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Chapter 3

ELEMENTS OF GROUP 3

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3.1 BORON

3.1.1 Boranes

Graph-theoretical techniques can be used to count 2-centre, 2-electron valence bond structures for boron hydrides. The heats of atomisation can be correlated using a four-term linear equation. This was based on the numbers of terminal and bridging BH bonds, nearest-neighbour boron atom pairs, and an estimate of the resonance energy.[1]

Ab initio molecular orbital calculations were carried out for H_2BXH, $HB(XH)_2$ and $(H_2B)_2X$, where X=O or NH. Gaussian-type basis functions, (7s,3p) for B,N and O, (4s) for H, contracted to a double-zeta basis (and augmented with d-orbitals for O and N) were used. The partial π-bond character was greater for B-N than for B-O bonds, and for H_2BXH compared to the other two types. In all cases the overall charge transfer gave B^+-X^- polarity, so that boron was acting as a strong σ-donor, but a weak π-acceptor.[2]

An ab initio molecular orbital study of the $C_2H_4+BH_3$ reaction show that hydroboration reactions go through a two-step process. First, a loose three-centre π-complex is formed (without an energy barrier), and then this is transformed to the product via a four-centre transition state - the latter process being rate-determining.[3]

Pyridine complexes of diborane, dichloroborane and $LiBH_4$ were investigated by conductometric titrations. The diborane complex is more stable towards hydrolysis than the other two.[4]

Diborane, or a mixture of B_2H_6 and B_5H_9, when irradiated by the R(16) line of the 10.6μm transition of a c.w. CO_2 laser (973.3cm^{-1}), undergo an apparent thermal reaction to give $B_{10}H_{14}$. Up to 65% of the starting material which reacts can be so converted. If B_2H_6/B_5H_9 mixtures are used, less than 1400 photons are needed to produce each $B_{10}H_{14}$ molecule.[5]

The unconventional base bis(trimethylphosphine)-diborane(4) reacts with B_2H_6 or B_4H_{10} according to equations (1) and (2).

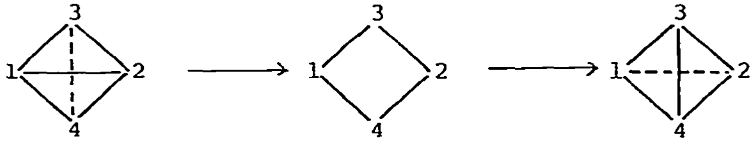
$$3/2B_2H_6 + B_2H_4(PMe_3)_2 \xrightarrow[CH_2Cl_2]{-20^oC} B_3H_6(PMe_3)_2^+ + B_2H_7^- \quad ... (1)$$

$$B_4H_{10} + B_2H_4(PMe_3)_2 \xrightarrow[CH_2Cl_2]{\text{room temp.}} B_3H_6(PMe_3)_2^+ + B_3H_8^- \quad ... (2)$$

The triboron complex cation has never been reported previously.[6]

Pentaborane(9) reacts with an excess of trimethyl-phosphine to give a mixture of $B_2H_4(PMe_3)_2$ and a new hypho-class compound, tris(trimethylphosphine)triborane(5), i.e. $B_3H_5(PMe_3)_2$. The latter sublimes under vacuum to give $B_6H_{10}(PMe_3)_2$. ^{11}B n.m.r. data were reported for all the borane adducts prepared.[7]

The degenerate rearrangement of tetrahedral B_4H_4 and B_4F_4 along a least motion pathway passes through a square-planar midpoint structure, equation (3). The rearrangement is accompanied by an orbital crossing of the HOMO-LUMO type, and this produces a



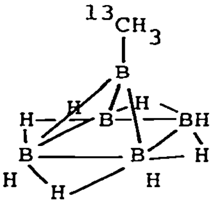
... (3)

sizeable energy barrier to the process. Approximate and ab initio calculations of this barrier yielded a value of about 355kJ $mole^{-1}$ for B_4H_4, with a smaller value for B_4F_4.[8]

Multinuclear (^1H, ^{11}B, ^{19}F and ^{31}P) n.m.r. studies have been carried out on $B_4H_8(PF_2X)$, where X=F,Cl,Br,I or H. Variable-temperature ^{19}F n.m.r. data showed that, except for X=H, all the molecules exist as geometrical isomers (with the phosphine placed endo or exo with respect to the folded B_4 framework) at ambient temperature. At low temperatures rotation about the P-B bond in the endo isomer becomes slow on the ^{19}F n.m.r. time-scale, and rotational isomers were observed - two when X-Cl or Br, only one when X=F or I. Rotation about the P-B bond was rapid at all temperatures in the exo isomer.[9]

Self-consistent charge calculations were carried out on derivatives of pentaborane(9) to examine multicentre bonding, and the application of the "isolobal, pseudo-isoelectronic" principles. Results were able to reproduce known photoelectron spectra quite well. The HOMO of B_5H_9 involved apical boron 2p orbitals, and correlated well with cluster orbitals in 1-$[(B_4H_8)Fe(CO)_3]$ and 1-$[(B_4H_8)Co(\eta^5-C_5H_5)]$, which involve mainly metal 3d orbitals. The next cluster orbital in B_5H_9, however, has no close counterpart in the metallo-derivatives.[10]

The first sign determination of a $^{11}B-^{11}B$ spin-spin coupling constant has been reported. Using $^{13}C-\{^1H,^{11}B\}$triple resonance, and several double resonance techniques, $^1J(^{11}B_a-^{11}B_b)$ was found to be +18.9Hz in 1-^{13}C-methyl-pentaborane(9),(1). Also $^2J(^1H-^{11}B_a)$



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(-6.8Hz) and $^1J(^{13}C - ^{11}B_a)$ (+73.1Hz) were found for the same molecule. The signs and magnitudes of the $^{13}C-^1H$ and $^1H-^{11}B$ coupling constants were also found in BMe_4^- and BPh_4^-.[11]

Investigation of the mercury-photosensitized reactions of selectively deuteriated pentaboranes (including 1-DB_5H_8 and μ-DB_5H_8) suggests that the primary reactive intermediate leading to decaborane (14) and -(16) is pentaborane(7), from direct loss of molecular H_2. The elimination of H_2 from any pair of H sites in pentaborane is a random, but not strictly statistical process. No evidence was found for the free-radical intermediate B_5H_8.[12]

Although derivatives of pentaborane(9) with bridging substituents μ-ER_3, where E=Si,Ge,Sn or Pb, have been known for some time, no carbon-bridged analogues μ-$(CR_3)B_5H_8$ have been reported. Calculations of m.o. energies for μ-$(CH_3)B_5H_8$ were unable to rationalise the non-existence of such compounds. However, reaction of allyl iodide or benzyl bromide with $B_5H_8^-$ gave 2-allyl- or 2-benzyl-pentaborane derivates, apparently via a short-lived bridging intermediate.[13]

Electrochemical studies on the arachno-boranes $B_{10}H_{10}L_2$ (where L=CNMe, SMe_2 or PPh_3) gave evidence for a new B_{10} species, formed in very small amounts. N.m.r. evidence suggested that it might be a nido-$B_{10}H_{10}L_2$ compound.[14]

Cyclohexane adds to $B_{10}H_{12}(SMe_2)_2$ to give 9-cyclohexyl-5(7)-(dimethyl sulphide)-nido-decaborane(11), $B_{10}H_{11}(C_6H_{11})SMe_2$. The unsymmetrical environment at B(5) gave rise to 2 methyl resonances in the n.m.r. spectrum. ^{11}B and ^{13}C n.m.r. spectra suggested a similarity in structure between this compound and the parent

$B_{10}H_{12}SMe_2$. The present compound reacts with NaH to form $2\text{-}(C_6H_{11})B_{10}H_9{}^{2-}$. Extended Hückel calculations suggest that the most likely positions for nucleophilic attack would be B(8) and B(9).[15]

