised by infrared and X-ray diffraction.[51]

Solubility has been studied at 25°C in the $K_2B_{12}H_{12}$-KBr-H_2O system. The only compound formed is the mixed salt $K_2B_{12}H_{12}.KBr$.[52]

3.1.3 Carba- and other Non-metal Heteroboranes

Ab initio m.o. calculations (using STO-3G basis sets) have been performed on the polymer systems $(HBX)_n$, where X=Be, BH, CH_2, NH or O. The conduction band has π-symmetry in each case, and the band gap increases in the order: X=Be<BH<NH<O<CH_2. Estimates of the energy of polymerisation suggest that HBNH is particularly stabilised by polymerisation. The electron distribution in $(HBBe)_n$ shows a σ-electron drift towards the boron atoms; in the other four systems the net electron transfer is away from boron.[53]

The aromatic-solvent-induced ^1H n.m.r. shifts observed for a series of closo-carbaboranes, $C_2B_nH_{2n+2}$, where n=3 to 10, can be correlated with PRDDO-MO calculations of hydrogen charges.[54]



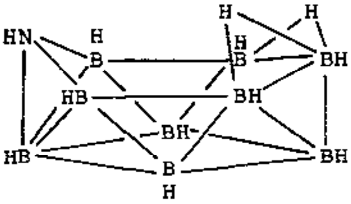
(9)

^{10}B, ^{11}B and ^{13}C n.m.r. parameters have been determined for the closo-pentaalkyl-1,5-dicarbapentaboranes(5), (9), where R = Et, R'=Me or Et; R=nPr, R'=Et. The chemical shifts show that neither the structure nor the electron distribution is significantly affected by alkyl substitution.[55]

$(\eta^5-C_5H_5)BeCl$ reacts with KB_5H_8 in pentane at -40°C to give good yields of $[\mu-(\eta^5-C_5H_5)Be]B_5H_8$. The crystal structure of this was determined, showing that the structure is like that of B_5H_9, with one bridge hydrogen replaced by $(\eta^5-C_5H_5)Be$.[56]

^{11}B n.m.r. data have been reported for $4-CB_8H_{14}$, $4-NB_8H_{13}$, $4-SB_8H_{12}$ and $4,6-C_2B_7H_{13}$, with detailed assignments proposed. The nature of the heteroatom bonding was discussed, in relation to these and to STO-3G and CNDO/2 density matrix properties.[57]

Lithiation of $1,2-C_2B_8H_{10}$ takes place preferentially at the six-coordinate equatorial (C(2)) site, rather than the five-coordinate apical (C(1)) site, in the approximate ratio 20:1. These data suggest that the relative acidities of C(1) and C(2) in this isomer are in the opposite order to that found in $1,6-C_2B_8H_{10}$.[58]



(10)

The aza-nido-borane, $6-NB_9H_{12}$, (10) can be prepared from $B_{10}H_{14}$ by treatment with sodium nitrite in THF (giving $NaB_{10}H_{12}NO_2$), followed by degradation with concentrated sulphuric acid. Hydrolysis of the new compound produces arachno-$4-NB_8H_{13}$, while addition of Lewis acids gives arachno-$9-L-6-NB_9H_{12}$, where L = Me_2S, MeCN or PPh_3).[59]

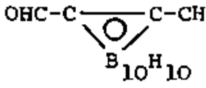
$6-NMe_3-6-CB_9H_{11}$ and sodium in liquid ammonia react to form $6-CB_9H_{12}^-$. The latter was a starting material for the preparation of $4-CB_8H_{14}$, $9-L-6-CB_9H_{13}$ (where L = Me_2S,MeCN or PPh_3), $1-(\eta^5-C_5H_5)-1,2-FeCB_9H_{10}^-$ and $2,3-(\eta^5-C_5H_5)_2-2,3,1-Co_2CB_9H_{10}^-$. The $4-CB_8H_{14}$ could be dehydrogenated at 623K to give the carbaborane $4-(7-)CB_8H_{12}$. Base degradation of $6-NMe_3-6-CB_9H_{11}$ in methanol gave 3,4-μ-NMe_3CH-B_5H_{10}. N.m.r. data and (for the transition metal complexes) X-ray diffraction were used to characterise these compounds.[60]

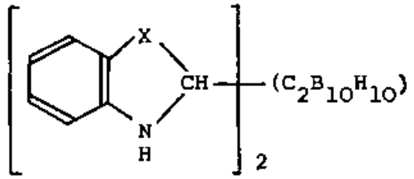
Controlled degradation of $Me_4C_4B_8H_8$ by air in 95% methanol produced $Me_4C_4B_7H_9$. Electrophilic bromination of the latter gave 11-$BrMe_4C_4B_7H_8$. X-ray diffraction shows this last compound to have an open-cage structure, with a bridging -CHMe- group across the open face. The last two compounds can both best be described as 11-vertex arachno-cages. Some of their reactions were described.[61]

Twelve C-SH and eight B-SH carbaborane thiols have been prepared and characterised, e.g. HS,X-1,2-$C_2B_{10}H_{10}$ (with 1-HS, X = H, 9-Hal, 12-Hal, 2-Me; 9-HS, X = 12-Hal or 1-Me; 12-HS, X = 1-Me), HS,X-1,7-$C_2B_{10}H_{10}$ (with 1-HS, X = H or 9-Hal; 9-HS, X = 10-Hal), 1-HS-1,2-$C_2B_{10}H_{11}$. The B-SH compounds were prepared as in equation (4).[62]

$$\text{1-Me-1,2-}C_2B_{10}H_{11} + S + AlCl_3 \xrightarrow[125^\circ C,5h]{\text{melt}} \text{1-Me-9-HS-1,2-}C_2B_{10}H_{10}$$

$$\text{or} \quad \text{1-Me-12-HS-1,2-}C_2B_{10}H_{10} \quad \ldots(4)$$

Condensation reactions between aromatic amines and 1,7-diformyl-1,7-dicarbadodecaborane(12),  $OHC\text{-}C\underset{B_{10}H_{10}}{\overbrace{\quad}}C\text{-}CHO$, have been studied. A variety of products were formed, such as (11), where X = -S- or



(11)

-C(=O)O-.[63]

Several meso-tetracarbaboranylporphyrins have been prepared, with meso-substituents 1-CH_2-1,2-$C_2B_{10}H_{11}$ or 1-CH_2-2-CH_3-1,2-$C_2B_{10}H_{10}$. The $-C_2B_{10}H_{10}Me$ cages of the latter were degraded by piperidine to produce $[-C_2B_9H_{10}Me]^-$ moieties, giving a water-soluble meso-tetracarbollylporphyrin.[64]

1-Amino-1,2-dicarbadodecaborane anions, o-$RCB_{10}H_{10}CNH_2{}^{2-}$ (where

R = H, Me or Ph) are oxidised by $KMnO_4$ in liquid ammonia to give 1,1'-azo-*o*-carbaboranes, $RC-B_{10}H_{10}CN=NCB_{10}H_{10}R$. Oxidation of $HCB_{10}H_{10}CCB_{10}H_{10}CNH_2{}^{4-}$ gave hydrazobis(*o*-carbaborane), $HCB_{10}H_{10}CCB_{10}H_{10}CNHNHCB_{10}H_{10}CCB_{10}H_{10}CH$, in the same solvent. The azo-derivatives can be reduced to the corresponding hydrazo-compounds while degradation using KOH gave *closo*,*nido*- or *nido*,*nido*-azacarbaboranes, $RCB_{10}H_{10}CN=NCB_9H_{10}CR^-$, $RCB_9H_{10}CN=NCB_9H_{10}CR^{2-}$ respectively.[65]

Closo,*closo*-1,1'-aza-*o*-carbaboranes, $RCB_{10}H_{10}CN=NCB_{10}H_{10}CR$ react with alkyl- or aryl-lithiums to form $RCB_{10}H_{10}CNHNR'CN_{10}H_{10}CR$, (R = H, Me or Ph; R' = alkyl or aryl). Further substitution of these (using alkyl halides) gave $RCB_{10}H_{10}CNR''NR'CB_{10}H_{10}CR$. All of these *closo*,*closo*-products can be converted into *closo*,*nido* ones in the presence of a base such as piperidine.[66]

1,2-(*O*-carbaboranylene)-4,4,6,6-tetramethyl-4,6-disila-5-oxacycloheptane, $C_8H_{26}B_{10}OSi_2$, forms monoclinic crystals (space group $P2_1/m$). The seven-membered cyclic substituent to the B_{10} cage is in the chair conformation.[67]

3.1.4 Metallo-heteroboranes

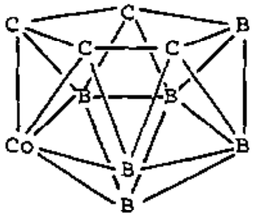
A generalisation of the Mingos-Wade skeletal electron counting schemes has been proposed for transition-metal heteroboranes, e.g. for situations where the transition-metal fails to conform to the eighteen-electron rule.[68]

Nido-cobaltacarbaborane anions $[(\eta^5\text{-}C_5R_5)Co(CH_3)_2C_2B_3H_4]^-$, where R = H or Me, react with $HgCl_2$ in THF to give (unstable) $[(\eta^5\text{-}C_5R_5)Co(CH_3)_2C_2B_3H_4.HgCl_2]^-$. These lose chloride ion rapidly to give isolable HgCl-bridged $\mu\text{-}[(\eta^5\text{-}C_5R_5)Co(CH_3)_2C_2B_3H_4]HgCl$. Symmetrisation of the latter produces $\mu,\mu'\text{-}[(\eta^5\text{-}C_5R_5)Co(CH_3)_2C_2B_3H_4]_2Hg$. For R = H the last transformation is rapid, but when R = Me it takes several days - and so the mono-metalloborane mercury complex is characterised best for the latter case. ^1H and ^{11}B n.m.r., infrared and mass spectra were used to characterise all the species, while X-ray studies were possible for $\mu\text{-}[(\eta^5\text{-}C_5Me_5)Co(CH_3)_2C_2B_3H_4]HgCl$ and $\mu,\mu'\text{-}[(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_4]_2Hg$.[69]

$Li^+C_5Me_5{}^-$, $CoCl_2$ and $Na^+\ Me_2C_2B_4H_5{}^-$ react in cold THF to give (mainly) *closo*-1,2,3-($\eta^5C_5Me_5$)$CoMe_2C_2B_4H_4$; the triple-decker sandwich complex 1,7,2,3-$(\eta^5\text{-}C_5Me_5)_2Co_2Me_2C_2B_3H_3$, and the novel complex $(\eta^5\text{-}C_5Me_5)_2Co_3Me_4C_4B_8H_7$. The last compound has no known counterpart. It contains two identical $(\eta^5\text{-}C_5Me_5)CoMe_2C_2B_4H_3$ units face-coordinated to the third cobalt atom, with a direct B-B bond

(1.758(5)Å) between the two ligands. The linked boron atoms have no terminal hydrogen atoms in the solid-state structure. In solution, ^{11}B and ^{1}H F.T. n.m.r., and infrared spectra, suggest that the "extra" hydrogen atom tautomerises between equivalent terminal positions on the (formerly) linked boron atoms on the two ligands, with cleavage of the B-B bond.[70]

Cobalt atoms react with boron hydrides in the presence of cyclopentadiene and sulphur reagents to form novel cobaltathiaborane and cobaltadithiaborane complexes. Thus C_5H_6 with B_5H_9 and Co atoms, followed by treatment with elemental sulphur, gives 6,8,7,9-$(\eta\text{-}C_5H_5)_2Co_2S_2B_5H_5$, whose structure was assigned spectroscopically. If cyclohexene sulphide replaces the sulphur, the same compound was formed, but also 2,3,6-$(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$. X-ray diffraction of the latter showed that its structure involved a tricapped trigonal prism, missing one equatorial vertex. It is the first time that such a structure has been seen for an eight-vertex, 2n+4 skeletal electron system. B_6H_{10} + C_5H_6 and cobalt atoms, followed by treatment with cyclohexene sulphide, form 7,6,8-$(\eta\text{-}C_5H_5)CoS_2B_6H_8$, with the expected structure for a 9-vertex 2n+6 skeletal electron system.[71]



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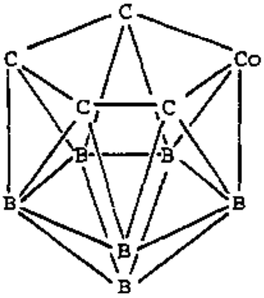


(13)

The structures of 2,7,8,10,11- and 9,7,8,10,11-$(\eta^5\text{-}C_5H_5)Co(CH_3)_4$-$C_4B_6H_6$ have been determined by X-ray diffraction. Both contain eleven-vertex CoC_4B_6 cages with icosahedral-fragment (capped pentagonal antiprism) geometry, and all four carbon atoms on the five-membered open face. There are no unusual distortions or anomalous features in the skeletal cage structures. These are (12), 2,7,8,10,11-isomer, and (13), 9,7,8,10,11-isomer.[72]

Na$[1,3\text{-}C_2B_7H_{12}]$ reacts with $[RhCl(PR_3)_2]_2$ or $[RhCl(PR_3)_3]$, where

R = Ph or *p*-tolyl, and Na(1,3-R^1_2-1,3-$C_2B_7H_{10}$, where R^1 = H or Me, reacts with [$IrCl(PPh_3)_3$] to form [*closo*-2,3-R^1_2-6,6-$(PR_3)_2$-6-H-6,2,3-$MC_2B_7H_7$], where M = Rh; R = Ph or *p*-tolyl; R^1 = H; M = Ir, R = Ph, R^1 = H or Me. When M = Rh, R = Ph, R^1 = H, the complex is a catalyst precursor for homogeneous hydrogenation of vinyltrimethylsilane under mild conditions. Na[1-R^1-3-R^2-1,3-$C_2B_7H_{10}$], where R^1 = R^2 = H or Me; R^1 = H, R^2 = Ph, and [$RhHCl(PPh_3)_2$] give unsaturated complexes [*hyper*-*closo*-2-R^1-3-R^2-6,6-$(PPh_3)_2$-6,2,3-$RuC_2B_7H_7$]. The complex with R^1 = R^2 = H is the most effective known catalyst for homogeneous hydrogenation of terminal alkenes. It also undergoes a number of interesting reactions with attendant polyhedral rearrangements.[73]

[$Co(PEt_3)_4$] reacts with *nido*-4,5-$C_2B_7H_{11}$ and *nido*-5,6-$C_2B_8H_{12}$ to give *closo*-[6,6-$(Et_3P)_2$-1,2,6-$C_2CoB_7H_9$] and *closo*-[1,1-$(Et_3P)_2$-1,2,4-$CoC_2B_8H_{10}$] respectively. Both products were characterised by single-crystal X-ray diffraction.[74]

The *arachno*-carbaborane, 1,3-$C_2B_7H_{13}$ reacts with [$Co(PEt_3)_4$] and with [$Rh(\eta\text{-}C_3H_5)(PEt_3)_2$] to form (respectively) [2-H-2,2-$(Et_3P)_2$-1,6,2-$C_2CoB_7H_9$] and [2-H-2,2-$(Et_3P)_2$-1,6,2-$C_2RhB_7H_9$]. X-ray diffraction shows that they crystallise with nearly identical unit cells, but they are not isostructural.[75]

A study has been made of the preferred structure of twelve-vertex, 28-electron, (*nido*) polyhedral cages, containing two electrons above the number required for regular *closo*-icosahedral systems. This was done by determining the structure of isomer III of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$ (the thermodynamically stable thermal rearrangement product of this system). This reveals a preference of the skeletal carbon atoms for low-coordinate vertices on the open rim, even though this requires three of the four carbon atoms to remain adjacent. The cobalt occupies a high-coordinate vertex.[76]

Trans-[$Ir(Co)Cl(PPh_3)_2$] reacts with *closo*-$[B_{10}H_{10}]^{2-}$ in methanol solution, giving rise to a number of novel structural types. Single-crystal X-ray diffraction revealed that one of these was the ten-vertex *iso*-*nido*-iridacarbadecaborane, $[\{IrC(OH)\overline{B_8H_6(OMe)\}(C}_6H_4PPh_2)(PPh_3)]$. This has been produced by oxidative insertion of the metal unit into the degraded *closo*-borane cluster.[77]

Reaction of 2,3-Me_2-2,3-$C_2B_9H_9$ with [$Fe(1,5\text{-}C_8H_{12})(\eta\text{-}C_5H_5)$] in benzene or other arene solvents gives the complexes [*closo*-1-(η^6-arene)-2,4-Me_2-1,2,4-$FeC_2B_9H_9$]. The toluene complex was characterised by X-ray crystallography. The η^6-naphthalene complex reacts with L(= CO or $P(OMe)_3$) to produce [closo-1,1,1-L_3-2,4-Me_2-1,2,4-$FeC_2B_9H_9$].[78]

[Closo-1,3-{μ-(η^2-3-CH_2=$CHCH_2CH_2$)}-3-H-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$] has been prepared. This contains a chelating 4-butenyl side-chain attached to the dicarbollide ligand, the alkenyl group formally replacing one PPh_3 of the parent compound [closo-3-H-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{10}$]. If the new complex is exposed to the conditions used for hydrogenating alkenes or alkynes, the alkenyl ligand is hydrogenated giving a non-coordinating butyl group. This leaves a vacant coordination site at the rhodium - which greatly enhanced the hydrogenation rate of added alkene. The complex did in fact act as a very efficient homogeneous hydrogenation catalyst. A crystal structure determination showed that the moleculae has closo-, twelve-vertex icosahedral geometry. The rhodium is bonded to one hydrogen, one triphenylphosphine, π-bonded to the carbon-carbon double bond, and symmetrically bonded to the C_2B_3 face of the C_2B_9 ligand.[79]