Single-crystal X-ray diffraction studies on the compound described in the last reference show that the boron atoms occupy a <u>nido</u>-decaborane framework, with 8 terminal and 3 bridging hydrogens (the latter at B(6)-B(7),B(8)-(9) and B(9)-B(10)). The B-B distances were similar to those in $B_{10}H_{13}{}^-$. The Me_2S (at B(5)) gave a B-S distance of 1.89(1)Å, while the B(9)-C(of C_6H_{11}) distance was 1.58(1)Å.[16]

The structures of the isomeric forms of the large neutral boranes, 2,2'- and 2,6'-bis(<u>nido</u>-decaboranyl), $(B_{10}H_{13})_2$, have been determined by X-ray diffraction. The 2,2'-isomer, is tetragonal (space group $I4_1cd$), with an intercluster B-B distance of 1.692(3)Å; the 2,6'-isomer is orthorhombic (space group Pbca), and has a B-B (intercluster) distance of 1.679(3)Å. $^1H\text{-}\{^{11}B\}$ and ^{11}B n.m.r. spectra were reported, and assigned in detail for the 2,2'-isomer.[17]

Selective $^1H\text{-}\{^{11}B\}$ n.m.r. spectroscopy was used, together with simple pulse and "partially relaxed" ^{11}B and $^{11}B\text{-}\{^1H\}$ data, to assign the ^1H and ^{11}B spectra of icosaborane oxide. These confirmed its structure as 6,6'-μ-oxo-bis(<u>nido</u>-decaboranyl), $(B_{10}H_{13})_2O$.[18]

It has been suggested that the structures of polymeric boranes, $(BH)_x$, where x is a large integer, may be built up by the linkage of structural units related to those of <u>nido</u>-boranes.[19]

3.1.2 <u>Borane Anions and Metallo-Derivatives</u>

SiF_4 reacts with a dichloromethane solution of $[^nBu_4N][BH_4]$ to give the $^nBu_4N^+$ salts of $BH_3SiF_3{}^-$ and $BH_2(SiF_3)_2{}^-$, equations (4) and (5). The new anions were characterised in solution by ^{11}B n.m.r. spectra.[20]

$$BH_4{}^- + 4BH_4SiF_4{}^- \rightarrow 4BH_3SiF_3 + BF_4{}^- + 4H_2 \qquad \ldots (4)$$

$$2BH_3SiF_3{}^- \rightarrow BH_2(SiF_3)_2{}^- + BH_4{}^- \qquad \ldots (5)$$

Complexes of $LiBH_4$ with dimethylformamide, tetrahydrofuran and diethyl ether were studied by coulometric titrations.[21]

The 25°C solubility isotherm has been determined for the system $Mg(BH_4)_2\text{-}Et_2O\text{-}$toluene. The phase crystallising at all concentrations is $Mg(BH_4)_2.2Et_2O$.[22] The non-solvated form of $Mg(BH_4)_2$

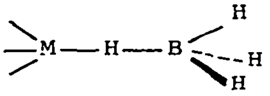
can be prepared, however, about 99% pure by the reaction of $NaBH_4$ and anhydrous $MgCl_2$ in Et_2O. The reaction involves excess $NaBH_4$, takes place on refluxing for 20-25h, and gives yields of over 80%.[23]

Inelastic electron tunnelling spectroscopy (IETS) was used to characterise $Zr(BH_4)_4$ supported on alumina. The νBH modes suggest that there are several different types of surface species, or that there is strong coupling involving BH_4 groups attached to a common Zr atom. There was also evidence for Zr-O and B-O vibrations.[24]

IETS experiments were also performed on $Zr(BH_4)_4/Al_2O_3$ over the temperature range 300-475K, to probe its interactions with H_2O, D_2O or D_2. The BH_4 groups attached to Zr or to Al all show bidentate coordination, and there was also evidence for $O\text{-}BH_2$ groups. Hydrolysis occurs rapidly, even at 300K, but there was no evidence for H/D exchange on the supported complex in the presence of D_2 or D_2O.[25] IETS was also used to study the interactions of C_2H_2, C_2H_4 and $MeCH{=}CH_2$ with $Zr(BH_4)_4/Al_2O_3$. There was evidence for C-C and C-H bonds in the surface species.[26]

Sodium borohydride reacts with $MoCl_3(PMe_3)$ to form $MoH(BH_4)(PMe_3)_4$. The BH_4^- ligand is shown by X-ray diffraction to be bidentate, and the solid-phase i.r. spectrum shows νBH_t and νBH_{br}, in agreement with approximately C_{2v} local symmetry for the $Mo(BH_4)$ unit. Thus, ν_s and ν_{as} (BH_t) are at 2290(A_1) and 2340 (B_1) cm^{-1}, with $\nu(BH_{br})$ giving a strong doublet at 1885 and 1935 cm^{-1}. Other vibrational modes associated with the MoH_2B unit gave bands at 1360 and 1165 cm^{-1}.[27]

The following tetrahydroborato-complexes have been prepared: $(BH_4)M^{I}(PMePh_2)_3$ (M=Cu or Ag), as well as the substituted species $[(EtO)BH_3]M^{I}(PMePh_2)_3$. In the solid-phase, i.r. spectra show that the BH_4 unit is unidentate, (2). In solution, however, an equilibrium is set up between singly- and doubly-bridged species (from i.r. and n.m.r. results).[28]



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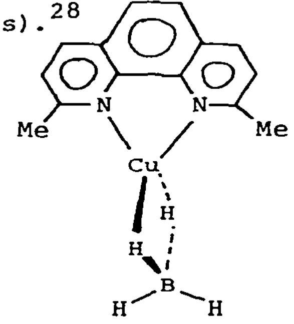

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(2,9-Dimethyl-1,10-phenanthroline)tetrahydroboratocopper(I), (3), forms orthorhombic crystals, space group Pnma. The Cu(I) has distorted tetrahedral coordination, with a bidentate BH_4^- ligand. The Cu-B distance is quite short, 2.08(2)Å.[29]

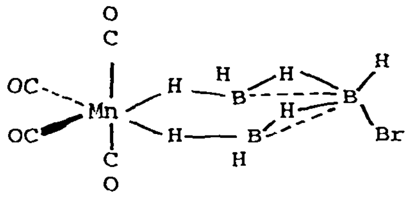
The $LiBH_4$-$Y(BH_4)_3$-THF system has been studied by isothermal solubility at 20°C. Crystallisation regions were found for the solvates: $Y(BH_4)_3.7THF$ and $Y(BH_4)_3.3THF$, together with the hitherto-unknown species $LiBH_4.Y(BH_4)_3.4THF$.[30] In the $Nd(BH_4)_3$-THF system, crystallisation regions were found for octa-, hexa- and tetra-solvates.[31]

U.v. irradiation (at 253.5nm) causes photolytic decomposition of $U(BH_4)_4$. No decomposition occurred, however, under the action of CW lasers in either the visible or infrared regions.[32]

The structure of $Np(BH_4)_4$ has been determined by single-crystal X-ray diffraction at 130K. The crystals are tetragonal, space group $P4_2/nmc$. The four BH_4 groups are arranged tetrahedrally about the neptunium, with an Np-B distance of 2.46(3)Å. The ligands are triply-bridging.[33] Solid-state, low-temperature infrared spectra (25-7400cm^{-1}) and Raman spectra (100-2600 cm^{-1}) of $Np(BH_4)_4$ and $Np(BD_4)_4$ could be assigned on the basis of T_d symmetry. A normal coordinate analysis gave a very similar force-field to those for $M(BH_4)_4$, where M=Zr or Hf.[34]

$B_3H_8^-$ reacts with amine or tertiary phosphine complexes of Co(I) or Co(II) halides to give arachno-triborane-ligand adducts, B_3H_7L, together with $B_2H_4L_2$ and BH_3L (where L=pyridine or tertiary phosphine). A similar reaction occurs with trans-$[M^I(CO)Cl(PPh_3)_2]$, where M(I)=Rh or Ir. The latter complex also gives a "borallyl" compound: $[Ir^{III}(\eta^3\text{-}B_3H_7)(CO)H(PPh_3)_2]$, which could alternatively be described as a nido-iridatetraborane: $[(IrB_3H_7)\text{-}(CO)H(PPh_3)_2]$.[35]

An X-ray structure determination has been carried out on $(OC)_4MnB_3H_7Br$, at -100°C. This shows that the B_3H_7Br ligand is bidentate, with the Br atom attached to the unique boron in an exo-fashion, (4). The molecular symmetry is C_s. The H atoms in this compound undergo exchange reactions at a rate suitable for n.m.r. study. Kinetic activation parameters for intramolecular hydrogen exchange are: $\Delta G^\ddagger$ (23°C) 51.0 ± 0.02 kJ $mole^{-1}$, $\Delta H^\ddagger$ 44.7 ± 1.5 kJ $mole^{-1}$, $\Delta S^\ddagger$ 11.1 ± 5.9 J $mole^{-1}$ K^{-1}.[36]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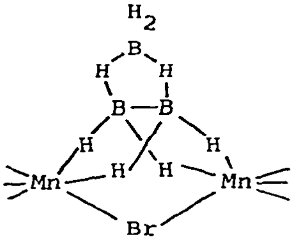
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The complexes $(\mu\text{-}X)(OC)_6(B_3H_8)Mn_2$ (where X=Cl or Br) have been prepared by the reaction of AlX_3 with $Mn(B_3H_8)(CO)_3$ in CH_2Cl_2 or (for X=Br) from $Mn_2(CO)_8Br_2$ and $Me_4N^+B_3H_8^-$. The crystal structure of the bromo-compound has been determined - showing that $B_3H_8^-$ acts as a bridging bidentate ligand, (5).[37]

Metal atom syntheses of metalloboron clusters have been examined, especially for Co with B_5H_9, B_6H_{10} or $B_{10}H_{14}$, in the presence of various other reactants. Thus Co, with B_5H_9 and C_5H_6 gave several known compounds, plus the new species: $1,2,3\text{-}(\eta\text{-}C_5H_5)_3Co_3B_5H_5$, $8\text{-}\sigma\text{-}(C_5H_9)\text{-}1,2,3\text{-}(\eta\text{-}C_5H_5)_3Co_3B_5H_4$ and $(\mu_3\text{-}CO)\text{-}1,2,3\text{-}(\eta\text{-}C_5H_5)_3Co_3B_3H_3$. The technique also permits the direct conversion of boranes and alkynes to metallacarbaborane clusters. Thus, Co + C_5H_6 + B_5H_9 + 2-butyne gives (among others) $2,5\text{-}(Me)_2\text{-}1,7,2,5\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5$.[38]

Extended Hückel m.o. calculations have been performed on trigonal prismatic platinaboranes and carbaplatinaboranes, $[B_8\{Pt(PH_3)_2\}H_8]^{2-}$ and $[B_6C_2\{Pt(PH_3)_2\}H_8]$. The observed conformations of these molecules can be explained in terms of the nodal characteristics of the frontier orbitals of the constituent $Pt(PH_3)_2$ and (carba)borane fragments.[39]

$B_9H_9^{2-}$ can be converted to the perhalogenated derivatives, $B_9X_9^{2-}$ (where X=Cl,Br or I) under aprotic conditions, equation 6

$$B_9H_9^{2-}\begin{cases}\xrightarrow{\text{"NCS"}} B_9Cl_9^{2-}\ (80\text{-}90\%\ \text{yield})\\ \xrightarrow{\text{"NBS"}} B_9Br_9^{2-}\ (90\text{-}95\%\ \text{yield})\\ \xrightarrow{I_2} B_9I_9^{2-}\ (70\text{-}80\%\ \text{yield})\end{cases}\qquad \ldots\ (6)$$

(where "NCS", "NBS" = N-chloro- or N-bromosuccinimide), all in CH_2Cl_2 solution. The chloro- and bromo-compounds can be oxidised (e.g. by thallium(III)trifluoroacetate) to neutral B_9X_9. The intermediate radicals $B_9X_9^{\cdot -}$ were also reported - the first examples of such species.[40]

The $B_{10}H_{12}^{2-}$ ligand in $Pt(B_{10}H_{12})(PMe_2Ph)_2$ has been investigated by ^{11}B, $^{11}B-\{^1H\}$, $^1H-\{^{11}B\}$ and $^1H-\{^{11}B, ^1H\}$n.m.r. spectroscopy. $^nJ(^{195}Pt-^{11}B)$ and $^{n+1}J(^{195}Pt-^1H)$ coupling constants were evaluated, and used to assign the ^{11}B spectrum.[41] Variable temperature $^1H-\{^{31}P\}$ and $^1H-\{^{11}B\}$ n.m.r. spectra show that the $(\eta^4-B_{10}H_{12}^{2-})$ ligand in this complex undergoes a novel type of dissociative rotation about an axis approximately in the Pt(II) coordination plane. This process has a $\Delta G^\ddagger$ value of (79 ± 5)kJ mol^{-1} at 71°C.[42]

The crystal structure of $(Et_3NH)_2(B_{12}H_{12})$ has been determined. The crystals belong to the space group $R\bar{3}$, and the anion forms an icosahedron which is very close to being regular - the distortions being much less than in the K^+ salt. The mean B-B bond length was 1.781(2)Å, and this will be useful for evaluating future theoretical studies.[43]

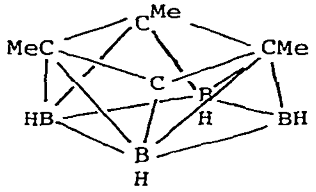
Alkali metal tetrahydroborates (MBH_4, where M=Na or K) react with $H_3B.NMe_3$ in high-boiling hydrocarbon solutions at 200-250°C. When the product is extracted with water and precipitated by CsOH, a 93-95% yield of $Cs_2B_{12}H_{12}$ can be achieved. This is an example of the formation of icosahedral $B_{12}H_{12}^{2-}$ from the simplest possible units.[44]

$K_2B_{12}H_{10}F_2 \cdot H_2O$ can be obtained by the fluorination of $K_2B_{12}H_{12}$ by liquid HF in an autoclave. Spectroscopic and X-ray powder diffraction data were listed. The infrared spectrum contained bands of the new anion at 405, 690, 885 and 1610 cm^{-1}.[45] The reaction of $K_2B_{12}H_{12}$ with liquid HF in an autoclave at elevated temperatures leads to further fluorination. From 60-90°C the product is $K_2B_{12}H_8F_4 \cdot H_2O$; from 90-150°C $K_2B_{12}H_7F_5$; and from 150-180°C $K_2B_{12}H_6F_6 \cdot 2H_2O$. This was the first recorded preparation of the last compound.[46]

3.1.3 Carba- and other Non-metal Heteroboranes

MNDO calculations have been carried out for all known carbaboranes up to $(B,C)_{12}$ which had not been reported earlier. The calculated geometries were in good agreement with experiment if appropriate symmetry constraints were applied.[47]

$1,5-C_2B_3H_5$ forms a dimer, $[2,2'-\{1,5-C_2B_3H_4\}_2]$ and a trimer, $[2,2'-3,2'-\{1,5-C_2B_3H_4\}_2-1,5-C_2B_3H_3]$ on pyrolysis. Both were characterised by n.m.r., i.r., u.v., and photoelectron spectra, and (for the dimer) Raman spectra. In addition, MNDO m.o. calculations were performed on both systems. Theory and experiment both suggest that the dimer possesses a single stable conformation (of D_{2d} symmetry). This results from a π-type interaction across the exopolyhedral B-B bond.[48]