A report has also been made of the related species [closo-1,3-μ-2,3-μ-{1,2-μ-(η^2-3,4-$CH_2CH_2C(Me)$=$CHCH_2CH_2CH_2$)}-3-H-3-PPh_3-3,1,2-$RhC_2B_9H_9$]. The two butenyl side-chains attached to the dicarbollide ligand have dimerised in a "head-to-tail" fashion. The resulting chelating alkene is bound to the rhodium so that the C=C bond is approximately parallel to the dicarbollide ligand. The initial rates of some alkene hydrogenations catalysed by this complex have been measured.[80]

Syntheses, properties and chemical behaviour have been reported for $(C_2B_9H_{11})_2Co^-$ derivatives, as anions containing -S- or -SS- bridges, or neutral species with -SR- or -S-SR- bridges (R = H, alkyl or aryl), as well as the $-S^+Me_2$ group. ^{11}B n.m.r. data suggest that on the n.m.r. timescale there is free rotation at the $(C_2B_9H_{11})_2Co^-$, oscillations at $-S_2-$ or $-S{=}{=}{=}CH{=}{=}{=}S-$, and rigid conformations at -S-, $-\overset{+}{S}R-$, Me_2S^+- and $-S-\overset{+}{S}R-$.[81]

Ionic compounds containing complex chromium(III) cations and $C_2B_9H_{12}^-$ decompose at about 100°C to form complexes containing a covalent bond between Cr^{3+} and the carbaborane unit.[82]

The thirteen-vertex supra-icosahedral metallacarbaborane, 1,1-$(PPh_3)_2$-1-H-1,2,4-$RhC_2B_{10}H_{12}$ (a hydrogenation catalyst precursor) has been prepared via routes analogous to those for 10-, 11- and 12-vertex phosphinorhodacarbaboranes. It was characterised by n.m.r. and X-ray diffraction. There is no bonding interaction between B(3) and B(8) - this is a significant departure from the normally triangulated polyhedral carbaboranes.[83]

3.1.5 Compounds containing B-C or B-Si Bonds

The He(I) resonance photoelectron spectrum has been recorded for the MeNC.BH_3 complex. The data were interpreted using results on free methyl isocyanide and 4-31G *ab initio* m.o. calculations on both species.[84]

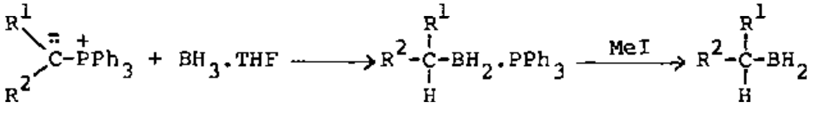
Raman and infrared spectra have been recorded for divinylmethylborane, $(CH_3)B(CH{=}CH_2)_2$. In the solid-phase there appears to be a planar heavy-atom skeleton, with C_s symmetry. In the fluid phases a second isomer is present, in which one or both of the vinyl groups are twisted slightly out of the BC_3 plane (C_1 symmetry). Variable-temperature ^{13}C n.m.r. studies were also carried out. The ^{13}C chemical shift for C_β of the vinyl group shows that there is little π-electron delocalisation. The low-temperature ^{13}C n.m.r. spectrum shows that there is only a low rotational barrier about the B-C(vinyl) bond.[85]

Me_nSnX_{4-n}, where n = 3, 2 or 1, dissolve in liquid BX_3 (where X = Cl or Br) at room temperature to give a reaction involving either X-exchange alone, or the cleavage of a methyl group from the alkyl tin as well as halogen exchange, as in equation (5). The

$$Me_3SnCl \ + \ BBr_3 \longrightarrow Me_2SnBr_2 \ + \ MeBBrCl \qquad ...(5)$$

products were identified by vibrational spectra.[86]

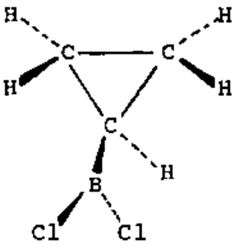
Preparatively useful monoalkyl boranes can be produced by the reaction of BH_3.THF with phosphorus ylides, equation (6), where



$$R^1R^2\overset{-}{C}-\overset{+}{P}Ph_3 + BH_3.THF \longrightarrow R^2-\underset{H}{\overset{R^1}{C}}-BH_2.PPh_3 \xrightarrow{MeI} R^2-\underset{H}{\overset{R^1}{C}}-BH_2 \qquad ...(6)$$

R^2 = H, R^1 = H, Me, n-C_5H_{11}, n-C_9H_{19} or Ph; $R^2 = R^1 = CH_3$. The products are useful sources of tertiary alcohols.[87]

Infrared and Raman spectra were recorded for gaseous and solid samples of cyclopropyldichloroborane, together with the Raman spectrum of the liquid. Only one conformation was found in all 3 physical states, identified as having C_s symmetry, (<u>14</u>). A

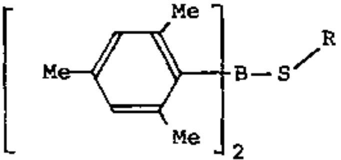


(14)

complete vibrational assignment was proposed.[88]

^1H, ^{11}B and ^{13}C n.m.r. data were reported and assigned for trimesitylborane, five aryl dimesitylboranes, ethenyl, allenyl, phenylethynyl and allyl dimesitylboranes. The unsaturated ligands stabilise the systems by π-electron back donation into the vacant boron p-orbital, in the order : aryl<<allenyl<alkenyl<alkynyl.[89]

The dimesityl boranes, (15), where R = Me, Et, CH_2Ph, Ph or p-MeC_6H_4, were prepared from $(MeS)_2BF$ and (RS)MgBr. When R = alkyl the compounds are readily hydrolysed in air, but greater stability is achieved when R = aryl. ^1H and ^{13}C n.m.r. data are consistent with significant B-S π-back-bonding.[90]



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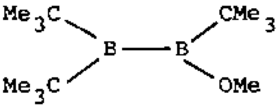
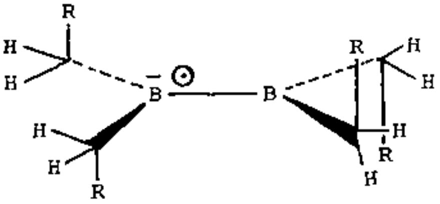


(16)

Tert-butylation of $B_2(OMe)_4$ by $LiCMe_3$ proceeds *via* $[(Me_3C)(MeO)B-B(OMe)CMe_3)]$ to produce (16). Tetra-alkylation of $B_2(OMe)_4$ can be achieved by *iso*-propyllithium, and no intermediates were detectable. Triethylaluminium reacts with $B_2(OMe)_4$ to give B_2Et_4, which is only stable below -30°C.[91]

The simplest B-B π-bond is found in the radical anion, (17), where R = $C(CH_3)_3$ or $C(CD_3)_3$. The one-electron π-bond was detected by e.s.r. measurements. It has a very similar structure to the isoelectronic C-C radical cation.[92]



(17)

Alkenylpentaboranes have been isolated for the first time, although they had previously been proposed as intermediates in thermally-induced carbaborane syntheses. B_5H_9 reacts under mild conditions with acetylene, propyne or 2-butyne, in the presence of catalytic amounts of $Ir(CO)Cl(PPh_3)_2$, to give $2-(CHR{=}CR^1)B_5H_8$, where R and R^1 = H or Me. The reaction corresponds to BH addition to the alkyne, in a *cis*-fashion, with the reaction of propyne occurring in a predominantly anti-Markownikoff manner. Thermolysis reactions of the alkenylpentaboranes showed that it was possible to get high yields of carbaboranes (predominantly alkyl derivatives of $2-CB_5H_9$) by passage through a hot tube (355°C).[93]

B_4Cl_4 reacts with lithium alkyls to form alkylated and peralkylated derivatives of the tetraboron framework. Examples included EtB_4Cl_3, $Et_2B_4Cl_2$ and ${}^tBu_4B_4$. These were characterised by infrared, n.m.r. and mass spectra.[94]

Reactions of several boron halides, methoxides, alkyls and hydrides with $(Me_3Si)_3SiLi.THF$ have been studied. It was possible to isolate $Me_2B{-}Si(SiMe_3)_3$ and $9-(Me_3Si)_3Si-9-BBN$, where 9-BBN = 9-borabicyclo[3.3.1]borane, together with $(Me_3Si)_3SiB(NMe_2)_2$, $[(Me_3Si)_3Si]_2B(NMe_2)$ and $[(Me_3Si)_3Si]_2B(OMe)$.[95]

3.1.6 Aminoboranes and other Compounds containing B-N Bonds

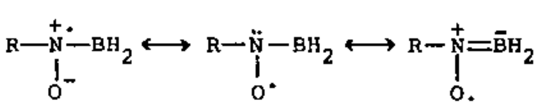
Ab initio m.o. calculations have been reported for $B(NH_2)_3$, $N(BH_2)_3$ and $B(OH)_3$. The molecules were assumed to be planar. The π-bond order was greater for B-N than for the B-O bonds.[96]

Microwave spectra have been obtained for $^{11}BH_3.NH_3$ and $^{10}BH_3.NH_3$. The B-N bond distance (r_{BN}) was found to be 1.66(3)Å. The molecular dipole moment was 5.216(17)D.[97]

Incomplete oxidation of $Et_3N.BH_3$ in toluene or hexadecane, or in the absence of a solvent, involves molecular oxygen. The product is a polymeric adduct of borate and triethylamine containing a B-N coordinate bond.[98]

Crystals of $C_5H_5N.BCl_3$ are monoclinic, space group $P2_1/c$. The pyridine ring is planar, while the boron has distorted tetrahedral coordination. Bond distances are, B-N, 1.592Å; B-Cl, 1.835(2)-1.839(3)Å.[99]

E.s.r. evidence was found for the formation of boronitroxides, (18), in the reaction of sodium borohydride with nitroso-compounds in alcoholic solutions.[100]



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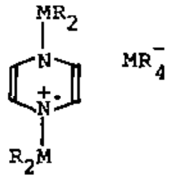
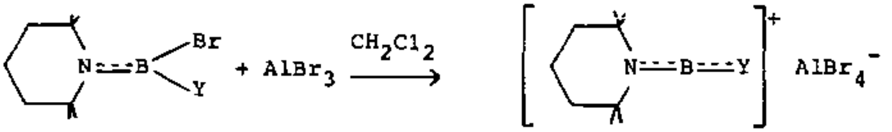


(19)

Alkyls MR_3 (M = B or Al; R = Et; M = Al, Ga or In, R = Me) react with pyrazine and sodium in THF, to give persistent radical complexes, (19). TlR_3 gave only Tl metal. All were identified by e.s.r. In the boron compound this gave evidence for $N \overset{\rightarrow}{-} B$ back-bonding.[101]

Chemical shifts ($\delta^{13}C$) of aminoboranes, $R_2BNR^1{}_2$, where R = Me, R^1 = H, Me, Et, $SiMe_3$, $SnMe_3$ or $R^1{}_2$ = HMe, H(CMe_3), Me($SiMe_3$), H($SiMe_3$); R = Et, R^1 = H, Me, Et, $R^1{}_2$ = HMe, H($SiMe_3$), and $X_2BNR^1{}_2$, where X = F, Cl, Br, R^1 = Et or X = Cl, Br, I, R^1 = Me, as well as borazines, can be explained by a γ-effect exerted by R or X on the shielding of $^{13}C(BC)$ and $^{13}C(NC)$.[102]

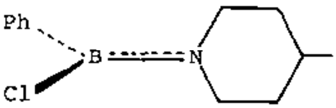
Hetero-allene analogues, containing a linear $>N{=}B{=}N<$ unit can be obtained, equation (7), where Y = NMe_2, NEt_2 or Ph. The structure was established by X-ray diffraction, and ^{11}B and ^{27}Al n.m.r. data were reported. ν_{as} BN_2 gave 2 bands in the range 1850-1900 cm^{-1} (splitting due to the $^{10}B/^{11}B$ isotope effect), consistent with this structure.[103]



(7)

A series of n.m.r. studies, chiefly ^{13}C, have provided evidence for restricted rotation about B-N bonds in a wide range of boron-nitrogen compounds. The compounds concerned were as follows:

dialkylaminofluorophenylboranes, $PhBF(NR_2)$, where R = Me, Et, *n*Pr; *i*Pr, *n*Bu, *s*Bu, *t*Bu, *iso*-pentyl, or R_2 = H*t*Bu;[104] aminodiphenylboranes, Ph_2BNR_2, where R_2 = Me_2, Et_2, *n*Pr_2, H*n*Bu, H*s*Bu, H*t*Bu, H(*neo*pentyl), $H(C_6H_{11})$, $H(NMe_2)$, $H(SiMe_3)$ or MeEt;[105] alkylaminodialkylaminophenylboranes, $PhB(NHR)(NR^1{}_2)$, where R = *n*Bu, *i*Bu, *s*Bu, *t*Bu; R^1 = Me or Et.[106] Such measurements on a series of chlorodialkylaminophenylboranes gave values for ΔG* for the rotational barrier about the B-N bond. Thus in (20) it was 17.7 kcal.mol.$^{-1}$.[107]



(20)

Electron diffraction has been used to determine molecular structures for $Me_{3-n}B(NHMe)_n$, where n = 1, 2 or 3. For n = 1, 2 or 3 respectively, the B-N bond distances were 1.397(2), 1.418(2) and 1.439(2)Å; i.e. all are shorter than expected for a formal single bond. The structures were all planar (or very close to it). There is thus significant B-N π-bonding, but this decreases in the sequence n = 1 > 2 > 3.[108]

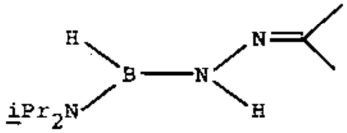
Based on infrared and Raman spectra, detailed vibrational assignments have been proposed for $B(NR_2)_3$, $B[N(CH_2)_4]_3$, $B(NR_2)_2Br$ and $B_2(NR_2)_4$, where R = Me or Et. Earlier discrepancies were resolved, showing that the antisymmetric B-N stretches always lie above 1500 cm^{-1}, with symmetric B-N stretches near to 1350 cm^{-1}. νB-B in the diboron compounds was at about 1230 cm^{-1}. In $B(NR_2)_3$ the internal vibrational modes of the three dialkylamino groups are strongly coupled together.[109]

Vibrational spectra were also reported for $(Me_2N)_2BX$, where X = H, D, CH_3 or CD_3, and assigned. The proposed assignment was supported by a normal coordinate analysis.[110]

Reactions of bis(dialkylamino)bromoborane with carboxylates (as K^+, Pb^{2+}, Ag^+ or trialkylammonium salts) gave bis(dialkylamino)-acyloxyboranes, $(R_2N)_2B(OCOR^1)$, where R = *i*Pr, R^1 = CF_3, CH_3 or CMe_3; R = Me or Et, R^1 = CMe_3. The compounds were characterised by infrared and ^1H n.m.r. spectra.[111]

Preparations and infrared spectra were reported for BCl_3 and AlX_3 (X = Cl, Br or I) complexes of 4-amino-benzophenone (=L):

$2BCl_3.3L$; $3AlCl_3.L.6H_2O$; $2AlCl_3.L.6H_2O$; $4AlCl_3.L$; $AlBr_3.3L$; $3AlBr_3.4L$; $AlI_3.4L$ and $AlI_3.L$. The ligand is coordinated via the NH_2 group in the BCl_3, $AlCl_3$ and $AlBr_3$ complexes. In the AlI_3 complexes, decreases in $\nu C{=}O$ suggest that here the carbonyl group is coordinated.[112]



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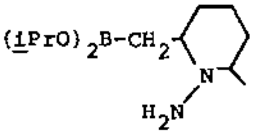
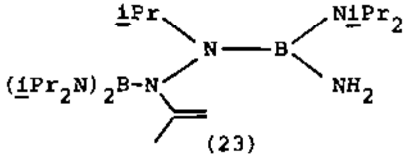


(22)

Pyrolysis of azidoboranes $(R_2N)_2BN_3$, where R = iPr or R_2 = $-CHMe(CH_2)_3CHMe-$, produces (21) or (22), respectively, both via boron imide intermediates. Photolysis of these two azides, however, yields (23) and (24) respectively.[113]



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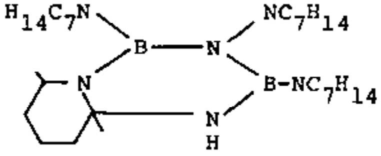


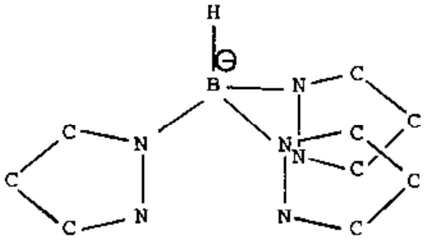
(24)

N-Silylated bis(amino)boranes, $(Me_2SiH)_2N$-B(Ph)NMe_2 and $Me_2SiCH_2CH_2SiMe_2NB(Ph)NMe_2$, can be prepared by the reaction of $Me_2NB(Ph)Cl$ with the N-lithium derivatives of the corresponding silylamines. Related compounds can be made from other boron starting materials.[114]

Dialkyl[(trimethylsilyl)(trimethylsilyloxy)amino]boranes, $R_2B-N(OSiMe_3)SiMe_3$, where R = Me, Et or Pr, can be prepared from R_2BCl and $(Me_3Si)_2N-OSiMe_3$. They are thermolysed at 70°C to give $(Me_3Si)_2O$ and a mixture of $R_2B-NR-BR-N(OSiMe_3)(SiMe_3)$ and $(RBNR)_3$. It is likely that these, and related reactions, can be explained by the intermediate formation of boron imides, RB=NR.[115]

The preparation of some amino(trimethylstannyl)boranes has been described, together with some of their properties, e.g. $Me_3SnB(NR_2)_2$ and $Me_3SnBCl(NR_2)$, where R = Me or Et. The $Me_3SnB(NR_2)_2$ are thermally stable, although the B-Sn bond is cleaved by H_2, halogens, chalcogens, or alcohols. The B-N bond is cleaved by HCl.[116]