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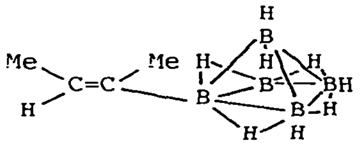
Photolysis of the nido-ferraborane, $(B_4H_8)Fe(Co)_3$, in the presence of RC≡CR gave a good yield of the tetracarbaborane $R_4C_4B_4H_4$. For R=Me, the species was characterised by mass and n.m.r. spectroscopy; the structure best explaining the results was (6). It was also possible to isolate as an intermediate $Me_4C_4B_4H_4$ $Fe(Co)_3$.[49]

The initial step in thermal reactions of pentaborane(9) with alkynes had been proposed to be hydroboration of the alkyne, to give an alkenyl-substituted pentaborane(9) derivative. Such a compound has now been isolated, i.e. 2-(cis-2-butenyl)pentaborane(9), (7). Further, this can be converted in high yield into monocarbon carbaboranes, e.g. (8).[50]



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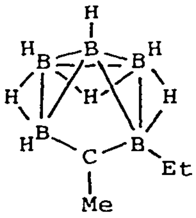

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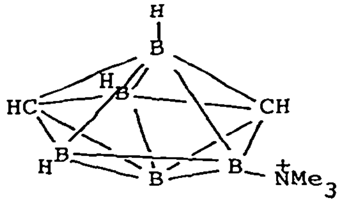

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A nitrogen derivative of *closo*-2,4-dicarbaheptaborane, $[5\text{-}Me_3N\text{-}2,4\text{-}C_2B_5H_6]^+$, (9), is prepared from $5\text{-}Cl\text{-}2,4\text{-}C_2B_4H_6$ and NMe_3, followed by removal of halogen in a two-step displacement reaction.[51]

Two-dimensional correlated $^{11}B\text{-}^{1}H$ n.m.r. spectra have been reported for $2,4\text{-}C_2B_5H_7$. One striking feature of the results (the first recorded use of this technique for B-H systems) is the approximate 3:1:1:3 intensity pattern for the ^{11}B-coupled proton quartets. It was possible to resolve heavily overlapped ^{11}B signals, and to correlate the resonances of individual ^{11}B and ^{1}H nuclei which are scalar-coupled to each other.[52]

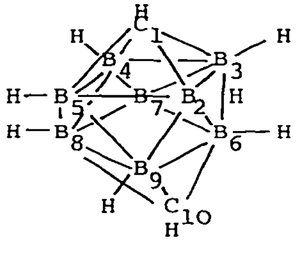
Ion-molecule reactions of *closo*-carbaboranes, $1,6\text{-}C_2B_4H_6$ and $2,4\text{-}C_2B_5H_7$, were investigated by pulsed ion-cyclotron resonance methods. Condensation reactions of the parent ion with itself are observed - with loss of H_2 for both molecules. $1,6\text{-}C_2B_4H_6$ also condenses with protonated acetone, again with loss of H_2. Proton affinities were estimated as follows: $1,6\text{-}C_2B_4H_6$:870 ± 4 kJ mol^{-1}; $2,4\text{-}C_2B_5H_7$: 723 ± 2 kJ mol^{-1}. The large difference was attributed to the fact that the molecule CB_5H_7 (isoelectronic with $C_2B_4H_7^+$) is known, but nothing isoelectronic with $C_2B_5H_8^+$ is known.[53]

Monochloro- and dichloro-derivatives of $1,6\text{-}C_2B_4H_6$ and $2,4\text{-}C_2B_5H_7$ have been prepared: 5-Cl-, 3-Cl- and $1\text{-}Cl\text{-}C_2B_5H_6$ (relative volatilities 3-Cl->1-Cl->5-Cl-), $2\text{-}Cl\text{-}1,6\text{-}C_2B_4H_5$, $2,4\text{-}Cl_2\text{-}1,6\text{-}C_2B_4H_4$ and $5,6\text{-}Cl_2\text{-}C_2B_5H_8$. The assignments of chloro-positions were based on ^{11}B n.m.r. measurements.[54]

KB_9H_{12} or $KB_{10}H_{11}Se$ react with As_2O_3 in basic solution to form $B_8H_8As_2S$, $B_8H_8As_2Se$ respectively. Base degradation followed by treatment with $C_5H_5^-$ and $CoCl_2$ converted the former to $B_7H_7As_2SCoCp$. The reaction of $B_7C_2H_{13}$ with AsI_3 and triethylamine produces a moderate yield of $B_7C_2H_9As_2$.[55]

Molecular orbital studies have been reported (using a minimum basis set) for the known azaboranes *arachno*-$4\text{-}NB_8H_{13}$, *arachno*-$B_9H_{12}NH^-$ and *nido*-$10\text{-}N\text{-}7,8\text{-}C_2B_8H_{11}$, as well as for the hypothetical *closo* species $1,12\text{-}NCB_{10}H_{11}$. The PRDDO calculations suggest that the most characteristic feature of the bonding in these molecules is the tendency of nitrogen to form polar, and whenever possible, two-centre bonds.[56]

Electron diffraction by gaseous 1,10-dicarba-closo-decaborane (10), $C_2B_8H_{10}$, (10), gave the molecular structure (based on the assumption that the C_2B_8 skeleton is a bicapped square antiprism, D_{4d}). The following bond distances were calculated: B-C 1.602(2)Å; B(2)-B(3) (basal) 1.850(5)Å; B(2)-B(6) (equatorial) 1.829(4)Å; B-H 1.164(14)Å; C-H 1.14(2)Å, with C-B-H 117.5 (1.8)°.[57]



(10)

2,3-Dimethyl-4,7-dihydroxy-10-bromo-2,3-dicarba-closo-undecaborane, $Me_2C_2B_9H_6(OH)_2Br$, forms crystals belonging to the space group Fddd (D_{2h}^{24}). The OH groups were located on adjacent vertex positions (B(4,7)), with the bromine at B(10). The configuration of the polyhedral cage is intermediate between the closo (C_{2v}) and nido (C_{5v}) icosahedral fragment. The distortion from the former is attributed to donation of electron density from the lone pair electrons on the oxygens to the m.o. framework of the polyhedron, i.e. this tends to increase the skeletal electron count from the closo total ((n+1) pairs of electrons) to the (n+2) pairs typical of nido structures (where n is the number of vertex positions).[58]

The crystal and molecular structures of caesium 9,10a,11-trimethyl-7,8-dicarba-nido-undecaborane, 9,10a,11-$(CH_3)_3$-7,8-$C_2B_9H_9^-$, have been determined. The crystals are triclinic, belonging to the space group $P\bar{1}$. All three boron atoms of the open face bear methyl substituents, with one (B(10)), also an H atom. The methyl group at B(10) is in an axial position - with the angle between Me-B(10) and the open face approximately 90°.[59]

$B_9H_{12}S^-$, when treated with potassium polyselenide, forms B_9H_9SSe. Similarly, with potassium polysulphide (in the presence of a small quantity of the polyselenide) $B_9H_9S_2$ is produced. ^{11}B n.m.r. data suggest that the structures are similar to that of the previously-known $B_9H_9Se_2$. Treating $B_9H_9Se_2$ or B_9H_9SSe with trimethylamine, C_5H_6 and $CoCl_2$ gives $B_9H_9SXCo(\eta\text{-}C_5H_5)$, where X=S or Se. The X-ray structure, for X=Se, shows it to have a twelve-vertex nido-cage. The closo-compound $[B_9H_9Se\ Co(\eta\text{-}C_5H_5)]_2$ is also isolated from the $CoCl_2$ reaction. Base degradation of B_9H_9SSe (with KOH) followed by addition of aqueous HCl yields B_7H_9SSe.[60]

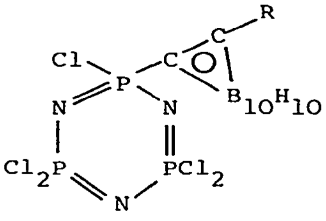
6-SB_9H_{11} undergoes facile hydroboration reactions with alkenes and alkynes. Alkenes give 9-R-6-SB_9H_{10} (R=alkyl). Alkynes such as acetylene, PhC≡CH, PhC≡CPh or 3-hexyne give 9-R'-6-SB_9H_{10}, where R'=alkenyl. Acetylene undergoes double hydroboration to form 9,9'-CH_3CH-(6-SB_9H_{10})$_2$. The coordination of R or R' at the 9 position was confirmed by ^{11}B n.m.r. results.[61]