^{11}B, ^{13}C, ^{14}N and ^{119}Sn n.m.r. data have been given for B- and N-(trimethylstannyl)aminoboranes, such as $Me_3Sn\text{-}B[N(CH_3)_2]_2$, $Me_2B\text{-}N[Sn(CH_3)_3]_2$ etc. Some rationalisations of both coupling constants and chemical shifts were attempted.[117]



(25)

He(I) and He(II) photoelectron spectra of the Na^+ and Tl^+ derivatives of hydridotris(1-pyrazolyl)borate, (25), have been reported. The spectra were assigned with the help of quantum-mechanical calculations.[118]

The crystal structure of $HB(Me_2pz)_3Mo(CO)_2SC_6H_4Cl$ shows that the hydridotris(3,5-dimethyl-1-pyrazolyl)borato ligand occupies three facial sites of the distorted octahedral molybdenum coordination polyhedron.[119]

3.1.7 Compounds containing B-P or B-As Bonds

Infrared and Raman spectra have been reported for $(CH_3)_2PH.BX_3$, $(CH_3)_2PD.BX_3$ and $(CD_3)_2PH.BX_3$, where X = Cl, Br or I. Fundamental modes were assigned on the basis of C_s symmetry. The calculated P-B stretching force constant was consistent with the structural change on adduct formation.[120]

Alkylation of triphenylphosphine-cyanoborane, $Ph_3P.BH_2CN$, by $Et_3O^+BF_4^-$ gave an N-ethylnitrilium salt which could be converted to the new phosphine-boranes: $Ph_3P.BH_2X$, where X = COOH, C(O)N(H)Et or COOEt. All of these were characterised by infrared, ^1H and ^{11}B n.m.r. spectra, as well as elemental analyses.[121]

A new borane-derived base, trimethylphosphine-[(dimethylamino)-methyl]borane, has been prepared, equation 8. This relies on the

$$Me_3P + Me_3N.BH_2CH_2NMe_2 \xrightarrow[12h]{hexane} Me_3N + Me_3P.BCH_2NMe_2 \qquad ...(8)$$

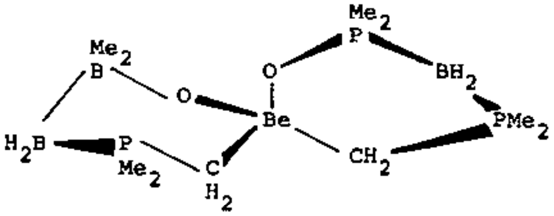
anomalously greater basicity of PMe_3 than NMe_3 towards boranes. Exposure of the product to diborane in hexane at −78°C produced the interesting species $Me_3P.BH_2CH_2NMe_2.BH_3$, containing two different dative bonds in the same compound.[122]

Trimethylphosphanechloroborane can be prepared by the route shown in equations (9) and (10). The product has νBH_2 infrared bands

$$BH_3.THF \;+\; HCl \longrightarrow BH_2Cl.THF \;+\; H_2 \qquad \ldots(9)$$

$$BH_2Cl.THF \;+\; PMe_3 \longrightarrow Me_3\overset{+}{P}-\overset{-}{B}H_2Cl \;+\; THF \qquad \ldots(10)$$

at 2395 and 2420 cm^{-1}, and it reacts with Me_2PCl to form $[Me_3\overset{+}{P}-\overset{-}{B}H_2-\overset{+}{P}(Cl)Me_2]^{+}Cl^{-}$. The bromo-analogue reacts with $K^{+}(Me_2PO)^{-}$ to give $[Me_3\overset{+}{P}-\overset{-}{B}H_2-P(=O)Me_2]$. Lithiation of this produces a derivative which forms a spirocyclic complex with beryllium chloride, (<u>26</u>).[123]



(<u>26</u>)

Infrared, Raman, ^{1}H and ^{13}C n.m.r. spectra have been reported and assigned for $R_3As.BX_3$, where R = Me or Ph; X = Cl, Br or I. The vibrational assignments were assisted by a normal coordinate analysis for $Me_3As.BX_3$.[124]

3.1.8 <u>Compounds containing B-O, B-S or B-Se Bonds</u>

The minimum energy path for the rearrangement LiOB →OBLi has been calculated, in an SCF approximation. It appears that LiBO is a "polytopic" molecule; with an excitation energy of about 12 kcal. $mol.^{-1}$ the Li atom will orbit about the BO core.[125]

Semi-empirical and <u>ab initio</u> m.o. calculations on the suboxides B_2O, B_2O_2, Al_2O and Al_2O_2 predict the following geometries: linear B-O-B, linear O-B-B-O, linear Al-O-Al and cyclic O-Al-O-Al. These calculations provide confirmatory evidence for the structures tentatively suggested from available thermochemical and spectroscopic data.[126]

$AgBO_2$ is prepared from a 1:1 mixture of Ag_2O and B_2O_3, at an oxygen pressure of 2 atm. The crystal structure (space group Pbcn) shows the presence of a ${}^1_\infty BO_2$-isopolyanion. The boron is coordinated in equal proportions tetrahedrally and trigonal-planar by the oxygens. At atmospheric pressure decomposition occurs, giving silver and B_2O_3.[127] The solid-state reaction of a 3:1 molar mixture of Ag_2O and B_2O_3 at high oxygen pressure gives Ag_3BO_3. This belongs to the space group R32, and contains BO_3 groups and Ag/O chains. As for $AgBO_2$, decomposition to silver and B_2O_3 occurs at atmospheric pressure.[128]

Accurate geometry determinations have been reported for H_2BOH, BF_2H, two conformers of FHBOH, F_2BOH, three conformers of $HB(OH)_2$ and three conformers of $FB(OH)_2$, all by SCF computation. Substitution of either F or OH increases the ionic character of both the B-F and the B-O bonds. The B-F bond is slightly more ionic than B-O. The OH group is a slightly stronger σ-acceptor and π-donor than is F.[129]

The molecular structure of $Me_2O.BF_3$ has been studied at 16°, 30° and 70° by gas-phase electron diffraction. The molecule has a staggered conformation, with $rB\text{-}O = 1.75\pm0.02$Å, an angle between the B-O bond and the COC plane of $40\pm8^\circ$, and an FBF angle of $117\pm2^\circ$ at each temperature. The B-F and C-O distances decrease with increasing temperature, and appear to converge on the corresponding values of the component molecules.[130] *Ab initio* calculations on the geometry of this molecule are consistent with these experimental results.[131]

Ab initio gradient calculations of the geometry and vibrational force field of B_2O_3 have been carried out at the double-zeta polarisation level of the restricted Hartree-Fock method. The molecule is planar with optimum bond lengths of 1.33Å (B-O), and 1.20Å (B=O). The central angle (136°) was very flexible. The O-B=O group was bent by 2°. The calculated vibrational wavenumbers only correlated very approximately with the limited experimental data now available.[132]

Further *ab initio* m.o. calculations on B_2O_3 also indicate a preferred planar geometry. This calculation predicts a "W"-shape, with a rather small inversion barrier at the central oxygen. MNDO calculations were in good agreement with the *ab initio* ones.[133]

Equilibrium geometries, barriers to skeletal linearity and conformational barriers for SiX_3 and BX'_2 rotation have been calculated for $X_3SiOBX'_2$ (X, X' = H, F or Cl), using the MNDO approximation. At equilibrium the calculsted SiOB angles were 180^o for $H_3SiOBCl_2$, F_3SiOBF_2, $F_3SiOBCl_2$ and $Cl_3SiOBCl_2$. The lowest value (140.5^o) was calculated for H_3SiOBH_2.[134]

45% conversion of trimethoxyborane to $HB(OMe)_2$ can be achieved by passing $B(OMe)_3/H_2$ mixtures through a carefully-controlled microwave discharge.[135]

Electron diffraction was used to determine molecular structures for $Me_{3-n}B(OMe)_n$ (n = 1, 2 or 3). The molecules all had planar (or nearly planar) conformations, with short B-O bonds, due to O→B back donation into the vacant boron p-orbital. The B-O distances were found as follows: 1.361(2)Å, 1.375(4)Å, 1.368(2)Å for n = 1, 2 or 3 respectively.[136]

^{11}B and ^{10}B n.q.r. spectra of $B(OH)_3$ have been reported. The quadrupole coupling and asymmetry parameters were found to be: ^{10}B, 5344(2) kHz, 0.0163(5); ^{11}B, 2768(8) Hz, 0.0163 (assumed).[137]

Ab initio LCAO-MO-SCF calculations were performed on the most likely interactions between F^- and H_3BO_3. The monofluoroborate ion, $[BF(OH)_3]^-$, is the most stable, but only by 33 kJ mol^{-1} compared to hydrogen-bonded $F^-....HOB(OH)_2$. Infrared analysis of solid $KF.H_3BO_3$ shows the latter to be the preferred form. ^{19}F and ^{11}B n.m.r. data on aqueous solutions of KF and H_3BO_3 are also most easily explained in terms of hydrogen-bonding, although $[BF_3(OH)]^-$ can be detected.[138]

In the course of hydrolysis of $B(OR)_3$, where R = Me, nBu or 2-ethylhexyl, by small amounts of H_2O in organic solvents, it has been possible to identify unambiguously both possible intermediates, $(RO)_2B(OH)$ and $(RO)B(OH)_2$, by Raman spectroscopy. Thus, bands due to $(MeO)_2B(OH)$ and $(MeO)B(OH)_2$ are seen at 772.8 cm^{-1} and 814.6 cm^{-1} respectively. Potentiometric and conductometric investigations confirm these results. OH^- in non-aqueous solvents converts $B(OR)_3$ to $B(OH)_4^-$, but in aqueous solutions it forms polyborates.[139]

Phase equilibria have been studied at 25°C for the systems: H_3BO_3-$HCONR_2$-H_2O (R = H or Me). There was no evidence for any chemical interactions between the components.[140]

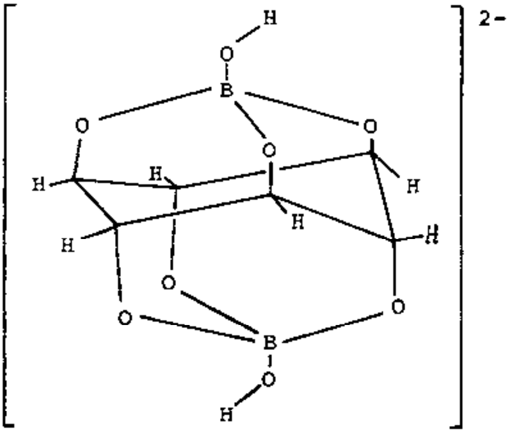
$BCl_n(ClO_4)_{3-n}$ (where n = 0, 1 or 2) and $B(ClO_4)_4^-$ can be synthesised by adding stoichiometric amounts of anhydrous $HClO_4$ to BCl_3, for the first three, or a large excess of $HClO_4$ to BCl_3-$MClO_4$

(where M = NO_2^+, NH_4^+) for the last. Infrared and Raman spectra show that all of the ClO_4^- ions are strongly bonded to the boron, and that all are unidentate.[141]

BCl_3 reacts with $HOTeF_5$ to give a 100% yield of $B(OTeF_5)_3$. This in turn reacts with $CsOTeF_5$ to form $Cs[B(OTeF_5)_4]$. Both were characterised by ^{11}B, ^{19}F and ^{125}Te n.m.r. spectra.[142]

$[(EtO)_2PO]_3B$ can be prepared from $BF_3.OEt_2$ and sodium triethylphosphite. Reactions and n.m.r. data (^{31}P, ^{11}B, ^1H) were reported for this new compound.[143]

A new complex borate has been identified: $Ca_3Er_3Ge_2BO_{13}$. An X-ray structural determination shows that the crystals are cubic (space group F$\bar{4}$3m), and that the boron occupies interstitial sites in the fluorite-related structure, as BO_4 units.[144]



(<u>27</u>)

A crystal structure determination has been carried out for sodium <u>scyllo</u>-inositol diborate decahydrate, $Na_2(C_6H_8B_2O_8).10H_2O$. The crystals belong to the space group Fdd2, and the anion has the structure (<u>27</u>), with B-OC distances of 1.48-1.51Å, and B-OH of 1.42Å.[145]

A metastable modification of $3MgO.B_2O_3$ has been prepared by the decomposition of mixtures of the corresponding methoxides. X-ray powder diffraction data were reported, and the infrared spectra of the stable and metastable forms compared.[146]

A note has been published, refuting earlier claims to have prepared mercury borates from the $HgO-B_2O_3-H_2O$ system.[147]

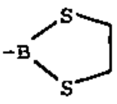
Orthoboric acid reacts with 2,2'-iminobis(ethanol) in aqueous solution at 25°C to give a substituted ammonium salt containing a cyclic trimetaborate anion: $[(HOC_2H_4)_2NH_2]^+[H_4B_3O_7]^-.2H_2O$.[148]

Dehydration of synthetic borax, $Na_2[B_4O_5(OH)_4].8H_2O$, takes place in four stages: 80-100°C, 80-150°C, 100-150°C and 150-500°C. One of the three intermediate phases is stable, the others are unstable. The final phase is crystalline and stable. The two stable phases are $Na_2[B_4O_5(OH)_4].3H_2O$ and (final) $Na_2B_4O_7$.[149]

Solubility and refractive indices have been measured for saturated solutions in the lithium tetraborate - 2-aminoethanol or 2,2'-iminobis(ethanol) or 2,2',2"-nitrilotris(ethanol) - H_2O systems;[150] and the $M_2B_4O_7$ - hexamethylenetetramine - H_2O (M = Li, Na or K) systems, all at 25°C.[151] All of the systems $Li_2B_4O_7$ - LiX - H_2O (where X = Cl, Br or I) are simple eutonic.[152]

The α-phase of $NH_4[B_5O_6(OH)_4].2H_2O$ is monoclinic (space group Pn). It is pseudo-isostructural with potassium pentaborate tetrahydrate.[153]

N.m.r. results for tris bis(organylthio)boryl amines, $N[B(SR)_2]_3$, where R = Me or $B(SR)_2$ = (28), (29) or (30), show that the RS groups are chemically equivalent in solution. This equivalence is lost in the solid state, as one $B(SR)_2$ group is strongly twisted out of the B_3N plane. This gives one longer, and two shorter B-N bonds. Mass spectra show that fragmentation occurs with preferential retention of B-N bonding. The crystal structures of the 1,3,2-dithiaborolane, 1,3,2-benzodithiaborole and 1,3,2-dithiaborolene ring systems show that only the last two possess planar rings.[154]



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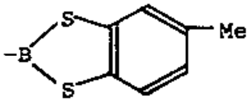

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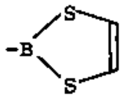


(30)

High-temperature flow pyrolysis reactions in the gas phase have been successful in detecting ClB=Se, the first in this family of compounds to be observed. Microwave spectra show that r(B=Se) = 1.751±0.002Å, with r(B-Cl) = 1.66±0.002Å.[155]

3.1.9 Boron Halides

The potential energy curve and dipole moment function have been calculated for BF near its equilibrium bond length. The dipole moment is predicted to be 0.89D (B^-F^+) at r_e. When the bond is stretched by about 0.2Å the sign of this changes.[156]

Ab initio m.o. calculations have been presented for $BF_n(OH)_{3-n}$, where n = 0, 1, 2 or 3, using restricted Hartree-Fock (3-21G) methods. The calculated geometries were in satisfactory agreement with experiment. The calculated value for the overall enthalpy of hydrolysis of BF_3 (to $B(OH)_3$) was +16.9 $kcal.mol^{-1}$.[157]

Boron trihalide adducts of acetate and benzoate esters readily exchange halogen to give mixed boron trihalide adducts: $D.BF_nCl_{3-n}$ (n = 0 to 3; D = carboxylic ester). Benzoate, but not acetate, esters also form DBF_2^+, probably by displacement of Cl from the BF_2Cl adduct.[158]

Ab initio m.o. calculations on BX_3 (where X = F or Cl) show that the π-contribution to the bonding is F>Cl.[159]

Solid BF_3 undergoes an enantiotropic phase transition at -147°C ($\alpha \rightleftharpoons \beta$). A third (γ) phase is metastable, or stable just below the melting point. The last forms monoclinic crystals (space group $P2_1/c$). The mean bond length is 1.287Å (1.319Å after correction for thermal motion). The crystal structures $BF_3.OH_2$ (monoclinic, $P2_1/n$) and $BF_3.O(Me)H$ (orthorhombic, Pbca) reveal unlimited 3- and 1-dimensional linking (respectively), by O-H---F bonds.[160]

A crystal structure redetermination has been carried out on boron trifluoride dihydrate. It is monoclinic ($P2_1/c$), and it is firmly established as hydroxytrifluoroboric acid monohydrate, $BF_3OH_2.H_2O$, and not $H_3O[BF_3OH]$. The B-F distances were 1.377-1.392Å, with B-O of 1.512Å.[161]

$HBF_4.2CH_3OH$ melts congruently at -41°C. A crystal structure determination shows that it is $[(CH_3OH)_2H^+][BF_4^-]$. The two cations and two BF_4^- ions in the unit cell are linked *via* hydrogen bonds to produce a cyclic dimer having an almost planar O_4F_2 ring.[162]

The heat capacity of NH_4BF_4 has been measured between 9K and 294K. There was no evidence for any phase transitions in this range.[163] Four phases can be isolated from the SnF_2-$BF_3.OMe_2$ systems, using acetonitrile as solvent. All contain the anion BF_4^-.[164]

Infrared spectra have been obtained for matrix-isolated $M^+BF_4^-$ ion pairs. When M = Cs there is a splitting (of about 200 cm^{-1}) of the t_2 BF_4^- stretching mode. The anion geometry is thought to be C_{3v}. A normal coordinate analysis was used to calculate the differences (ΔK) in stretching force constant of the coordinated and non-coordinated B-F bonds. The ΔK values lay in the sequence $M = Tl^+ < Cs^+ < K^+$.[165]

Crystal structures have been determined for three oxonium tetrafluoroborates: $[H(CH_3OH)_2][BF_4]$ - also discussed above; $[H_3O][BF_4]$: triclinic ($P\bar{1}$), in which the ions are linked by hydrogen bonds (O-H---F) to give ribbons of condensed rings; and $[H_5O_2][BF_4]$: monoclinic ($P2_1/c$), with a three-dimensional network of linked anions and cations.[166]

$(OC)_5ReFBF_3$ can be made from $(OC)_5ReX$ and $Ph_3C^+BF_4^-$ (where X = H or Me). Treatment of this with water produced the trifluorohydroxoborato complex $(OC)_5ReOHBF_3$. Infrared, ^{11}B and ^{19}F n.m.r. data were given for the two rhenium complexes.[167]

Unstable dihaloboranes, HBX_2, where X = Cl or Br, are generated in the gas-phase by almost quantitative reactions of BX_3 with solid $NaBH_4$ at about 250°C. He(I) photoelectron spectra were reported, and assigned with the help of ab initio m.o. calculations.[168]

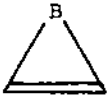
Boron trichloride and dimethyl sulphide form a 1:1 adduct; this exchanges with excess BCl_3 by a displacement mechanism (activation energy 5.0±0.5 kcal. mol^{-1}) and with excess Me_2S by a dissociation mechanism (activation energy 20±1 kcal. mol^{-1}). The 1:1 $AlCl_3.Me_2S$ complex exchanges very rapidly with excess Me_2S. Equilibria and exchange reactions of $AlCl_3.Me_2O$, $AlCl_3.2Me_2O$ and Me_2O were also described. All exchanges for the gallium analogues were very fast. BCl_3 and Cl^- give BCl_4^- and $B_2Cl_7^-$, which exchange rapidly with excess BCl_3. $AlCl_3$, on the other hand, reacts with Cl^- or BCl_4^- to give only $AlCl_4^-$, which does not exchange with $AlCl_3$.[169]

Tetramethoxydiborane(4) and BBr_3 react at room temperature to give a 50% yield of B_2Br_4. This is a very convenient method of preparation for the latter compound.[170]

The first neutral boron-iodide cluster compound has been prepared: B_9I_9. It is formed by the reaction of thallium(III) trifluoroacetate on $B_9I_9^{2-}$. It can be characterised by elemental analysis, infrared (very similar to B_9Cl_9, B_9Br_9) and mass spectra. The oxidative powers of B_9X_9 lie in the order: $B_9I_9 > B_9Br_9 > B_9Cl_9$. Thus the iodines are the least able to relieve the electron deficiency.[171]

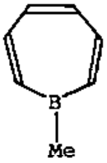
3.1.10 Boron-containing Heterocycles

Ab initio m.o. calculations have been carried out on the small-ring Hückel 2π aromatic compounds $(CH)_2BH$, (31) and $(CH)_2(BH)_2$, for which the most stable isomer was calculated to be 1,3-diboretene (32). The results were compared with those for isoelectronic carbocations. (32) has a puckered skeleton, with C_{2v} symmetry, like $C_4H_4^{2+}$. These puckerings are due to 1,3-σ-type repulsive interactions in the planar forms. A similar puckering was predicted for 1,3-diboretane, $(CH_2)_2(BH)_2$.[172]



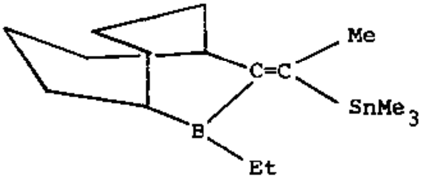
(31)

(32)



(33)

1-Methylborepin, (33), and its 3,6-dideuterio-derivative, are formed in the reactions between methylboron dibromide and the products of hydrostannation of a 1:1 *cis*/*trans* mixture of 1,5-hexadiyn-3-ene.[173] (33) is calculated to be aromatic on the basis of (i) the value of its Hückel M.O. resonance energy and (ii) the ring current effect in its ^1H n.m.r. spectrum.[174]

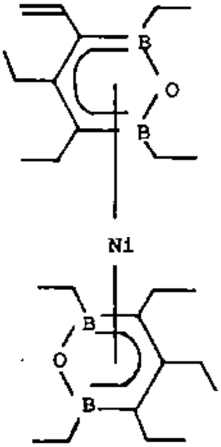


(34)

A number of the boron-containing alkenes have been prepared from the reaction of 9-ethylborabicyclo[3.3.1]nonane and alkynyl stannanes e.g. (34).[175]

Bis[1-oxa-2,6-diboracyclohexenyl]nickel having one vinyl and 9 ethyl substituents has been prepared from $Ni(CO)_4$ and 1,3-diborolene, followed by exchange of an CHMe group of the ring for oxygen of inserted CO, and migration of an H atom from the >CH=CHMe group of one ring to that of the other. X-ray diffraction showed that the structure is (35), in which the C_3B_2O rings are non-planar.[176]

N.m.r. data (^1H, ^{11}B and ^{13}C) have been reported for the triple-decker sandwich complex (36), and its anion. They show that it behaves like metallocenes. There is one unpaired electron - which is equally distributed between the two nickel atoms (on the n.m.r. timescale).[177]



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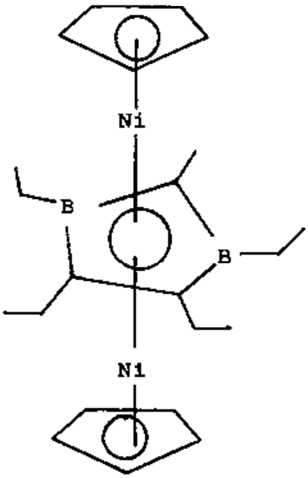
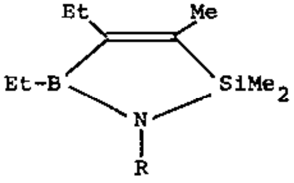


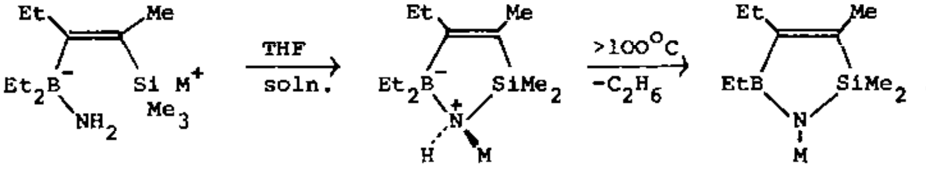
(36)

INDO-SCF m.o. calculations have been carried out on d^5 metallocene and bis-borabenzene systems, $M(C_5H_5)_2$ and $M(C_5H_5BH)_2$, ($M = Cr^-$, Mn or Fe^+). The results are consistent with previous suggestions about the relative bonding capabilities of these two ligands.[178]



(37)

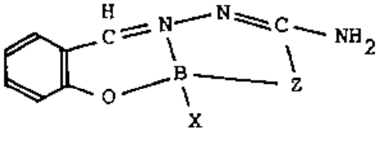
The new five-membered C_2BNSi compounds, (37), where R = Me or $SiMe_3$, can be prepared by a new type of ring-closure reaction,



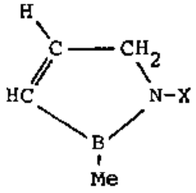
...(11)

equation (11), where M = Na or K. This is followed by treatment with methyl iodide or $SiMe_3Cl$ to give the final products.[179]

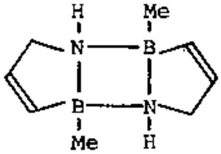
Boron trifluoride diacetic acid reacts with semicarbazones or thiosemicarbazones to produce FB(L). Boron triacetate gives analogous complexes (AcO)B(L). These can be formulated as (<u>38</u>), with X = F or AcO, Z = O or S.[180]



(<u>38</u>)

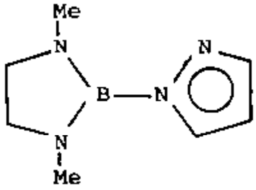


(<u>39</u>)

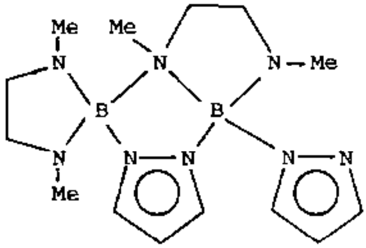


(<u>40</u>)

2-Methyl-1-trimethylsilyl-Δ^3-1,2-azaboroline, (<u>39</u>, X = $SiMe_3$) is prepared from $LiCH{=}CH{-}CH_2{-}N(SiMe_3)_3$ and $MeBBr_2$. It can be converted to 2-methyl-Δ^3-1,2-azaboroline (<u>39</u>, X = H) by elimination of $SiMe_3$ with ethereal HCl. The latter compound dimerises at room temperature to form (<u>40</u>); this dissociates again >60°C. Both of the monomers give π-complexes with iron carbonyls.[181]



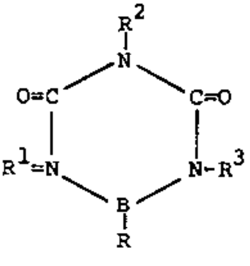
(<u>41</u>)



(<u>42</u>)

The synthesis of several new monomeric <u>N</u>-borylated pyrazole and imidazole derivatives has been reported. Structural proposals were based on spectroscopic data. For example (<u>41</u>) appears to be in equilibrium (below −40°C) with the new species (<u>42</u>).[182]

Several 1,3,5-triaza-2-boracyclohexa-4,6-diones, (<u>43</u>), where $R = R^1 = R^2 = R^3 = H$; R = Me or Ph, $R^1 = R^2 = R^3 = H$; R = Me, $R^1 = H$, $R^2 = R^3$ = Et, Ph etc, have been prepared by condensation reactions of boranes with biurets. They were characterised spectroscopically.[183]



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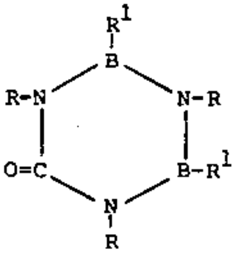
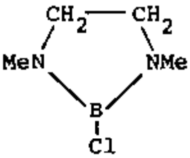


(44)

Numerous cyclic ureidoboranes, some analogous to (43), together with (44), R = Me, R^1 = Me, nBu or Ph; R = Et, R^1 = Me, and analogues containing C=S groups have been prepared from N,N'-diorganylureas or N,N'-diorganylthioureas and haloorganylboranes.[184]

Detailed vibrational assignments have been proposed for (45), where X = Cl, Br or NMe_2. These were generally in accord with C_{2v} symmetry, although there was some evidence for a slight breakdown of the selection rules, as some "A_2" modes were seen in the infrared spectra. The wavenumbers of the symmetric (near 1300 cm^{-1}) and antisymmetric (near 1500 cm^{-1}) BN_2 stretches were consistent with a large degree of B-N π-bonding.[185]

2-Chloro-diazaborolidine, $(CH_2NMe)_2BCl$, (45, X = Cl), reacts with N-silylated sulphur-nitrogen compounds (with sulphur in the oxidation state +4 or +6) to give the boranes $Me_2S(O)=N-B(NMe-CH_2)_2$, $(CH_2-CH_2)_2S[=N-B(NMe-CH_2)_2]_2$, $O=S=N-B(NMe-CH_2)_2$ etc. These are all thermally stable. Other chloroboranes, such as $(Me_2N)_2BCl$, Ph_2BCl etc, give less stable species.[186]



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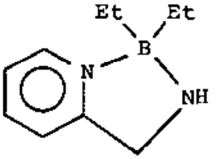

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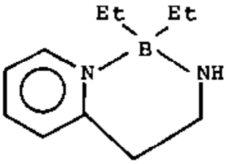
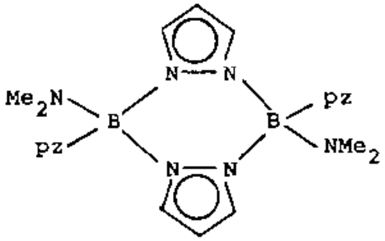


(47)

2-Aminomethylpyridine or 2-aminoethylpyridine react in 1:2 mole ratio with trialkylboranes to give compounds which pyrolyse to form $C_5H_4N-2-(CH_2)_n-NHBR_2$, where n = 1 or 2, R = Et or nPr. When R = Et, n.m.r. data are consistent with the structures (46) and (47). For R = nPr, a mixture of open and bicyclic forms are given when

$n = 1$, but the open form only when $n = 2$.[187]

Tris(dimethylamino)borane reacts with pyrazole (Hpz) to give a number of products, depending upon the reaction conditions, e.g. cis and trans-isomers of (48). Intermediates are believed to include $(Me_2N)_2Bpz$ and $(Me_2N)B(pz)_2$.[188]



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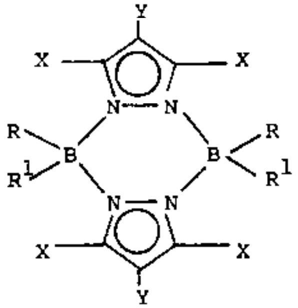
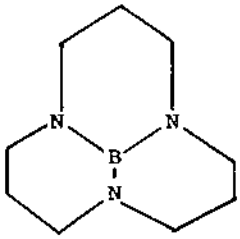


(49)

The B_2N_4 ring of compounds of the general type (49) is cleaved symmetrically when the boron-bonded hydrogen is replaced by strongly electron-donating amino-substituents. The products are monomeric pyrazol-1-ylboranes containing trigonal boron. If amino-substituents of weak donor ability are used, however, the above 'pyrazabole' structure is maintained.[189]

Crystal and molecular structures have been determined for (50), i.e. 1,5,9-triaza-13-bora-tricyclotridecane. The BN_3 system is approximately planar, but the carbon atoms lie out of this plane (by 0.3 to 0.4Å for the 3-, 7- and 11-carbon atoms, less for the others). The mean B-N bond length is 1.431(6)Å, suggesting a B-N bond order of about 1.4.[190]



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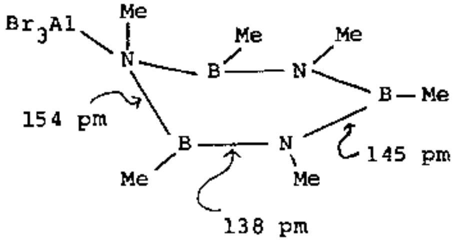


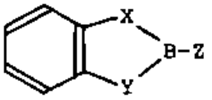
(51)

$AlBr_3$ forms a 1:1 adduct with hexamethylborazine - being coordinated to one nitrogen atom. This results in loss of planarity for the B_3N_3 system, and the B-N bond lengths now vary between 138 and 154 pm, (51).[191]

Boron nitride films are produced by the pyrolysis of various B-N compounds: borazines, such as $(ClBNH)_3$; $(C_3H_7)_2NBBr_2$ etc. The products are mixtures of hexagonal and cubic modifications, with more of the latter at lower thermolysis temperatures.[192]

Infrared and Raman spectra have been reported for $(BF\text{-}NH)_3$, $(^{10}BF\text{-}NH)_3$, $(BF\text{-}ND)_3$, $(BCl\text{-}NH)_3$, $(^{10}BCl\text{-}NH)_3$, $(BCl\text{-}^{15}NH)_3$, $(^{10}BCl\text{-}^{15}NH)_3$, $(BCl\text{-}ND)_3$, $(BCl\text{-}^{15}ND)_3$ and $(^{10}BCl\text{-}^{15}ND)_3$. Most previous assignments were confirmed, and hitherto-missing Raman bands due to modes of A_1' and E'' symmetry were detected.[193]

^{13}C chemical shifts of benzanellated heteroborolenes, (52), where X = Y = O, NR or S; X = NH, Y = S or O; Z = alkyl, Cl, NMe_2 etc, show that the BX(pp) π-interaction weakens the mesomeric donor ability of X (= O, N or S) towards the C_6 ring.[194]



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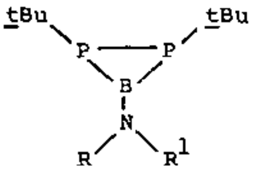
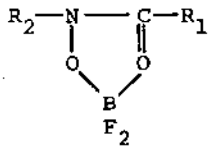


(53)

Reaction between K(*t*Bu)P-P(*t*Bu)K and diorganylaminodichloroboranes produces a new 1,2-di-*tert*-butyl-3-diorganylamino-1,2,3-diphosphaborinanes, (53), where R = R^1 = Et or Ph, R = Me, R^1 = *t*Bu, *n*Bu, Ph or C_6H_{11}. The three-membered systems are quite stable towards dimerisation (giving 6-membered P_4B_2 rings with opposite boron atoms).[195]

Several new boron-containing heterocycles have been reported: (54), where R_1 = Ph; R_2 = Ph, *o*-, *m*- or *p*-MeC_6H_4; R_1 = *o*-, *m*- or *p*-MeC_6H_4, R_2 = Ph, from the appropriate hydroxylamine derivatives and $BF_3.OEt_2$ in dry benzene (reflux for 2 hours).[196]



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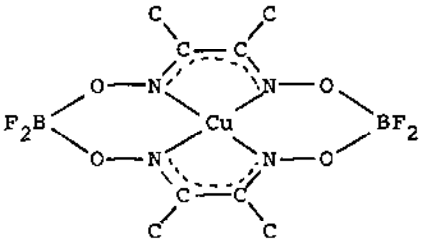
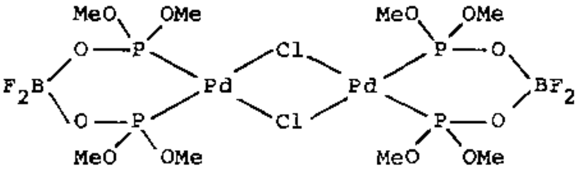