Aqueous polyselenide or polytelluride solutions react with $B_9H_{13}.SMe_2$ to form $B_9H_{12}X^-$ (X=Se or Te). These are oxidised by I_2 to $B_9H_{11}X$ (in benzene) or $B_9H_{11}X.MeCN$ (in acetonitrile). The latter, with X=Se, forms a triethylamine adduct, $B_9H_{11}Se.NEt_3$. $B_9H_{11}Se$ decomposes on pyrolysis to B_9H_9Se and $B_{11}H_{11}Se$. The formation of $B_9H_{12}Se^-$ is accompanied by small amounts of $B_8H_{10}Se_2$.[62]

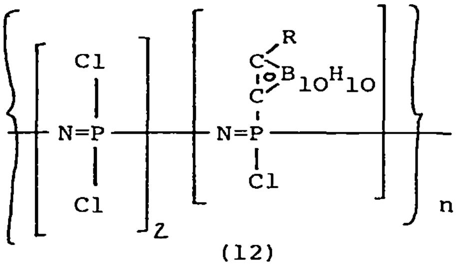
He(I) and Ne(I) photoelectron spectra have been reported for the thiaboranes: 1-SB_9H_9, 1-$SB_{11}H_{11}$, 6-SB_9H_{11}, 10-CH_3-1-SB_9H_8, 10-Br-1-SB_9H_8 and 6-Br-1SB_9H_8, together with the He(I) spectra of the related species: 1,10-$C_2B_8H_{10}$, 1,12-$C_2B_{10}H_{10}$ and $B_{10}H_{14}$. The observed substitution effects can be used to define the availability of electron density at the 6- and 10-positions of 1-SB_9H_9 relative to other borane frameworks. The nature of the highest energy m.o.'s for 1-SB_9H_9 was deduced - they consist of a pair of framework orbitals involving B 2p and S 3p functions lying on the surface of the sphere containing the cage atoms.[63]

The crystal structure of 9-methylsulphonyl-1,7-dicarbacloso-dodecaborane(12) has been determined. The crystals are orthorhombic, and belong to the space group Pnma. The B-S distance in 9-CH_3SO_2-1,7-$C_2B_{10}H_{11}$ is 1.876Å, and there was no evidence for an abnormally long B(2)-B(3) distance, as had been found for e.g. 9,10-Br_2-1,7-$C_2B_{10}H_{10}$.[64]

Gamma-ray induced polymerisation of a 1:3 molar solution of solid 1-vinyl-o-carbaborane and styrene formed a co-polymer containing a 1-vinyl-o-carbaborane molecule and nine styrene molecules per co-polymer molecule. The structure was related to that of polystyrene, but with no unsaturated end-group.[65]



(11)



(12)

Both cyclic, (11), and polymeric, (12), phosphazenes containing carbaborane side chains have been prepared for the first time.[66]

3.1.4 Metallo-heteroboranes

The crystal and molecular structures have been determined for 2,3-Me$_2$-1,2,4,5-(η^5-C_5H_5)$_2$$Co_2C_2B_3H_3$ and 2,3-Me$_2$-1,2,4,5-(η^5-C_5H_5)$_2$-CoFe(H)$C_2B_3H_3$. Both contain seven-vertex, pentagonal bipyramidal $M_2C_2B_3$ cages, with Co at an equatorial vertex and Co or Fe at an apical vertex. In both cases the framework carbon atoms occupy adjacent equatorial positions. Previous n.m.r. data had suggested these structures. These results, however, give the first definite evidence for the presence of equatorial metal atoms in pentagonal bipyramidal metalloboron cages, and the smallest metallocarbaboranes established to contain M-M bonds.[67]

Co(PEt$_3$)$_4$ reacts with closo-1,7-$C_2B_6H_8$ or closo-1,5-$C_2B_3H_5$ to form 2,2,2-(H)(Et$_3$P)$_2$-2,1,8-$CoC_2B_6H_8$ and 2,2-(Et$_3$P)$_2$-2,1,6-$CoC_2B_3H_5$ respectively. The structures were established by X-ray crystallography, the former containing a tricapped trigonal prism, with C(1), B(6) and C(8) occupying capping sites.[68]

Sealed-tube pyrolysis of [nido-$\mu_{4,5}$-{trans-(Et$_3$P)$_2$Pt(H)}-$\mu_{5,6}$-H-2,3-Me$_2$-2,3-$C_2B_4H_4$] produces the closo-carba-metalloborane, [1,1-(Et$_3$P)$_2$-2,3-Me$_2$-1,2,3-$PtC_2B_4H_4$]. X-ray diffraction of the product showed that the crystals were monoclinic (space group $P2_1/a$). The molecular structure is a highly-distorted pentagonal-bipyramidal cage, with a novel (C_{2v}) conformation of the Pt(PEt$_3$)$_2$ fragment. By contrast, pyrolysis of [nido-$\mu_{4,5}$-{trans-(Et$_3$P$_2$)Pt(H)}-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$] leads to separation of the cage carbon atoms, yielding [closo-1,1-(Et$_3$P)$_2$-1,2,4-$PtC_2B_4H_6$].[69]

CoCl$_2$ or FeCl$_2$, on simultaneous treatment with 2,3-Me$_2$$C_2B_4H_5^-$ and $B_5H_8^-$ in tetrahydrofuran, at room temperature, yields mixed ligand metallacarbaboranes. With CoCl$_2$, the chief product was

$[Me_2C_2B_4H_4]CoH[Me_2C_2B_7H_7]$. $FeCl_2$ gives several products: $Me_4C_4B_8H_8$ (known), with the new species $[Me_2C_2B_4H_4]FeH_2[Me_2C_2B_5H_5]$ and $Me_4C_4B_{11}H_{11}$. The last was thought to have 15-vertex *nido*-cage geometry.[70]

The crystal and molecular structures of 4,5,7,8-Ph_4-1,4,5,7,8-$(\eta\text{-}C_5H_5)CoC_4B_3H_3$ (in which there are more carbon than boron atoms) have been studied. The cage framework can be described as a bicapped square antiprism missing two vertices (one cap and one equatorial position). This structure could not be predicted from simple electron-counting rules, but it is consistent with some other eight-atom twenty skeletal electron systems.[71]

SCCC molecular orbital calculations on [π-(3)-1,2-dicarbollyl]-tricarbonylmanganese, $(Cb)Mn(CO)_3^-$, confirm previous work on $(Cp)Fe(Cb)^-$ in showing that the dicabollide anion should be regarded formally as a σ-electron donor, and only in a secondary manner as a π-electron donor.[72]

Reactions of [*hyper*-*closo*-2-R^1-3-R^2-6,6-$(PPh_3)_2$-6,2,3-$RuC_2B_7H_7$] with (*o*-styryl)diphenylphosphine, when R^1, R^2=H or Me; R^1=H, R^2=Ph; (*o*-allylphenyl)diphenylphosphine, when R^1,R^2=H or Me; and $Ph_{3-n}P(CH_2CH_2CH{=}CH_2)_n$, when n=1 or 2, R^1,R^2=Me, give sixteen-electron ruthenacarbaborane complexes, [*hyper*-*closo*-$RuL(C_2B_7H_7R^1R^2)$]. The crystal structure of [2,3-Me_2-6-$(CH_2{=}CHCH_2C_6H_4Ph_2P)$-6,2,3-$RuC_2B_7H_7$] was determined. The C_2B_7 fragment has *arachno*-geometry, occupying nine vertices of an 11-vertex octadecahedron, with a Ru atom in a "non-vertex" position, and within bonding distance of six atoms in the open face. The observed distortion from the common ten-vertex bicapped square antiprismatic structure was probably due to the perturbation of the polyhedral skeletal bonding induced by the sixteen-electron ruthenium(II) centre.[73]