(55)

Tetraethylammonium carbonylbis[difluoro(glyoximato)borato]copper(I) forms monoclinic crystals (space group $P2_1/c$). The macrocyclic ligands are sverely puckered into a boat conformation, (55).[197]



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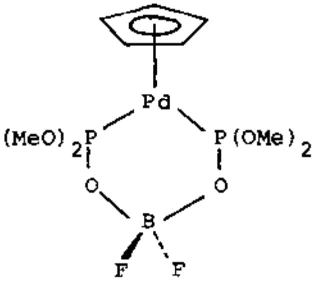
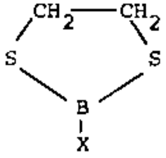


(57)

[ClPd{P(OMe)$_2$O}$_2$H]$_2$ reacts with $BF_3.OEt_2$ to give a binuclear complex (56). With cyclopentadienylthallium(I) the latter forms (57).[198]

Infrared and Raman spectra have been reported for 2-X-1,3-dithia-2-boracyclopentanes, (58), where X = Cl, Br, Ph or NMe_2. The rings modes can all be assigned in terms of a "twisted ring" conformation, of C_2 symmetry. The internal B-Ph modes are in accord with C_{2v} "local" symmetry, but those of B-NMe_2 suggest considerably lower symmetry.[199]



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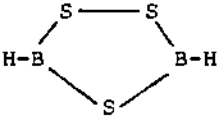
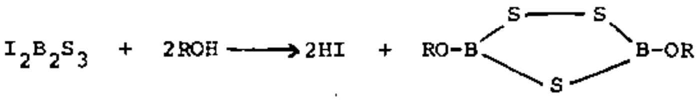


(59)

Various boranes (BH_3.THF, tetraphenyldiborane, 9-borabicyclo-[3.3.1]nonane (9-BBN)) react with 3,5-substituted 1,2,4,3,5-trithiadiborolanes in order to produce (59). The best mixture is $(Me_2N)_2B_2S_3$ + 9-BBN. The product is volatile, and condensed phases are always polymerised. Monomeric adducts $H_2B_2S_3.nNMe_3$, where n = 1 or 2, are formed, however.[200]

Reactions between trithiadiborolanes, $Y_2B_2S_3$, and boranes BX_3 occur with exocyclic substituent exchange of Y and X, and with an endocyclic process *via* ring opening and BY/NX exchange. ^{10}B-labelling was used to differentiate between the two routes.[201] Similar experiments were performed on reactions between $X_2B_2S_3$ and Y $Y_2B_2S_3$. Again two routes were found: X and Y can exchange rings by an exo-process, and mixed compounds XYB_2S_3 are formed with no exchange of boron atoms. In the endo-process, B atoms are also exchanged, leading to a statistical distribution of boron isotopes.[202]

The first two examples of hitherto unknown 1,2,4-trithia-3,5-



...(12)

diboralanes with B-O-C bonds have been prepared, equation (12), R = $Me_2C_6H_3$, and characterised.[203]

3.2 ALUMINIUM

3.2.1 Aluminium Hydrides

Potential energy curves for low-lying doublet states of AlH^+ (dissociating to $Al^+(^1S)$ + H, $Al^+(^3P)$ + H, $Al^+(^1P)$ + H or $Al(^2P) + H^+$) have been determined by *ab initio* configuration interaction calculations. The B' $^2\Sigma^+$ state was predicted to be bonding (bond length 2.06Å). A shallow minimum was found for the $3^2\Sigma^+$ state, and another for $2^2\pi$, while quasi-bound minima were found for $4^2\Sigma^+$ and $3^2\pi$.[204]

The structure of $Na[Me_3Al-H-AlMe_3]$ reveals a novel Al-H-Al bridge bond. The Al-H distance is 1.65Å, comparable to that in "normal" electron-deficient bridges, e.g. $[Me_2AlH]_2$. However, the Al-H-Al angle is accurately 180°, and there is no Al---Al interaction (distance = 3.30Å). Thus, metal-metal interaction need not be significant in "electron-deficient" bonding.[205]

The heat capacity of $LiAlH_4$ has been measured in the temperature range 12-320K. The plot of C_p against T is given by a smooth curve, with no anomalous regions.[206]

Hydrogen abstraction from AlH_4^- or $AlH(\underline{t}BuO)_3^-$ forms (respectively) $H_3Al\cdot^-$ and $(\underline{t}BuO)_3Al\cdot^-$. These were investigated in solution by e.s.r. spectroscopy. $H_3Al\cdot^-$ resembles $H_3B\cdot^-$ and $H_3Si\cdot$ very closely.[207]

Solutions of $LiAlH_4$ in THF, mono-, di- or triglyme, and $LiAlH_4$/THF in toluene were investigated by ^{27}Al n.m.r. $\delta^{27}Al$ and $^1J_{AlH}$ were both approximately independent of the solvent, although the line width of the ^{27}Al resonance is solvent and temperature dependent. Intermolecular hydride exchange is rapid in mono- or triglyme at room temperature.[208]

^{11}B and ^{27}Al n.m.r. were used to study the systems AlH_3/BH_3/THF and $LiAlH_4/BH_3$/THF. For the former, the data are explicable in

$$AlH_3 + \underline{n}BH_3 \rightleftharpoons AlH_{3-n}(BH_4)_n \qquad ...(13)$$

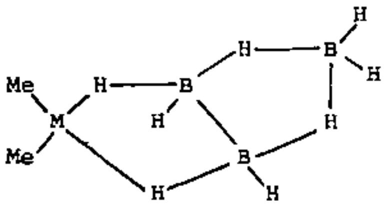
$$2AlH_{3-n}(BH_4)_n \rightleftharpoons AlH_{3-(n+1)}(BH_4)_{n+1} + AlH_{3-(n+1)}(BH_4)_{n-1} \qquad ...(14)$$

terms of the equilibria (13) and (14), where all of the species are solvated by THF. In the second system there was evidence for $LiBH_4$ and $AlH_{3-n}(BH_4)_n$ in equilibrium with $LiAlH_{3-n}(BH_4)_{n+1}$. At high n values, some of the coordinated THF is displaced from BH_3 by BH_4^-, to give $B_2H_7^-$.[209]

$Al(BH_4)_3$ reacts with volatile boron hydrides to produce numerous aluminoboranes of very great thermal stability. Thus, $Al(BH_4)_3$ and B_2H_6 in benzene solution form amorphous involatile "AlB_4H_{11}", which is also produced from $AlMe_3$ and B_2H_6. The structure is thought to be analogous to $(AlH_3)_x$, with a boron framework similar to that of B_5H_{11}. Aluminium occupies the apex(1) BH_2 position of B_5H_{11}, and the polymerisation involves six-coordination (hydrogen-bridged) at aluminium. B_5H_9 reacts with $Al(BH_4)_3$ to form "AlB_5H_{12}". This interacts with H_2O or gaseous HCl to produce species containing BH_2^+ cations. Thermal decomposition of $(H_4B)Al(B_3H_8)_2$ gives "AlB_6H_{13}".[210]

The structures of $Me_2MB_3H_8$, where M = Al or Ga, have been determined by electron diffraction. The skeletons are analogous to B_4H_{10}, the metal atom being linked to each of two boron atoms of B_3H_8 by a single hydrogen bridge, (<u>60</u>). The chief structural parameters are: (M = Al) rAl-C, 193.2(0.8)pm; rAl-B, 230.7(0.8)pm;

rAl-H_b, 190.6(4.1)pm; (M = Ga) rGa-C 193.0(0.7)pm; rGa-B 234.4(0.9)pm; rGa-H_b 198.9(4.8)pm.[211]



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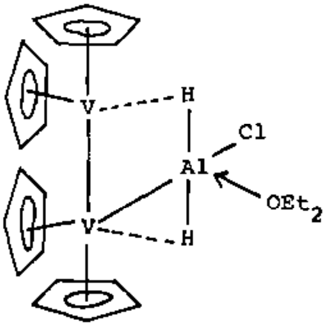


(61)

The reaction of $LiAlH_4$ and Cp_2VCl has been studied. It was possible to isolate two new species: $(Cp_2V)_2AlH_2Cl.OEt_2$ and $(Cp_2V)_2Al_2H_6.OEt_2$. The infrared spectra of these, and the deuterio-analogues, were obtained and partly assigned. The suggested structure for the former is (61).[212]

3.2.2 Compounds containing Al-C or Al-Si Bonds

S.C.F.-M.O. calculations have been carried out on the reactants and products of the reaction (15), on a symmetrical π-complex

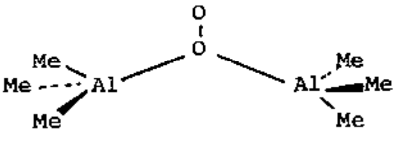
$$H_2AlH^* + HC{\equiv}CH \longrightarrow H_2Al\text{-}CH{=}CHH^* \qquad ...(15)$$

formed from the reactants, and on the system at various points on the reaction pathway. The reaction is best explained as one in which bonds are broken and formed in a concerted fashion. In the transition state the four reacting atoms (Al, H*, C and C) are joined by fractional bonds. The symmetric π-complex is at a shallow minimum, and therefore a possible intermediate rather than the transition state.[213]

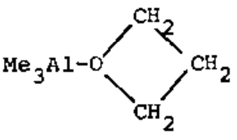
Exposure of Me_2AlX, (X = Cl, Br or I), in solid solutions in tetramethylsilane, to γ-rays at 77K leads to formation of a species with a six-line e.s.r. spectrum. The results were compatible with the formation of pyramidal $Me_2AlX\cdot^-$. The unpaired electron occupies a π*-orbital mainly derived from Al 3s and 3p orbitals.[214]

Crystal and molecular structures have been determined for

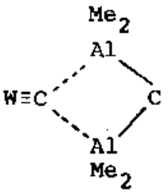
[K(dibenzo-18-crown-6)] $[Al_2Me_6O_2].1.5C_6H_6$. The O_2 must be regarded as O_2^- for charge balance, but a new structural mode is found, (<u>62</u>), with a very long O-O bond (1.47Å), and νO_2 at 851 cm^{-1}. Thus the O-O bond is very weak. The Al-O bond lengths (1.852(9), 1.868(9)Å) are normal. The geometry is very similar to that of $[Al_2Me_6(N_3)]^-$.[215]



(<u>62</u>)



(<u>63</u>)



(<u>64</u>)

The molecular structures of (<u>63</u>) and Me_3AlSMe_2 have been determined by gas-phase electron-diffraction. The bond distances in the former are Al-C, 1.965(7)Å; Al-O, 2.03(4)Å; O-C, 1.465(2)Å. In the latter they are: Al-C, 1.985(5)Å; Al-S, 2.55(2)Å; S-C, 1.817(5)Å.[216]

A single-crystal X-ray diffraction has been reported for the dialumina-methylidyne complex: $W(CAl_2Me_4Cl)(CH_3)(PMe_3)_2(\eta^2\text{-}C_2H_4)$. The tungsten geometry is approximately trigonal bipyramidal, with axial trimethylphosphine ligands. The best simple explanation of the $W(CAl_2Me_4Cl)$ unit involves a $W{\equiv}C{:}^-$ fragment, linked by a three-centre, two-electron bond to the two aluminium atoms of a $[Me_2Al(\mu\text{-}Cl)AlMe_2{}^+]$ group, (<u>64</u>).[217]

The complexes $Me_4(MeC{\equiv}C)_4Al_2M$, where M = Be or Mg, have been prepared from $[Me_2AlC{\equiv}CMe]_2$ and $(MeC{\equiv}C)_2M$ in 1,4-dioxan. They have low conductivity, and hence largely covalent bonding. It is believed that four alkynyl groups are bonded to M <u>via</u> σ and π bonds to alkynyl groups.[218]

The reagents $Al(SiMe_3)_3.Et_2O$ and $LiAl(SiMe_3)_4/AlCl_3$ can be used for directed nucleophilic silylation of carbonyl compounds giving α-hydroxytrimethylsilyl derivatives.[219]

The alkylaluminium compound in Ziegler-Natta catalysts can be replaced by silylaluminium compounds, e.g. $TiCl_4/Al(SiMe_3)_3.Et_2O$ (in the ratio 5:2) has proved to be an efficient catalyst for the polymerisation of ethene.[220]

3.2.3 Compounds containing Al-N, Al-As or Al-Sb Bonds

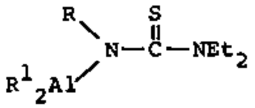
Infrared, Raman, ^{81}Br and ^{27}Al n.m.r. studies have been carried out on the $AlBr_3$ - CH_3CN system, for molar ratios $CH_3CN : AlBr_3$ in the range 4.7 to 64. The only anion present is $AlBr_4^-$, with three octahedral cations characterised: $AlBr_n(CH_3CN)_{6-n}^{(3-n)+}$ with n = 1, 2 or 3.[221]

Infrared and Raman spectra for $AlX_3.2py$, where X = Cl or Br; py = C_5H_5N or C_5D_5N, are consistent with the formulation $[AlX_2py_4]^+[AlX_4]^-$. The cation seems to possess a helical *trans*-octahedral conformation.[222]

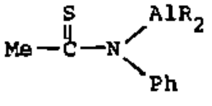
Mixed solvation-counterion complexes of the aluminium chloride system in MeCN or PhCN have been studied by high-field ^{27}Al n.m.r. spectroscopy. In the MeCN system, signals were identified due to *cis*- and *trans*-$[Al(MeCN)_4Cl_2]^+$, $[Al(MeCN)_5Cl]^{2+}$ and $[Al(MeCN)_6]^{3+}$.[223]

Similar techniques were also reported for AlX_3, where X = Cl, Br or I, in MeCN solution. The anion was always AlX_4^-, together with mixed hexa-coordinated cations: $[AlX_nS_{6-n}]^{3-n}$, where S = MeCN. These all have characteristic ^{27}Al shieldings. Geometric isomers could be detected for both $[AlCl_2S_4]^+$ and $AlCl_3S_3$. Addition of small amounts of H_2O displaces Cl^- or Br^- from the cations, to give $[AlS_n(H_2O)_{6-n}]^{3+}$.[224]

N-Silylated derivatives of thiourea, containing three organic substituents on both nitrogen atoms, react with R_2AlCl, where R = Me, Et or *i*Bu, to give monomeric thioureido-alanes, (*65*), where R = Me, Et or Ph, R^1 = *i*Bu, Et, Me. Analogous reactions gave smaller yields of (*N*-phenylthioacetimido)alanes, (*66*), where R = Me, Et or *i*Bu.[225]



(*65*)



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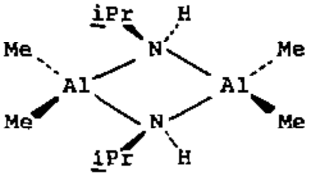

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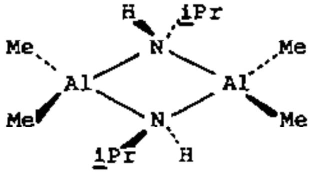
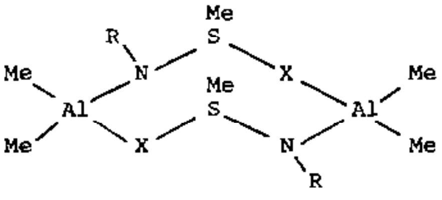


(*68*)

Triethylaluminium and isopropylamine react to form $[AlMe_2(NHPr^{i})]_2$. A crystal structure determination revealed that the molecules contain four-membered $(AlN)_2$ rings, and that *cis*-, (67), and *trans*-, (68), isomers crystallise together, in the mole ratio 2:1. N.m.r. studies showed a similar mixture in solution over a wide concentration range.[226]

Crystal and molecular structures have been determined for the pentamer $\{(HAlN^{i}Pr)_2(H_2AlNH^{i}Pr)_2[HAlNCH(CH_3)CH_2N(CH_3)_2]\}$. The molecule is built up from four $(AlN)_3$ and two $(AlN)_2$ rings. The nitrogen atom of the side-chain NMe_2 group is bonded to an aluminium atom, which is thus five-coordinate. Al-N distances were in the range 1.859(5) to 2.162(5)Å. For the hexamer $[HAlN(CH_2)_3N(CH_3)_2]_6 . 2LiH$; the structure consists of an "open cage", $(AlN)_6$, to which the two LiH molecules are linked by Li-H-Al bridges. The Al-N bond distances here are from 1.845(6) to 1.947(8)Å.[227]



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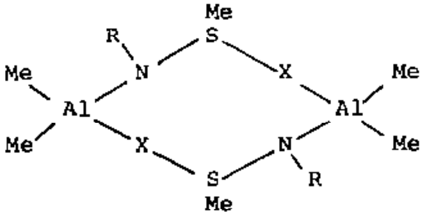


(70)

Sulphurdi-imines, RN=S=NR, and sulphinylanilines, RN=S=O, react with hexamethyldialuminium to produce $[Me_2Al\{RNS(Me)NR\}]_2$, where R = 4-MeC_6H_4, 4-ClC_6H_4 or 2,6-$Me_2C_6H_3$, and $[Me_2Al\{RNS(Me)O\}]_2$, where R = Me, Ph, 4-MeC_6H_4, 4-ClC_6H_4, 2,6-$Me_2C_6H_3$ or 2,4,6-$Me_3C_6H_2$. The former compound reacts with $HgCl_2$ or $SnCl_2$ to form dimeric $[Cl_2Al\{RNS(Me)NR\}]_2$, for R = 2,6-$Me_2C_6H_3$. The dimethylaluminium dimers exist in two conformations, (69) and (70).[228]

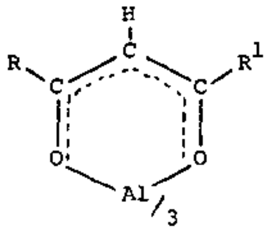
The limits of the vitreous range of the $CaO-SiO_2-AlN$ system have been investigated at 1400°C.[229]

Chains of $AlAs_4$ tetrahedra have been detected in the intermetallic compound Ca_3AlAs_3. Such groups can thus occur in Zintl phases - and not only in silicates and polyphosphates.[230]

Crystals of $Ca_5Al_2Sb_6$ are orthorhombic (space group Pbam); they contain $AlSb_4$ tetrahedra linked into chains *via* common corners. Two are linked by Sb_2 groups to form double chains. In monoclinic crystals of $Ca_3Al_2As_4$ (space group C2/c), the $AlAs_4$ tetrahedra are joined by common corners and edges to produce an infinite layer structure.[231]

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

Dissolving $(Me_2N)_3SiCl.AlCl_3$ in THF produces the adduct $AlCl_3.2THF$. Crystals of this belong to the orthorhombic space group Pbcn. The molecules possess nearly idealised trigonal bipyramidal geometry, with the THF molecules occupying axial sites. The Al-Cl bond lengths are 2.153 to 2.164Å, with Al-O 1.990Å. The Cl-Al-Cl angles are close to 120°, and the O-Al-Cl angles are close to 90°, giving D_{3h} effective symmetry for the $AlCl_3O_2$ unit.[232]



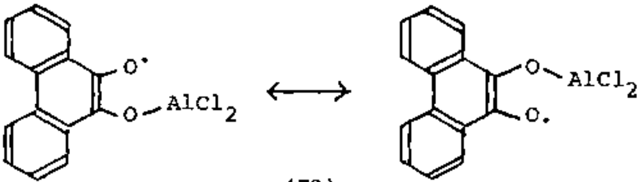
(71)

Eight tris(β-diketonato)aluminium(III) complexes, (71), with $R^1 = CF_3$, R = Me, Ph, 2'-C_4H_3S, p-MeC_6H_4, p-FC_6H_4, p-$MeOC_6H_4$ or 2'-$C_{10}H_7$; $R^1 = CHF_2$, R = Ph, have been studied by ^{19}F n.m.r. spectroscopy. All are stereochemically non-rigid, and there was evidence for ^{19}F resonances from cis and trans isomers.[233]

2H-$AgAlO_2$ forms hexagonal crystals, space group $P6_3/mmc$. It is isostructural with 2H-$AgFeO_2$, and contains aluminium atoms in octahedral sites.[234] Infrared spectra of some aluminates of rhombohedral and orthorhombic perovskite types have been analysed. A complete vibrational analysis was reported for $NdAlO_3$.[235]

Tris(diethylthiophosphato)aluminium(III) can be prepared by treating hydrated $Al(ClO_4)_3$ with a large excess of triethylthiophosphate. The product was characterised by infrared spectroscopy, which indicated coordination of aluminium by both oxygen and sulphur atoms of the ligands.[236]

A persistent radical is formed by the reaction of aluminium trichloride with 9,10-phenanthraquinone. E.s.r. studies show that it can be formulated as a pair of tautomers, (72).[237]



(72)

Equilibrium constants have been determined for reactions of Al^{3+}, Ga^{3+} and In^{3+} with *o*,*o*',*p*'-trihydroxyazo-compounds. The values are in the order: $Ga^{3+} > In^{3+} > Al^{3+}$. It was suggested that the spectrophotometric properties of the different complexes are sufficiently distinct to enable equilibrium concentrations of the components to be determined in mixed soutions.[238]

Formation constants and thermodynamic stability constants have been determined for aluminium(III) complexes of iminodiacetic (IDA) and nitrilotriacetic (NTA) acids. For IDA, log K, and log K_2 are 8.84 and 7.52 respectively; for NTA they are 10.66 and 8.73.[239]

The crystal structure has been determined for *trans*-bis(μ-acetato-*O*,*O*')-bis[μ-(tetraisopropoxy)aluminate-*O*,*O*']dimolybdenum, $[(\mu\text{-}O_2CMe)_2Me_2\{\mu\text{-}(OCHMe_2)_2Al(OCHMe_2)_2\}_2]$. The crystals are monoclinic, space group $P2_1/a$. No marked differences were found between terminal and bridging Al-O distances.[240]

Potentiometric measurements on the system Al(III)-gallic acid $(C_7H_6O_5;H_3L)\text{-}OH^-$ system can be explained in terms of the presence of $AlHL^+$, Al(OH)(HL) or AlL, AlL_2^{3-}, AlL_3^{6-}, $Al_2(OH)_2(HL)_3^{2-}$, $Al_2(OH)_2(HL)_2L^{3-}$, $Al_2(OH)_2(HL)L_2^{4-}$, and $Al_2(OH)_2L_3^{5-}$.[241]

The system $Na_2SO_4 - Al_2(SO_4)_3$ has been studied by DTA and infrared spectroscopy. It was established that $NaAl(SO_4)_2$ undergoes peritectic fusion at 750°C. The $Na_2SO_4 - NaAl(SO_4)_2$ eutectic melts at 660°C.[242] Equilibria in the $Al(III) - CO_2 - OH^-$ system have been studied by e.m.f. titrations in 0.6M NaCl solution. Data were consistent with the presence of the complexes $AlOH^{2+}$, $Al_3(OH)_4^{5+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_2(OH)_2CO_3^{2+}$ and $Al_3)OH)_4HCO_3^{4+}$.[243]

X-ray crystal structure determinations have been carried out for two new sodium aluminates. These are: Na_5AlO_4, which is orthorhombic (space group Pbca), and contains discrete AlO_4 tetrahedra; and $Na_7Al_3O_8$, which is triclinic (space group $P\bar{1}$), and contains a novel ring structure, derived from six AlO_4 tetrahedra, linked by oxygen bridges to form an infinite chain.[244]

$Ni_3Al_2SiO_8$ (phase IV) is orthorhombic (space group Imma). One third of the aluminium atoms are in octahedral, and two-thirds in tetrahedral sites. The structure is based on a slightly distorted cubic close-packed lattice of oxygen atoms, and is related to spinel and modified spinels.[245] Phase $\overline{\underline{\mathrm{V}}}$ of $Ni_3Al_2SiO_8$ is also orthorhombic (space group Pmma) and its structure is closely similar to that of phase $\overline{\underline{\mathrm{IV}}}$.[246]

Single crystals of $SrAl_2O_4$ can be prepared from $Al_2O_3/SrCO_3$ mixtures subjected to CO_2 laser irradiation (giving temperatures above 2000°C). The crystals belong to the space group $P2_1(C_2^2)$. The structure is derived from that of tridymite.[247]

Thermogravimetric measurements have been made on $Al_2(OH)_5Cl$. Decomposition takes place chiefly in the range 240 to 340°C (giving $AlO(OH)$, $Al(OH)_2Cl$ and H_2O). The final decomposition (to Al_2O_3) occurs below 600°C. The physical properties of aqueous solutions of the compound were also examined.[248]

${}^{3}_{\infty}[Al(H_2PO_4)_3]$ has been prepared and characterised as a second modification of aluminium tris(dihydrogen phosphate). The crystal structure is a three-dimensional Al-O-P network of AlO_6 octahedra, linked by common vertices through $O_2P(OH)_2$ tetrahedra and six further octahedra.[249]

X-ray powder diffraction for $Rb_2[M_2O(OH)_6]$, where M = Al or Ga, shows that they are isostructural, with four formula units per unit cell. The probable space group is Aba2.[250] Similar results are reported for $Cs_2[M_2O(OH)_6]$.[251]

Crystals of natural natrolite, $Na_2Al_2Si_3O_{10}.2H_2O$, are orthorhombic, space group Fdd2. Silicon and aluminium atoms are both four-coordinated by O. The average Al-O distance is 1.746(2)Å, the average Si-O distance is 1.619(2)Å.[252]

The hitherto-unknown $Pb_9Al_8O_{21}$ was prepared from 90 mol.% PbO and 10 mol.% Al_2O_3 at 950°C, followed by 72 hours at 850°C, and then rapid cooling to room temperature. The crystals belong to the space group $Pa3(T_h^6)$. The AlO_4 tetrahedra form a three-dimensional network with large cavities containing $[Pb_9O_{16}]^{14+}$ cations.[253]

Y_2O_3 and Al_2O_3 react in the solid phase to produce yttrium aluminates: $Y_4Al_2O_9$, $YAlO_3$ and $Y_3Al_5O_{12}$ (formed in that sequence).[254] Treatment of CuO/Al_2O_3 solid mixtures at 930°C for 8 days in the presence of PbO produces $Cu_2Al_4O_7$. Crystals of these are cubic, space group $F\bar{4}3m$, and AlO_4 tetrahedra are present.[255]

High-resolution ^{27}Al n.m.r. spectra of polycrystalline aluminates were studied at 70.4 MHz, using "magic-angle" spinning. Isotropic shifts depend on the Al-O coordination. Thus, AlO_4 tetrahedra give shifts of 55-80ppm., compared with AlO_6 octahedra (near 0 ppm.).[256] The observed ^{27}Al n.m.r. resonances in solutions of aluminosilicates can be assigned to AlO_4 tetrahedra with different numbers of Si-O-Al bonds.[257]

A new structural model proposed for zeolite A (rhombohedral $R\bar{3}$) differs from the one currently accepted (cubic Fm3c) in that each tetrahedrally-coordinated Si^{4+} is surrounded, via oxygen bridges, by 3 (not 4) Al^{3+} and one Si^{4+}, and each Al^{3+} by 3 (not 4) Si^{4+} and one Al^{3+}.[258]

A number of papers have appeared on the study of Al(III) hydrolysis by means of ^{27}Al n.m.r., along with other physical techniques. Thus, evidence was found for at least four components, including $Al(OH_2)_6{}^{3+}$ and $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$, in the solutions formed by dissolving aluminium metal in $AlCl_3$ aqueous solutions. Hydrolysis of $AlCl_3$ solutions by Na_2CO_3 gave only the Al_{13} cation, together with high-molecular weight polymeric ions.[259]

Decomposition of two different types of hydrolysed Al(III) solutions by the addition of acid was followed by ^{27}Al n.m.r. and pH measurements. The mechanism of decomposition of $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$ seems to involve as a rate-determining step the exchange of water ligands on Al^{3+}. High-molecular weight material decomposes more slowly than the Al_{13} cluster.[260]

Hydrolysis of aluminium(III) solutions, carried out in the shortest possible time, and without subsequent ageing, gives solutions whose composition depends upon the degree of hydrolysis achieved, and containing varying proportions of $[Al(H_2O)_6]^{3+}$, $[(H_2O)_4Al(OH)_2Al(OH_2)_4]^{4+}$ and $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$. New species were quickly formed on ageing, however.[261] ^{27}Al n.m.r. spectroscopy at 104.2 MHz gave definite evidence for $[(H_2O)_4Al(OH)_2Al(OH_2)_4]^{4+}$ and $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$ in hydrolysed Al(III) solutions.[262] ^{27}Al data on solutions obtained by the relatively slow hydrolysis of $AlCl_3$ solutions with aluminium metal in the presence of mercury showed that a variety of readily interconvertible species were present.[263]

The preparations of $[AlW_{12}O_{40}]^{5-}$ and $[AlMo_6O_{21}]^{3-}$ were monitored by ^{27}Al n.m.r. spectroscopy. For the former, four species containing aluminium are produced - one is the desired product, one a protonated form of it, while one of the others may be the 2:18(Al:W) anion.[264]

A water-soluble chloride can be prepared from the sparingly-soluble basic aluminium sulphate, $[Al_{13}O_4(OH)_{25}(OH_2)_{11}](SO_4)_3.xH_2O$, by reaction with barium chloride. Kinetic and ^{27}Al n.m.r. measurements suggest that the chloride (both as the solid and in solution) contains only the $Al_{13}O_{40}$ cation.[265]

Measurements of the kinetics of reaction with ferrone, and ^{27}Al n.m.r. data were used to determine the influence of the method of preparation, concentration and ageing on the constitution of solutions of basic aluminium salts. In all cases the proportion of polymeric species decreases at equal basicity with increasing aluminium concentration. The $Al_{13}O_{40}$ species is only formed in solutions prepared by the addition of alkali.[266]

Solid-state, high-resolution ^{27}Al n.m.r. data show that in the basic aluminium chloride, with OH/Al = 2.5, cations of the type $[Al_{13}O_4(OH)_{25}(H_2O)_{11}]^{6+}$ exist. Aqueous solutions give a single peak due to such a cation. Addition of HCl produces decomposition to low molecular weight species. Alkali, however, gives higher molecular weight particles not accessible to ^{27}Al n.m.r.[267]

Tetragonal aluminium sulphide, crystallising with the defect spinel structure, has been prepared at ambient pressure from the elements. Infrared and Raman spectra of this species, and of Al_2S_3, were reported and discussed in relation to their crystal structures.[268]

Single crystals of α-$ZnAl_2S_4$ (spinel structure) can be obtained by a chemical transport reaction at 740°C. Heating (800-900°C) produces a two-phase system. In the range 830-860°C the two phases are $Zn_{0.98}Al_{2.01}S_4$ (cubic, α-phase) and $Zn_{1.80}Al_{1.47}S_4$ (hexagonal, Wurtzite-phase).[269]

Crystal structure determinations have been determined for the following: $BaAl_2Se_4$ (tetragonal, P4/nnc); $BaGa_2Se_4$(orthorhombic, Cccm); $CaGa_2Se_4$ (orthorhombic, Fddd); and $CaIn_2Te_4$ (tetragonal, I4/mcm). All of the structures are closely related to that of TlSe.[270]

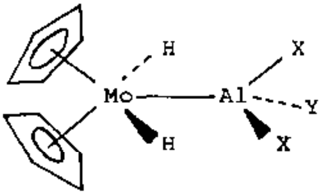
3.2.5 Aluminium Halides

The crystal structure of $KAlF_4$ has been determined by neutron diffraction at room temperature. The crystals are tetragonal, space group P4/mbm. The structure is derived from that of $TlAlF_4$, and contains a sequence of $[AlF_{4/2}F_2]^{-}_{\infty}$ layers of AlF_6

octahedra, sharing four corners in the (001) phase. K^+ ions lie between the layers. The Al-F distnaces are 1.752(1)Å (axial) and 1.817(1)Å (equatorial).[271]

Hydrothermal synthesis in HF produces single crystals of $Rb_2AlF_5.H_2O$ or $Tl_2AlF_5.H_2O$. These are isostructural and orthorhombic (space group Cmcm). The structure contains infinite chains of AlF_6 octahedra along the $\vec{c}$ axis; the octahedra share two trans fluorine atoms.[272]

The enthalpy of formation of the NMe_4^+ salt of $Cl_3Al(ClO_4)^-$ has been determined from thermochemical measurements: $\Delta H^o_{f,298.15}\{Me_4N^+[Cl_3Al(OClO_3)]\}_{cryst} = -246.87 \pm 0.36$ kcal.mol^{-1}. The enthalpy of addition of crystalline $AlCl_3$ to crystalline Me_4NClO_4 is -40.8 kcal. mol^{-1}.[273]



(73)

The complexes $Cp_2MoH_2AlX_3$ and $Cp_2MoH_2AlHX_2$ (where X = Cl or Br) have been prepared from Cp_2MoH_2 and the etherate of the appropriate aluminium compound. They contain a direct Mo-Al bond, (73), where X = Y = Cl or Br or X = Cl or Br, Y = H_2. Both νMo-H and (where appropriate) νAl-H are in the regions expected for terminal hydrogens e.g. for $Cp_2MoH_2AlHCl_2$, νAlH is at 1795 cm^{-1}, for $Cp_2MoH_2AlDCl_2$, νAlD is at 1320 cm^{-1}.[274]

The binary $AlCl_3$-$CaCl_2$ system has been examined. A eutectic was found at 24.5 mole % $CaCl_2$, 110°C, and a peritectic at 30.0 mole % $CaCl_2$, 280°C. The latter corresponds to the incongruent melting of $CaCl_2.AlCl_3$.[275]

Some vibrational assignments have been proposed from the infrared spectra of crystalline $(CpTiCl)_3AlCl_{3-n}H_n.S$ (where n = 0 or 1; S = Et_2O or NEt_3). The hydrido-complexes presumably involve bridging hydrogens, as no νAlH_t modes could be seen.[276]

Potentiometric measurements on the NaCl-$AlCl_3$ system are explicable

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \quad ...(16)$$

$$3Al_2Cl_7^- \rightleftharpoons 2Al_3Cl_{10}^- + Cl^- \qquad ...(17)$$

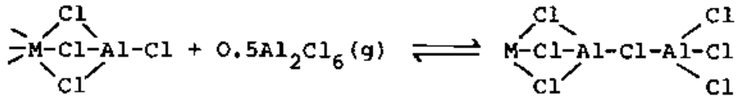
$$2Al_3Cl_{10}^- \rightleftharpoons 3Al_2Cl_6 + 2Cl^- \qquad ...(18)$$

in terms of the equilibria (16)-(18).[277]

^{27}Al n.m.r. spectra have been obtained for liquid samples of the $AlCl_3$/*n*-butylpyridinium chloride system. Previous suggestions about the structures of species present were confirmed, and ^{27}Al n.m.r. parameters of $AlCl_4^-$ and $Al_2Cl_7^-$ were determined.[278]

Raman spectra of PCl_5-$AlCl_3$ melts (containing 30, 50, 63.7, 70, 80 or 90 mole % $AlCl_3$) gave bands due to the species PCl_5, PCl_4^+, $AlCl_4^-$, $Al_2Cl_7^-$ and Al_2Cl_6. A higher complex, $Al_xCl_y^{2-}$, was found when more than 70 mole % of $AlCl_3$ was present. The last gave bands at 100, 297 and 395 cm^{-1}.[279]