$NaC_2B_8H_{11}$ reacts with $[IrClL_n]$, (n=2, L=PMe_2Ph, $AsMe_2Ph$; n=3, L=PPh_3) to give eighteen-electron Ir(III) complexes 1,1-L_2-1-H-1,2,4-$IrC_2B_8H_{10}$. $RhClL_3$, on the other hand gives sixteen-electron Rh(I) complexes [*nido*-9,9-L_2-9,7,8-$RhC_2B_8H_{11}$], where L=PPh_3 or P(*p*-tolyl)$_3$, and the eighteen-electron Rh(I) complexes [*nido*-9,9,9-L_3-9,7,8-$RhC_2B_8H_{11}$], where L=$AsMe_2Ph$, PMe_2Ph, PMe_3, $AsMe_3$, $SbMe_3$ or PEt_3. In solution, reversible dissociation of [*nido*-$Rh(PEt_3)_3(C_2B_8H_{11})$] occurs to give [*nido*-$Rh(PEt_3)_2(C_2B_8H_{11})$]. The latter partially isomerises to [*closo*-1,1-$(PEt_3)_2$-1-H-1,2,4-$RhC_2B_8H_{10}$] on standing.

$NaC_2B_8H_{11}$ and $[RhHCl(PPh_3)_3]$ form [closo-1,1,3-$(PPh_3)_3$-1-H-1,2,4-$RuC_2B_8H_9$], in which a PPh_3 ligand has displaced a terminal B-H of the carbaborane.[74]

5,6-Dicarba-nido-decaborane and [Pt_2(μ-cyclo-octadiene)$(PEt_3)_4$] form 9-H-9,9-$(Et_3P)_2$-$\mu_{10,11}$-H-7,8,9-$C_2PtB_8H_{10}$. Pyrolysing this at 100°C leads to loss of H_2 and formation of 9-H-9,10-$(Et_3P)_2$-7,8,9-$C_2PtB_8H_9$. The structures were determined by X-ray diffraction.[75]

$(Ph_3P)M(C_2B_8H_{11})$, where M=Cu or Au, or $(Ph_3P)_2Ag(C_2B_8H_{11})$, were prepared from reactions of $[5,6\text{-}C_2B_8H_{11}]^-$ with $[PPh_3CuCl]_4$, $(PPh_3)AuCl$ and $(PPh_3)_2AgBr$ respectively. The silver compound loses triphenylphosphine on recrystallisation to form "$(Ph_3P)Ag(C_2B_8H_{11})$". This is a dimer, containing two enantiomeric arachno-AgC_2B_8 cages linked by a pair of Ag-H-B bridges derived from B-H (terminal) groups.[76]

The crystal and molecular structures have been determined for isomer 1 of $(Ph_2PCH_2)_2NiMe_4C_4B_8H_8$ and isomer 2 of $(\eta^5\text{-}C_5H_5)CoMe_4C_4B_7H_7$. The nickel compound contains a nido thirteen-vertex NiC_4B_8 cage, which is related structurally to a fourteen-vertex closo polyhedron, by removal of one vertex from the bicapped hexagonal antiprism. This is the first example of a nido-thirteen-vertex cage. The cobalt compound also has unprecedented geometry - an irregular basket-shaped framework, with one carbon atom bridging three framework atoms across the open top of the basket. The two compounds are related, since removal of one BH from the MC_4B_8 system, with linkage of two carbon atoms, produces the CoC_4B_7-type.[77]

4-$[\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]$-2,3,7,8-$Me_4C_4B_8H_7$, from the reaction of $Me_4C_4B_8H_8$ with sodium naphthalenide, $FeCl_2$ and Na^+Cp^- in THF, contains a C_4B_8 distorted icosahedral cage, very like that of previously reported $Me_4C_4B_8H_8$ species, with a ferrocenyl group at B(4).[78]

A new rationalisation of the unusual structure of $CpCoFeMe_4C_4B_8H_8$ has been presented, which removes previous inconsistencies. Two models cannot be distinguished - one involving true covalent bonding interactions involving B(8) and B(2')/B(6'), the other an apparent or pseudo-double face capping caused by geometric or steric constraints.[79]

It has been found that cage exchange reactions can occur quite easily in formally six-coordinate rhodium(III) carbaborane complexes, containing C_2B_9 cage systems.[80]

A complete assignment has been proposed for the ^{11}B n.m.r. (111.8MHz) spectrum of 3,3-$[(C_2H_5)_3P]_2$-3-H-3,1; 2-$RhC_2B_9H_{11}$. This was obtained using data on specifically deuteriated derivatives of this, and comparison with 3,3-$(Ph_3P)_2$-3-H-9,12-Br_2-3,1,2-$RhC_2B_9H_9$ and 6-Ph-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{10}$. The parent compound gives five ^{11}B resonances in tetrahydrofuran solution, with relative intensities 1:1:2:2:3 (reading upfield). These were assigned to B(10), B(8), B(9,12), B(4,7), B(6,5,11) respectively.[81]

Treatment of the ion-pair $[Ir(COD)(PR_3)_2][$*nido*-7,8-$C_2B_9H_{12}]$, where R=phenyl or *p*-tolyl, with H_2 yields *closo*-3,3-$(PR_3)_2$-3-H-3,1,2-$IrC_2B_9H_{11}$, and the novel *nido*-metallocarbaborane 3,9-[*cis*-$(H)_2$-*trans*-$(PR_3)_3$-Ir]-3,9-μ-(H_2)-*nido*-7,8-$C_2B_9H_{10}$. The former was characterised by n.m.r. and i.r. spectroscopy and elemental analyses. The crystal structure of the latter was determined for R=p-tolyl. The iridium atom interacts with the B(3)-H(3) and B(9)-H(9) bonds to give octahedral coordination about the metal.[82]

$[PtCl(Ph_2PC_2B_{10}H_{10})(Ph_2PC_2B_{10}H_{11})]$ forms monoclinic crystals, space group I2/a. The complex contains a $\overline{\text{Pt-P-C-B}}$ metallocycle, obtained by insertion of Pt into a B-H bond of a diphenyl (ortho-carbaboranyl)phosphine. The coordination at the platinum is a distorted square-plane, with the third and fourth sites occupied by a phosphorus atom of a second $Ph_2PC_2B_{10}H_{11}$ ligand and a chlorine atom. The following bond distances were determined: Pt-Cl 2.415(3)Å, Pt-B 2.073(9)Å, Pt-P(chelate) 2.279(3)Å, Pt-P(non-chelate) 2.305(2)Å.[83]

3.1.5 Compounds containing B-C or B-Si Bonds

Spectroscopic (^1H, ^{11}B, ^{13}C, ^{31}P n.m.r.; mass) data were reported for 6 simple phosphanealkyleneboranes, $R_3P^+CHR'BH_3^-$, where R'=H, R=Me, Et, iPr, nBu or tBu; R'=Me, R=iPr.[84] The zwitterion $Me_3P^+CH_2BH_3^-$ forms orthorhombic crystals, space group $Pna2_1$. The P-CH_2 bond length (175.6pm) is close to the single bond value, compared to that in $Me_3P{=}CH_2$, 164pm, which has double bond character.[85]

Electrolysis of an acetonitrile solution of $Na[BH_3(CN)]$ at an iron electrode gives $[Fe\{BH_3(CN)\}_2(NCCH_3)_4]$, but at a molybdenum or vanadium anodes, $Na[BH_3(CN)]$ is oxidised to $Na[BH_3(CN)BH_2(CN)]$. Chemical oxidation, using Hg_2Cl_2 or $HgCl_2$, also produces the latter species.[86]