A number of papers have been published by Schäfer and co-workers on gaseous complexes of aluminium halides with a variety of metal halides. Thus it has been suggested that the addition of $AlCl_3$ to gaseous $MCl_x.nAlCl_3$ complexes in which M is coordinatively saturated is independent thermodynamically of the nature of and the charge on M. If M is six-coordinate, then for all the equilibria


...(19)

(19), $\Delta H^o = -8(\pm3)$ kcal. mol^{-1} and $\Delta S^o = -16(\pm4)$ cal. K^{-1}.[280]

The equilibria (20) have been studied by mass-spectrometry for

$$MCl_x(s) + 0.5nAl_2Cl_6(g) \rightleftharpoons MCl_x.nAlCl_3(g) \qquad ...(20)$$

$MCl_x = TiCl_3$, VCl_3, $ScCl_3$, $NdCl_3$, $ZrCl_4$, $TaCl_5$ or $\frac{1}{2}Nb_2Cl_{10}$. $n = 1$ in every case. For $MoCl_3$ and WCl_6 no complex formation was detected.[281] Mass spectrometric or spectrophotometric measurements gave $\Delta H^o(298)$ and $\Delta S^o(298)$ for (20), in which $MCl_x = VCl_3$,[282] or $HgCl_2$.[283] Similar data were deduced for the equilibria (21), in which M = Cr,[284] or Ni.[285] In the latter case

$$MCl_2(s) + Al_2Cl_6(g) \rightleftharpoons MAl_2Cl_8(g) \qquad ...(21)$$

it was also possible to characterise the equilibrium (22).

$$NiAl_2Cl_8(g) + 0.5Al_2Cl_6(g) \rightleftharpoons NiAl_3Cl_{11}(g) \qquad ...(22)$$

Some mass spectral data were also obtained for (21), in which M = Fe, Zn, Cd or Pt. Relationships were found here between the thermodynamic data obtained from these and the coordination of M and Cl in the solid dichlorides.[286] For M = Pd, (21) was studied, and also the equivalent equilibria involving the bromides or iodides. Differences between the chloride and bromide systems on the one hand, and iodides on the other, could be traced to structural differences between the dihalides.[287]

$AlCl_3$ is formed by the reaction of metallic aluminium with $PbCl_2$ in a molten salt mixture. If chlorine gas is also present, the halogen carrier is recovered in good yield. Thus a continuous process can be developed.[288]

The visible spectra of $CoAl_2Cl_nI_{8-n}$ contain bands at wavenumbers intermediate between those of $CoAl_2Cl_8$ and $CoAl_2I_8$. The crystal structure of $PdAl_2Cl_8$ shows that it is monoclinic (space group $P2_1/c$).[289]

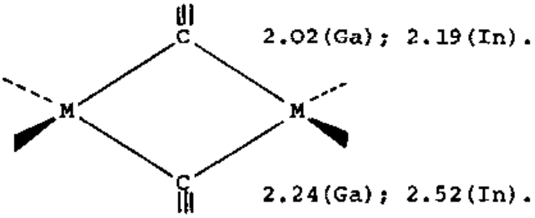
Phthalocyanine-aluminium and -gallium fluorides doped with iodine give $(PcMFI_x)_n$, where M = Al, x = 0.012 to 3.4; M = Ga, x = 0.048 to 2.1. They were characterised by resonance Raman spectra (both I_3^- and I_5^- are present). Iodine-doping leads to a marked increase in conductivity.[290]

3.3 GALLIUM

3.3.1 Compounds containing Ga-C Bonds

Detailed vibrational assignments have been proposed for trimethylgallium, based on infrared and Raman spectra in solid, liquid and gaseous phases. The spectra of the solid are very simple, suggesting that the molecule remains monomeric, at a site of C_3 symmetry.[291]

The molecular structure of monomeric trivinylgallium, $Ga(CH{=}CH_2)_3$, has been determined by gas-phase electron diffraction. No evidence was found for dimers. The best fit with the data was given by a model of C_3 symmetry, and rGa-C = 1.963(3)Å, rC=C = 1.335(3)Å, rC-H = 1.094(8)Å. The torsion angle CGaCC is 24(5)°, compared with a value of 0° for a planar skeleton. The Ga-C and C=C distances give no evidence for any delocalisation of π-electron density to Ga.[292]



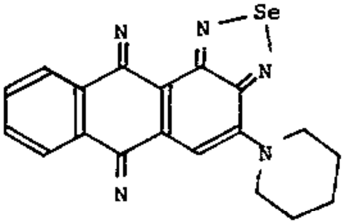
(74)

Gas-phase electron diffraction experiments have been carried out on dimethyl(propynyl)-gallium and -indium, $[Me_2M(\mu\text{-}C\equiv CMe)]_2$. The results are consistent with dimeric molecules of C_{2h} symmetry. The M_2C_2 ring is rectangular, (74). The structures are analogous to that of the aluminium compounds, and can be described as distorted monomer units joined by donation of C≡C π-electrons into the vacant p_z-orbital on the metal.[293]

3.3.2 Compounds containing Ga-N or Ga-P Bonds

The infrared and Raman spectra of solid Me_3NGaMe_3 and $Me_3{}^{15}NGaMe_3$, have been reported, with the Raman spectra of the liquids at about 50°C, and a low-resolution microwave spectrum. All of the data are consistent with C_{3v} molecular symmetry. All of the vibrational modes were assigned except for the methyl torsions.[294]

The complexes $GaX_3.L$ and $InCl_3.L.2H_2O$, where X = Cl or Br, and L = (75), have been prepared. Infrared and electronic spectra suggest that coordination occurs *via* the carbonyl and the nearest nitrogen of the heterocyclic ring. The gallium complexes are best represented by an ionic form $[GaL_2X_2][GaX_4]$.[295]



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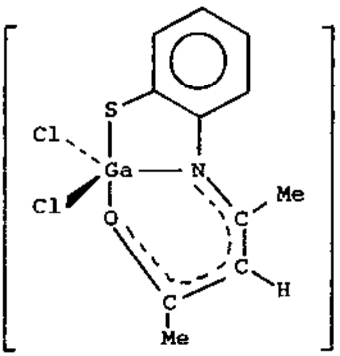
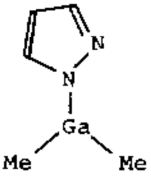


(76)

1:1 Complexes are formed by $MeGa^{2+}$ or Ga^{3+} with tridentate ligands (H_2L, with ONO or SNO donor atoms). The infrared data are generally consistent with trigonal bipyramidal environments at the metal centre, e.g. (76).[296]



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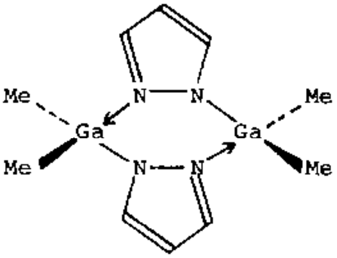
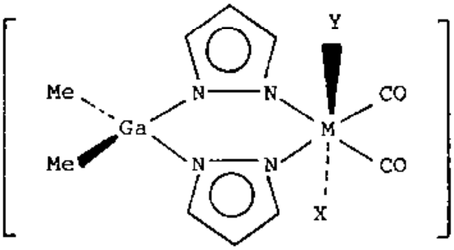


(78)

A series of N-dimethylgallylazoles has been prepared from azoles (imidazoles, benzimidazoles, pyrazoles etc.) and trimethylgallium. The structure, whether monomeric, dimeric or polymeric, depends on the positions of the nitrogen atoms in the azole group. For the pyrazolyl derivatives, n.m.r. studies on acetone or acetonitrile solutions show that there is an equilibrium between monomer, (77), and dimer, (78).[297]

A report has appeared on the preparation, n.m.r. spectra and X-ray diffraction of (79), where M = Mn; Y = $N_2C_3H_4$, $N_2C_5H_8$; X = CO, n = 0; M = Mo or W, X = CO, Y = $N_2C_3H_4$ or $N_2C_5H_8$, or X = η^3-C_3H_5 or η^3-C_7H_7, Y = $N_2C_3H_8$, n = 1. The n.m.r. data reveal interesting differences in behaviour between the manganese and molybdenum species in solution.[238]



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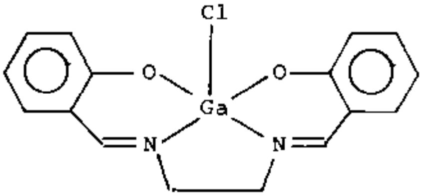
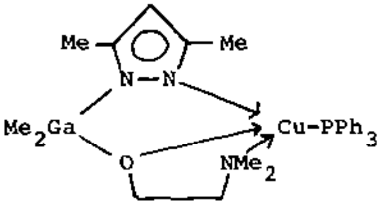


(80)

N,N'-Ethylenebis(salicylideneiminato)chlorogallium(III), (80), forms monoclinic crystals (space group $P2_1/a$). The gallium coordination geometry is intermediate between square pyramidal and trigonal bipyramidal. Important bond distances are Ga-Cl, 2.228(2)Å;

Ga-O, 1.868(4), 1.883(4)Å; Ga-N, 2.019(6), 2.035(5)Å.[299]

The crystal structure of the copper(I) complex: $[Me_2Ga(OCH_2CH_2NMe_2)N_2C_5H_7]Cu.PPh_3$, (81), shows that there is distorted tetrahedral geometry at the copper. Bond distances involving gallium are : Ga-O, 1.896(3)Å; Ga-N, 2.005(3)Å; Ga-C, 1.972(5), 1.987(5)Å.[300]



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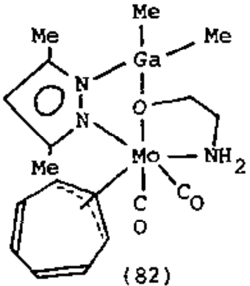
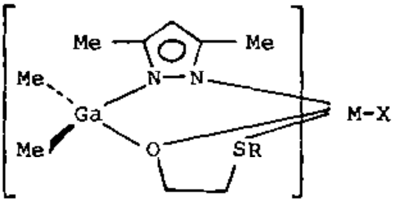


(82)

New tridentate anionic organogallate ligands have been prepared: $[Me_2Ga(N_2C_5H_7)(OCH_2CH_2SR)]^-$, where R = Et or Ph, from $Na^+[Me_3Ga(N_2C_5H_7)]^-$ and $HOCH_2CH_2SR$ in refluxing THF. When R = Et, the ligand forms *fac*-octahedral complexes with molybdenum, tungsten and manganese carbonyls, and it also acts as a tridentate ligand (L) in $LCu(PPh_3)$ and LNi(NO). When R = Ph, the number of complexes formed is much less, due to steric effects.[301]

Crystal and molecular structures have been reported for the closely related complexes (82),[302] and (83), where R = Et, M = Ni, X = NO or M = Mo, X = $(\eta^3-C_7H_7)(CO)_2$; R = Ph, M = Mn, X = $(CO)_3$.[303]



(83)

The reactivity of 1-dimethylgallylpyrazole towards alkyl halides and acid chlorides has been studied.[304]

Infrared and Raman spectra have been obtained for $(CH_3)_3GaPH_3$ and $(CH_3)_3GaPD_3$. The data were consistent with molecular symmetry of

C_{3v}. A normal coordinate analysis revealed only slight coupling between the GaC_3 stretches and CH_3 deformations. Other modes were essentially "pure".[305] Similar experiments on $(CH_3)_3GaP(CH_3)_3$ again showed that the symmetry was C_{3v}, but revealed extensive vibrational coupling between the Ga-P stretch, the PC_3 and the GaC_3 deformations. The solid-phase data were consistent with the presence of only one molecule per unit cell; a rhombohedral space group such as R3m is consistent with all of the observed data.[306]

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

Crystals of $LiGaO_2.8H_2O$ are trigonal (space group P3cl). The gallium atoms are tetrahedrally coordinated by oxygens (with Ga-O distances 1.85-1.89Å). Two of the oxygen atoms are linked together, and to the others by hydrogen bonds.[307]

A study of the $LiBO_2$ - $LiGaO_2$ system by D.T.A., X-ray diffraction etc. shows that a single intermediate compound is formed: Li_2GaBO_4. This melts incongruently at 896°C.[308]

The mixed-oxide species $CuGaInO_4$ forms hexagonal crystals (space group $R\bar{3}m$). The Ga^{3+} ions have trigonal-bipyramidal coordination (distorted; C_{3v} symmetry), while the In^{3+} lies between cubic close-packed oxygen layers and has trigonally-compressed octahedral coordination.[309]

Detailed vibrational assignments have been proposed for $(CH_3)_3GaO(CH_3)_2$ and $(CH_3)_3GaO(CD_3)_2$, based on infrared and Raman spectra, and a molecular symmetry of C_s. The Ga-O stretch could not be assigned to a specific mode, as it contributed significantly to four features (in the range 279-148 cm^{-1}).[310]

Pyridinium and ammonium hexamolybdogallates, i.e. containing the anion $[Ga(OH)_6Mo_6O_{18}]^{3-}$, have been characterised by T.G.A., X-ray diffraction, infrared and ^1H n.m.r. spectroscopy.[311]

β-$SrGa_2O_4$ forms monoclinic crystals (space group $P2_1/c$). All of the gallium atoms are four-coordinate, with Ga-O distances in the range 182.6 to 186.7pm.[312] Single crystals have been obtained of the hitherto-unknown $Ca_3Ga_4O_9$. These are orthorhombic, belonging to the space group Cmm2. The anions are formed by circles of four and five GaO_4 tetrahedra, giving a network arrangement.[313]

The Ga_2S_3-PbS system was studied for 30 to 100 mole % PbS. One ternary compound is formed: $PbGa_2S_4$, which melts without decomposition at 875°C.[314]

The formation of Ga(III) and In(III) complexes with sulphur-containing ligands, such as acetylacetone-2-mercaptoanil or salicylaldehyde-2-mercaptoanil, has been reported. All of the complexes are Schiff-base derivatives, with the ligand being dibasic and tridentate.[315]

The first ternary compound to be characterised structurally in the Cs-Ga-Se system is $Cs_{10}Ga_6Se_{14}$. Discrete $[Ga_6Se_{14}]^{10-}$ anions are present - comprising six linearly edge-linked $GaSe_4$ tetrahedra. The overall length of the hexameric species is 1900pm.[316] $EuGa_2Se_4$ crystals are orthorhombic, and their magnetic properties show that the Curie-Weiss law is obeyed, with a characteristic temperature of -4K.[317]

3.3.4 Gallium Halides

Studies on the ternary system BaF_2-MnF_2-GaF_3 at 600°C show that the presence of four quaternary fluorides: $BaMn_2Ga_2F_{12}$, $BaMnGaF_7$ (monoclinic), Ba_2MnGaF_9 and $Ba_{3+x}Ga_{2-2x}Mn_{2x}F_{12}$. D.T.A. studies on the GaF_3-BaF_2 system show that the fluorides $BaGaF_5$ and $Ba_3Ga_2F_{12}$ are formed.[318]

GaTeCl crystals contain GaTeCl tetrahedra, sharing common Te vertices with six neighbouring equivalent tetrahedra. Chlorine atoms are in terminal positions. The Ga-Te distances in the tetrahedra are 262.5 to 263.8pm, while Ga-Cl is 218.2pm.[319]

Values have been found for the enthalpies of solution of the following: $GaCl_3$ and GaI_3 in H_2O, MeOH and Me_2SO; $InCl_3$ and InI_3 in H_2O and several non-aqueous solvents.[320]

Crystals of $GaCl_3.SbCl_3$ are monoclinic (space group ($P2_1/c$). The $GaCl_4^-$ units are very distorted, due to strong interactions with $SbCl_2^+$, *via* Ga-Cl---Sb bridges, to give an infinite polymeric chain.[321]

^{69}Ga, ^{71}Ga and ^{115}In n.m.r. spectra have been obtained for the anions MX_4^-, where M = Ga or In, X = Cl, Br or I, in dichloromethane solution. For each element, mixtures of two halo-anions produces a statistical distribution of mixed halo-species. For gallium, a mixture of three halo-anions contains all 15 possible species in statistical amounts. Quadrupole effects meant that line widths were in the sequence $^{71}Ga < {}^{69}Ga < {}^{115}In$.[322]

The equilibria (23) established between ACl(s) (where A = Li, K

$$ACl(s) + GaCl_3(g) \rightleftharpoons AGaCl_4 \qquad ...(23)$$

or Cs) and $GaCl_3(g)$ were studied by mass spectrometry. The following thermodynamic data were obtained: $\Delta H^{\circ}(298) = 5.6(Li)$, $3.2(K)$, $\lesssim -2.2(Cs)$ kcal. mol^{-1}; $\Delta S^{\circ}(298) = 1.6(Li)$, $6.1(K)$, $\sim 4(Cs)$ cal. K^{-1}.[323]

Etherates and pyridine adducts have been isolated for a number of mixed tetrahalogallates, $H[GaX_3Y].2Et_2O$ and $H[GaX_3Y].4py$, where X = Cl, Y = I; X = I, Y = Cl; X = Br, Y = I; X = I, Y = Br. It is believed that the ether molecules form $(Et_2O)_2H^+$, with GaX_3Y^- anions, while the pyridine adducts contain py_2H^+ and $[GaX_3Ypy_2]^-$.[324]

^{71}Ga n.m.r. data have been reported for four-coordiante anions $[GaX_nY_{4-n}]^-$ and $[GaX_2YZ]^-$, where X, Y and Z = Cl, Br or I. Halide exchange between GaX_4^- and GaY_4^- in dichloromethane solution is slow, and the equilibrium proportions reported here do <u>not</u> correspond to a statistical distribution. No resonances were seen for $Ga_2X_6^{2-}$ (X = Cl or Br), which have a staggered ethane-like structure.[325]

A crystal structure determination has been carried out on *trans*-dichlorotetrakis(pyridine)gallium(III) tetrachlorogallate(III), The crystals are orthorhombic, space group $Pna2_1$. It is the first example of a *trans*-octahedral gallium(III) complex. In the cation, the Ga-Cl distances are 2.308 and 2.317Å, with Ga-N distances in the range 2.074-2.125Å. The anionic Ga-Cl distances are 2.154 to 2.159Å. The Raman spectrum of the complex was recorded, and the following assignments were: νGaN, $263 cm^{-1}$ (A_{1g}) and $248 cm^{-1}$ (B_{1g}), and νGaCl, $194 cm^{-1}$ (A_{1g}). The last was rather low, but there was no other candidate.[326]

The mixed metal compounds $InGaX_4.2L$, where L = py, piperidine, piperazine, 1,4-dioxan, tetrahydrofuran, have been prepared, together with $[(\underline{n}Bu)_4N]_2[InGaX_6]$, where X = Cl or Br. Raman spectra reveal that all of these contain In-Ga bonds, although precise assignment of individual modes to particular wavenumbers is not possible, because of extensive mixing. Features in the range 128 to 151 cm^{-1} were chiefly due to νInGa.[327]

A vibrational assignment of $Ga_2Cl_7^-$ has been proposed from infrared and Raman data on solid KGa_2Cl_7. Spectra of the molten salt (at 200°C) were also obtained - these show some cation dependence on the vibrations even here.[328]

The systems $GaBr_3$-MBr (where M = Na or Tl(I)) have been studied. For M = Na, four compounds were detected: $NaGa_2Br_7$, $NaGaBr_4$, Na_2GaBr_5 and Na_3GaBr_6. For M = Tl(I), two compounds are formed:

$TlGa_2Br_7$ and $TlGaBr_4$.[329]

3.3.5 Intermetallic Phases Containing Gallium

Li_5Ga_4 is a new phase found in the Li-Ga system. It crystallises in the trigonal system, and belongs to the space group $P\bar{3}m1$. The structure is related to those of LiGa and Li_3Ga_2.[330]

$RbGa_3$ can be prepared by heating a mixture of the elements to 700°C in a tantalum tube. The crystals are tetragonal, and belong to the space group $I\bar{4}m2$. Gallium triangular faced dodecahedra are stacked, *via* direct and bifurcated Ga-Ga bonds, to give a non-compact network interlocked with a sublattice of rubidium atoms.[331]

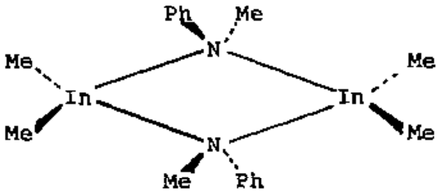
A related species, $RbGa_7$, forms monoclinic crystals, space group C2/m. This structure can be described in terms of a packing of icosahedra (of gallium atoms) around inversion centres in a sheet-like non-compact netting. This leaves channels where rubidium atoms are situated, forming zig-zag chains parallel to the *y*-axis.[332]

3.4 INDIUM

3.4.1 Compounds containing In-C Bonds

A significant improvement has been reported in the synthesis of cyclopentadienylindium(I). The new process involves metathesis of LiCp with a slurry of InCl in diethyl ether.[333]

All of the compounds $[(CH_3)_2MN(CH_3)(C_6H_5)]_2$, where M = Al, Ga or In, exist in solution as mixtures of *cis* and *trans* geometrical isomers. *Cis* was the main isomer for aluminium and gallium, *trans*- for indium. X-ray diffraction of the solid indium compound showed that only the *trans*-form was present in the crystals, (84).[334]



(84)

The novel indium(I) compounds $NaIn(CH_2SiMe_3)_2$ and $NaIn(CH_2SiMe_3)_2.MeOC_2H_4OMe$ are prepared from $In(CH_2SiMe_3)_3$ and sodium hydride in the appropriate solvent. If aromatic or hydrocarbon solvents were used, the hexamer $[NaIn(CH_2SiMe_3)_2]_6$ was formed. The second species above was isolated from dimethoxyethane solution, and it was associated in solution. The extent was concentration-dependent. Chemical and spectroscopic properties were consistent with models in which the association involved In-In interactions.[335]

3.4.2 Compounds containing Bonds between Indium and Elements of Group VI

The vibrational spectra of the double oxides $LnInO_3$, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, have been studied (all have the orthorhombic perovskite structure), as well as those with Ln = Eu, Gd, Tb or Dy, as modifications having the $LnMnO_3$ structure. Although the former contain InO_6 units, and the latter InO_5, there is little difference in the νIn-O stretching region.[336]

$M_3[In(OH)_6]_2$, where M = Ca or Sr, have been prepared by treating a mixture of MCl_2 and $InCl_3$ with boiling KOH solution. Thermal decomposition (when M = Ca) leads to the formation of $CaIn_2O_2(OH)_4$ (320°C) and then $CaIn_2O_4$ (520°C). νInO modes in $[In(OH)_6]^{3-}$ are seen at 480, 405 and 300 cm^{-1}.[337]

Electrochemical oxidation of metallic indium in the presence of DMSO or CH_3CN and tetrafluoroboric acid leads to formation of $[InL_6]^{3+}[BF_4]_3^{3-}$, where L = DMSO or CH_3CN.[338]

The macrocycles 6,7,9,10,17,18,20,21-octahydrodibenzo[b,k]-[1,4,7,10,13,16]-hexaoxacyclo-octadecin(dibenzo-18-crown-6) and 1,4,8,11-tetra-azacyclotetradecane (cyclam) form adducts with InX_3 and InX_2, but not with InX (X = Cl, Br or I). The products In_2X_4L (L = macrocycle) are in fact $[InL][InX_4]$ (by infrared spectroscopy). For InX_3 and dibenzo-18-crown-6, infrared data show the presence of InX_4^- anions and linear InX_2^+ species - the latter being part of a mono- or polynuclear complex cation. Cyclam and InX_3 give $[In(cyclam)_2][InX_4]_3$.[339]

Complex formation between In(III) and H_3PO_4 has been studied in the pH range 2-3. $InHPO_4^+$ and $In(HPO_4)_2^-$ were both detected. In(III) has a greater tendency to coordinate a second HPO_4^{2-} than has Fe(III).[340]

X-ray scattering intensities from indium(III) sulphate in aqueous solution have been analysed. The data suggest that inner indium sulphate complexes, $In(H_2O)_{6-z}(OSO_3)_z^{+3-2z}$, exist, together with a hydrogen-bonded structure outside the In^{3+} inner coordination sphere.[341]

The preparations of $M(SO_3F)_3$, (M = In or Tl) and $Tl(SO_3F)$ have been reported. The In(III) and Tl(I) compounds are formed by the action of excess HSO_3F on $InCl_3$ or TlCl. The thallium(III) fluorosulphate is made by the reaction (24). The M(III) compounds

$$TlSO_3F \ + \ S_2O_6F_2 \longrightarrow Tl(SO_3F)_3 \qquad \ldots(24)$$

both form adducts with oxygen or nitrogen donor ligands.[342]

Ammonium and indium(III) selenates form $(NH_4)In(SeO_4)_2$. In an excess of ammonium selenate, hydrolysis occurs to give basic salts of variable composition.[343]

The vibrational spectra of $^{40}CaIn_2O_4$ and $^{44}CaIn_2O_4$ have been studied. In-O stretches lie in the region 450-650 cm^{-1}. Ca-O stretches (identified by isotopic shifts) and In-O deformations lie in the range 300-450 cm^{-1}.[344]

Various compounds $In_2S_xSe_y$ and $In_2Se_xTe_y$ (where $x+y \approx 3$) have been synthesised from the elements. Continuous substitutional solid solution is possible: $In_2S_{3-x}Se_x$ (for $0 \ngtr x \ngtr 2$). In_2Se_2Te has a crystal structure which is a modification of a known form of In_2Se_3(hexagonal). All of the phases studied were semiconductors.[345]

Phase diagrams have been constructed for the systems In_2X_3-InY_3, where X = Se or Te; Y = Cl, Br or I. All are quasibinary, and contain intermediate ternary compounds InXY (which all melt incongruently).[346]

3.4.3 Indium Halides

Fusion of InX, where X = Cl, Br or I, has been studied by DTA, calorimetry, conductometry and chemical analysis. All undergo partial decomposition (disproportionation) or fusion.[347]

Metallic indium reduces $InCl_3$ to In_2Cl_3. The latter is indium(I) hexachloroindate(III), $In^I_3[In^{III}Cl_6]$, and it crystallises as orthorhombic crystals (space group Pnma). The In(III) occupies octahedral holes, with an average In^{III}-Cl distance of 251pm. In(I) atoms have coordination numbers 7-11, with In^I-Cl distances of from 329 to 359pm. The crystal structure is isotypic with α-Tl_2Cl_3.[348]

The Raman spectrum of a single crystal of $K_3InCl_6.H_2O$ has been assigned, using knowledge of the crystal structure. The main feature is the splitting of ν, of $InCl_6{}^{3-}$ into two components. These could be assigned to indium atoms occupying different sites.[349]

Crystals of $4(NH_3Me)^+.(InBr_6)^{3-}.Br^-$ are monoclinic (space group $P2_1/c$). They are isomorphous with $(MeNH_3)_4InCl_7$. The In-Br distance in $InBr_6{}^{3-}$ is 2.670Å.[350]

3.5 THALLIUM

3.5.1 Thallium(I) Compounds

Dissociation curves have been calculated for TlH, using fully relativistic quantum methods. The results show that the "orthogonal triplet interaction" makes no significant contribution to the bonding.[351]

Formation of the non-radiative exciplex $*(UO_2Tl)^{3+}$ in aqueous solution occurs by a simpler mechanism than for $*(UO_2Ag)^{3+}$. This is due to the absence of a primary hydration shell for Tl^+, and to the fact that its $6s^2$ electron pair is more suitable for electron transfer than their equivalent on Ag^+.[352]

Infrared spectra have been recorded for Tl_2SO_4, Tl_2MoO_4 and In_2MoO_4 in nitrogen matrices at 12K. All are thought to have D_{2d} symmetry.[353]

Anhydrous thallium(I) formate, TlHCOO, forms orthorhombic crystals, space group $Pna2_1$. The coordination polyhedron of the Tl^+ is best described as an elongated trigonal bipyramid.[354] The thallium(I) acetate complex of the channel-forming antibiotic gramicidin in p-dioxan solution gives a ^{205}Tl resonance at the lowest value ever recorded for Tl^+.[355]

The mixed phosphite $LiTlPO_3H$ can be prepared from the individual salts. The crystals are monoclinic, space group C2. The Tl^+ has five oxygen atoms as nearest neighbours (2.76(2) to 2.84(2)Å), with three further oxygens at distances from 3.02Å to 3.43Å.[356]

Tl_4SnS_3 crystals have been isolated from the SnS-Tl_2S system. They are tetragonal, and belong to the space group P4/ncc. The structure is built up of sheets, containing Tl-S bonds in the range 2.87Å to 3.04Å. Interactions between the sheets are very weak (Sn---S 3.15Å; Tl---Tl 3.574, 3.602Å).[357]

$Tl^I_2Sn_2S_5$ was prepared by fusion of a stoichiometric mixture of the elements, followed by prolonged heating at 300°C. The crystals are monoclinic, space group C2/c. The Tl atoms are located in channels parallel to the <u>b</u> axis, and surrounded by nine sulphur atoms (Tl-S, 3.073Å to 3.807Å).[358]

Phase studies have been carried out on the systems Tl_2X-TlS (where X = Cl, Br or I). These quasibinary systems all contained the new type of compound Tl_6X_4S. For X = I, a further species, Tl_3SI was also detected.[359]

Crystals of Tl_3PS_4 are orthorhombic (space group Pnma). The thallium atoms are coordinated by either five or seven sulphur atoms (Tl-S: 3.05 to 3.48Å; average 3.27Å).[360] Phase diagrams have been established for the systems: Tl_3SbS_3-Tl_3AsS_3 and $TlSbS_2$-$TlAsS_2$. The former gave a complete series of solid solutions, the latter a eutectic.[361]

The new phase $Tl_4Ge_4Se_{10}$ gives monoclinic crystals, space group C2/c. The crystal structure contains Tl^+ and adamantane-like $Ge_4Se_{10}{}^{4-}$. The thallium is nine-coordinated by selenium atoms (with Tl-Se distances of from 3.115Å to 4.049Å).[362] A study of the Cu-Tl-Se phase diagram reveals the existence of the new phases CuTlSe, Cu_2TlSe_2 and Cu_4TlSe_3. All possess some metallic character.[363]

(85)

Reaction of KTlTe with 2,2,2-crypt (= 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) in ethylenediamine, gives dark brown crystals of $(2,2,2\text{-crypt-}K^+)_2(Tl_2Te_2)^{2-}$.en. X-ray studies show that the $Tl_2Te_2{}^{2-}$ ring has the geometry (85), with Te-Tl bond lengths of 2.929 - 2.984Å, TlTeTl angles of 75° and TeTlTe angles of 96°. A square-planar form would have produced severe Te-Te non-bonded distortions.[364]

Studies on the TlBr-$PbBr_2$ system indicated the formation of three compounds: Tl_3PbBr_5, Tl_2PbBr_4 and $TlPb_2Br_5$.[365] Single crystals of the low-temperature modification of Tl_3PbBr_5 were obtained. They were orthorhombic, and belonged to the space group $P2_12_12_1$.[366]

3.5.2 Thallium(III) Compounds

The solvent dependence of ^{205}Tl, ^{13}C and ^{1}H n.m.r. parameters in dimethylthallium(III) derivatives, Me_2TlX, where X = BF_4, OAc or F, has been measured. The solvents used were $BuNH_2$, H_2O, MeCN, Me_2CO, py, THF, MeOH, Me_2SO and DMF. Attempts were made to correlate the n.m.r. results with solvent parameters such as the Drago parameters E_B and C_B - these gave a good correlation.[367]

^{205}Tl chemical shifts for Me_2TlX, ($X = NO_3$, BF_4, OAc), were also studied as a function of temperature, solute concentration and (in some cases) added anion concentration in several solvents. The changes with temperature are greater than those induced by concentration changes. The temperature effects were ascribed to vibrational effects within the Me_2Tl^+ cation, and/or vibrational effects involving interaction of the cation with coordinated solvent molecules.[368]

The ^{205}Tl spin-lattice relaxation in some dialkylthallium(III) derivatives is dominated by the chemical shift anisotropy relaxation mechanism.[369]

Crystals of {2-exo-bicyclo[2.2.1]hept-exo-3-acetato-5-enyl}-5,10,15,20-tetraphenylporphinatothallium(III) are monoclinic, space group $P2_1$. The organothallium group is above the porphyrin ring, with the thallium atom 0.9Å above the N_4 plane. The thallium atom and the acetato-group are cis-exo to the bicyclo[2.2.1] unit.[370]

The behaviour of thallium in zeolites following treatment with ozone has been studied. X-ray powder diffraction showed that all the thallium(III) was present as Tl_2O_3, with no TlO^+ or $Tl(OH)_2{}^+$.[371]

The crystal structure of di-μ-pentafluorobenzoatobis[bis(pentafluorophenyl)(triphenylphosphine oxide)thallium(III)], $\{(C_6F_5)_2TlO_2CC_6F_5(OPPh_3)\}_2$, shows that the dimeric structure involves unsymmetrical pentafluorobenzoate bridging (Tl-O = 2.531Å and 2.789Å). The pentafluorobenzoate groups are also unsymmetrically chelated to thallium (TlO = 2.389Å and 2.531Å), which has an overall coordination number of six (irregular geometry).[372]

Thallium(III) acetate reacts with ketones ($RCOCH_3$, R = Me, Et, *n*Pr, *i*Pr, *n*Bu, *i*Bu, *t*Bu) in methanol, giving thallation at CH_3 or at the α-carbon of R (detected by n.m.r.) $J(^{203/205}Tl-^1H)$ in $RCOCH_2X$, ($X = Tl(OAc)_2$), is independent of R, and about 1290Hz, but in $R^1CHXCOCH_3$ (R^1 = H, Me or Et) it increases with increasing chain length.[373]

Interaction of thallium(III) with DL-glutamic acid (at pH values 0.76 to 2.4, and 25.0±0.1°C) has been studied. If L^{2-} is the deprotonated acid, Tl^{3+} forms complexes $Tl(HL)^{2+}$ and $Tl(HL)_2^+$, the logarithms of the stability constants being 8.25±0.07 and 13.34±0.14 respectively.[374]

Several new anionic complexes of thallium(III) have been prepared. They are: $[TlCl_3Brpy_2]^-$, $[TlCl_3Br(aniline)_2]^-$, $[TlCl_3Br(quinoline)_2]^-$ and $[TlCl_4(quinoline)_2]^-$. The compounds were analysed by u.v. and infrared spectroscopy.[375]

Solution and solid-state ^{205}Tl n.m.r. have been used to study the formation and geometries of $TlX_n^{(3-n)+}$, for X = Cl or Br. The existence of $TlCl_5^{2-}$ and $TlCl_6^{3-}$ in solution, and (for X = Br) at least one species higher than $TlBr_4^-$ were shown. $TlCl_3$ is less-shielded (by 300-400p.p.m.) in aqueous solution than in the solid - implying structural differences.[376]

Far-infrared transmission spectra of thin films (thickness approx. 18μm) of aqueous solutions have been obtained, using a multiple-scan Fourier-transform infrared spectrometer. Solutions containing Tl(III) and Cl^- (with Cl^-:Tl ratios between 4.1 and 6.4) provided evidence for the presence of $TlCl_5^{2-}$.[377]

All of the vibrational wavenumbers of TlI_4^- have been reported for the first time. They are (all in cm^{-1}): $\nu_1(a_1)$ 128 (Raman, polarised); $\nu_2(e)$ 45 (Raman); $\nu_3(t_2)$ 150 (infrared and Raman); $\nu_4(t_2)$ 52 (infrared).[378]

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