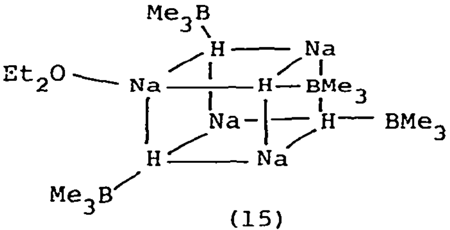
Infrared and Raman spectra were reported for the anion $[(F_3C)_2BF_2]^-$, including $^{10}B/^{11}B$ isotopic data. The assignment was used as the basis for a normal coordinate analysis.[87]

Electron diffraction measurements were reported for cis- and trans-1,2-dimethylborane,(13) and (14). There was appreciable Me...Me repulsion in the cis compound.[88]

(13)

(14)

The crystal structure of the etherate of tetrameric sodium hydridotriethylborate, NaBMe$_3$H $_4$.OEt$_2$ has been determined. Alternating Na and H atoms form the corners of a very distorted cube, with one of the Na atoms coordinated to the diethyl ether molecule,and all the hydridic hydrogens bonded to the boron of the BMe$_3$ group,(15). All of the hydrogen atoms are formally four-coordinate.[89]



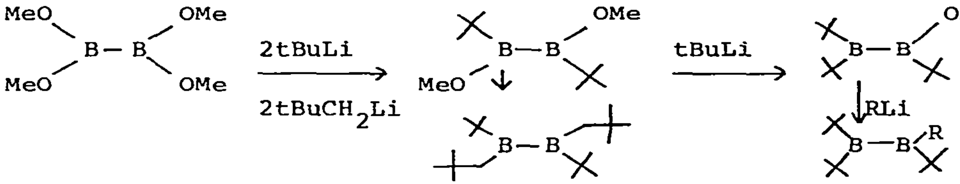
(15)

The relationship between the ^{11}B chemical shifts of the trigonal boranes BR$_2$R' (R,R'=Me or Et;R=Me,R'=CH=CH$_2$,C≡CMe,C≡CPh),δ^{11}B, and the ^{13}C$^+$ chemical shifts of carbenium ions is more complex than at first thought. However, comparison of δ^{13}C data of organoboranes and carbenium ions can be useful in conformational studies.[90]

Microwave,infrared,Raman and n.m.r.(^{1}H,^{11}B,^{13}C,^{19}F) spectra have been reported for (cyclo-C$_3$H$_5$)^{10}BF$_2$ and (cyclo-C$_3$H$_5$)-^{11}BF$_2$. The following structural parameters were obtained: r(B-F)1.328±0.004Å; r(B-C)1.589±0.004Å; r(C$_2$-C$_3$)1.496±0.003Å; F-B-F 115.9±0.9°; C2-C1-B 115.0±0.8°,angle of tilt 2.9±1.8°. Vibrational assignments were proposed.[91]

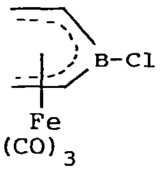
The crystal structure of ammonium tetraphenylborate has been determined at 120K. The ammonium ion is situated at a site of D_{2d} symmetry, and oriented as expected by simple contombic calculations.[92]

The boron compounds (alkyl)$_2$B-B(alkyl)$_2$ have been prepared for the first time; equation (6). The process involves stepwise replacement of methoxy-groups by alkyls, where R=Me, tBuCH$_2$ or SiMe$_3$.[93,94]



...(6)

Chlorovinylborane (prepared in situ from BCl_3 and $Me_2Sn(CH=CH_2)_2$) reacts under photochemical conditions with $Fe(CO)_5$ or $CpCo(CO)_2$, forms (16) and (17) respectively. The chlorine can be readily substituted by e.g. OCH_2Ph, under basic conditions.[95]



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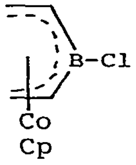


(17)

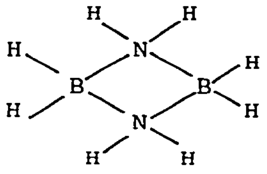
Attempts to synthesise $B(SiMe_3)_3$ from $LiSiMe_3$ and $B(OMe)_3$ in hexane led to formation of $[B(SiMe_3)_4]^-$. This is due to the formation of the strongly nucleophilic anion $SiMe_3^-$ by $LiSiMe_3$ in hexane.[96]

3.1.6 Aminoboranes and other Compounds containing B-N Bonds

Infrared and Raman spectra, together with a normal coordinate analysis, were reported for $BX_2{}^{14}NCS$, where X=Cl, Br or I, $BCl^{15}NCS$, $BBr_2{}^{15}NCS$ and BCl_2NCO. There is B-N bonding in all cases and B,N,C and Y (Y=S or O) are colinear. The B-N stretching force constant was approx. 6.5mdyn. $Å^{-1}$ – consistent with some B-N π-bonding, giving a bond intermediate between single and double. For BCl_2NCO there is extensive mixing of modes involving B-N, N-C and C-O, but for BX_2NCS the vibrational modes are more localised.[97]

$Na[BH_3(NCS)]$ has been prepared. It was found to be a stronger reducing agent than $Na[BH_3(CN)]$.[98]

Vibrational wavenumbers were calculated for a number of boron-containing molecules, from BH and BH^+ to (e.g.) $B_3N_3H_6$, 2,4-$C_2B_5H_7$, $B_{12}H_{12}{}^{2-}$ etc. Correlations with observed spectra gave a series of group corrections. These were used in assigning infrared spectra of aminoborane, BH_2NH_2, and $B_2N_2H_8$, (18), and in predicting wavenumbers for vinylborane and $B_2N_2H_4$ (formally the inorganic analogue of cyclobutadiene).[99]



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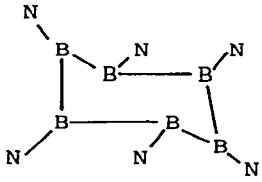


(19)

N.m.r. and vibrational spectroscopic data for the monomeric iminoboranes $R_2C = N\text{-}BR'_2$ ($R=CF_3$; $R'=NMe_2$, Me, iPr, Ph) show that the C=N-B skeleton is linear. There was no evidence for particular strengthening of the N-B bond in this allene-like arrangement.[100]

Vibrational spectra were reported for $(Me_2N)_2BX$ (where X=Cl, Br or I). Some general assignments were proposed, which were fairly consistent with an approximate normal coordinate analysis. The B-X stretching wavenumbers were coupled extensively with other skeletal vibrations involving the boron.[101]

Hexakis(dimethylamido)cyclohexaborane crystallises from residues obtained on dehalogenation of $(Me_2N)_2BCl$. This is the first homocyclic boron compound, and also the first B(I) compound which does not exhibit electron deficiency. The B_6 ring is found to have a chair conformation, (19).[102]

The B-B bonds in $(Me_2N)_2B\text{-}B(NMe_2)_2$, $(Me_2N)ClB\text{-}BCl(NMe_2)$ and $Cl_2B\text{-}BCl_2$ are cleaved by the chloramines Me_2NCl, $MeNCl_2$ and $EtNCl_2$. BCl_3 or the corresponding aminoborane and diborylamines are produced.[103]

An X-ray determination of the structure of ammonia-carboxyborane, $H_3N.BH_2(CO_2H)$, has been carried out. This boron analogue of the protonated form of glycine has monoclinic crystals (space group $P2_1/c$), containing centrosymmetric dimers.[104]

The boron cations $A_3BH^{2+}X_2^{\ 2-}$ (A=py or substituted pyridine; X=Br,I,PF_6) have been prepared by nucleophilic displacement on $Me_3N.BHBr_2$ or dihaloboron adducts of pyridine or substituted pyridines. The B-H bond in these cations is less susceptible to halogenation than that in singly-charged boron cations.[105] It was suggested that intermediates were formed which were bis(amine)-adducts of $BHBr^+$ or $BBr_2^{\ +}$ - and these were indeed isolated.

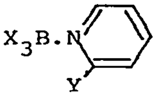
Their reactivities were examined, and the reaction scheme of the type shown in equations (8) to (10) was proposed.[106]

$$Me_3N.BHBr_2 + R\text{-}py \longrightarrow Me_3N + R\text{-}py.BHBr_2 \qquad ...(8)$$

$$R\text{-}py.BHBr_2 + R\text{-}py \longrightarrow (R\text{-}py)_2BHBr^+ + Br^- \qquad ...(9)$$

$$(R\text{-}py)_2BHBr^+ + Br^- \longrightarrow R\text{-}py \quad (R\text{-}py)_3BH^{2+} + 2Br^- \qquad ...(10)$$

2-X-Pyridines form adducts with BH_3 or BBr_3 (X=Br,Cl,F or CN), except for BBr_3/2-cyanopyridine, (20, X=H or Br; Y=Br,Cl,F or CN). Spectral parameters (infrared, ^1H and ^{11}B n.m.r.) were reported.[107]



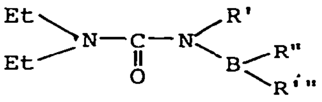
(20)

Dimethylsulphideborane reacts with various Lewis acids (quinoline, isoquinoline, 2-, 3- or 4-aminopyridine or aniline) to form borane adducts. These were characterised by i.r., ^1H and ^{11}B n.m.r. spectra. Detailed studies on the aminopyridine boranes showed that the BH_3 group was coordinated to the ring nitrogen.[108]

$Me_2B\text{-}N(Me)Li$ can be used to synthesise a large number of borylamino-element compounds, e.g. $Me_2B\text{-}NMe\text{-}BMe\text{-}NMe_2$, $Me_2Si\ NMe\text{-}BMe_2\ _2$, $Me_2B\text{-}NMe\text{-}SiMe_2\text{-}NMe\text{-}SiMe_2Br$, etc.[109]

$Hg[NMe\text{-}BMe_2]_2$ and $MeHg\text{-}NMe\text{-}BMe_2$ are both volatile compounds, prepared from $Me_2B\text{-}N(Me)Li$ and $HgCl_2$ or MeHgCl. They do not decompose on heating below 80°C, although very sensitive to air and moisture. There is no evidence for association via Hg-N or B-N interaction in either the gaseous phase or in solution.[110]

N.m.r. and photoelectron studies were reported on the new bis(boryl)hydrazines, XMeB-NMe-NMe-BMeX (where X=F,Cl,Br,SMe,NMe_2 or Me). The ^{14}N n.m.r. results can only be rationalised in terms of planar coordination at the nitrogens, while the He(I) photoelectron spectra are consistent with a gauche conformation.[111]



(21)

The preparation, n.m.r.(^1H,^{11}B,^{13}C), mass and i.r. spectra were reported for the ureidoboranes, (21, R'=R"=R'"=Ph or Me; R'=Ph or iPr, R"=R'"=NMe_2; R'=iPr or Me, R"=R'"=Me).[112]

N-Sulphinylamines react quantitatively with (methylthio)organylboranes according to equation (11), i.e. insertion of N=S into the

$$R\text{-}N{=}S{=}O + 3R'_2BSMe \rightarrow RN(BR'_2)SSMe + MeSSMe + (Me_2B)_2O \qquad ...(11)$$

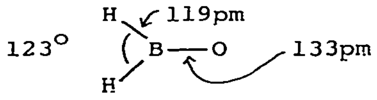
$$(R{=}t\text{-}Bu,Ph,2\text{-}F\text{-}C_6H_4,C_6F_5 \text{ etc; } R'{=}Me)$$

B-S bond, and complex redox reaction. The products are monomeric.[113]

Triethylenediamine (TED) precipitates BF_3 from diethyl ether solution as TED• $2BF_3$, and from THF as $TED.BF_3$. N,N,N',N'-Tetramethylethylenediamine (TMED) and TED precipitate BH_3 from both diethyl ether and THF as $TMED.2BH_3$ or $TED.2BH_3$. From diethyl ether, TMED precipitates AlH_3 as $TMED.2AlH_3$, while in THF the TMED reacts with AlH_3 to form $TMED.AlH_3$. The last is somewhat soluble, so the precipitation of AlH_3 is incomplete in this case. TED, however, precipitates AlH_3 quantitatively from both Et_2O and THF (as $TED.AlH_3$).[114]

3.1.7 Compounds containing B-O Bonds

Ab initio self consistent field m.o. calculations on H_2BO suggest the optimised geometry of (22) for the radical.[115]



(22)

Infrared (gas, solid) and Raman (liquid, solid) spectra were reported for divinylboronic anhydride, $[(CH_2{=}CH)_2B]_2O$. $^{16}O/^{18}O$ isotopic shifts were used to assist in arriving at an assignment, although the molecule possesses C_1 symmetry. The B-O-B unit appears to be linear, which is also in agreement with ^{11}B and ^{13}C n.m.r. data; thus there appears to be (p-p)π bonding between the boron and the oxygen.[116]

The infrared and Raman spectra of three crystalline forms of metaboric acid, HBO_2 have been obtained. The behaviour the antisymmetric ν(OH) mode, and the in- and out-of-plane deformations (δ(OH) and γ(OH) respectively) show that hydrogen bonds of different strengths are present in these 3 forms - in agreement with X-ray diffraction results. The remaining vibrational modes could be related to the analogous modes in borates and polyborates of known structure.[117]

Studies of solubility, viscosity, density and refractive index of lithium metaborate aqueous solutions, and its interactions with formamide and dimethylformamide have been carried out. The incongruently soluble compounds $2LiBO_2.HCONR_2.2H_2O$ (R=H or Me) were identified.[118] Solubilities were determined in systems $HCONR_2-KBO_2-H_2O$ (R=H or Me) at 25°C; there was no evidence for any new phases.[119]

Boron acids form 1:1 complexes with a variety of bidentate

$$RB(OH)_2 + H_2L \rightleftarrows RB(OH)L^- + H_3O^+ \qquad \ldots (12)$$
$$(R{=}m\text{-}NO_2C_6H_4\text{-},\ Ph, OH\ \text{or}\ Me)$$

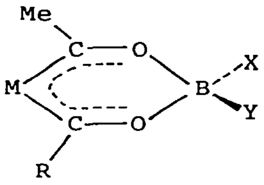
chelating ligands according to equation (12). Stability constants were calculated by pH titration methods, and the reaction kinetics were measured at μ=0.1M (KNO_3) and 25°C. The ligand H_2L = oxalic acid, malonic acid, salicylic acid, tartaric acid, catechol, mannitol etc.[120]

^{17}O chemical shifts have been reported for thirty B-O compounds, containing three-coordinate boron. They could be interpreted in terms of B-O, $(p-p)\pi$ interaction. The decrease in π bond order was found to be in the sequence: $(R_2B)_2O > (RBO)_3 > R_2BOR > RB(OR)_2 > B(OR)_3$ (where R=Me or Et).[121]

$Li[B(SO_3Cl)_4]$ forms monoclinic crystals, space group $P2_1/c$. There is approximately tetrahedral coordination at the B, with B-O distances of 1.460(3)-1.478(3)Å, and unidentate chlorosulphato ligands.[122] It has been pointed out that $K[B(SO_3Cl)_4]$ has monoclinic (Cc) rather than triclinic (P1) symmetry reported by Mairesse and Drache (Acta Crystallogr., B34 (1978)1771).[123]

The crystal and molecular structures of $[(\eta^5-C_5H_5)(CO)Fe(CH_3CO)-(i-C_3H_7CO)]BF_2$ - a metalla-β-diketonate complex of boron - have been determined. The crystals are monoclinic, belonging to the space group $P2_1/c$. The BF_2 unit is attached to the ferra-β-diketonate through the two oxygen atoms of the metallachelate ring. This ring is in a boat conformation, and is the second example of a non-planar metalla-β-diketonate ring structure, giving relief of internal angle strain within the ring due to the bonding preferences of the iron and boron.[124]

If a metalla-β-diketone, e.g. [cis-$(OC)_4Re(CH_3CO)(RCO)$]H, where R=Me,iPr or CH_2Ph, or [Cp(OC)Fe$(CH_3CO)(RCO)$]H, where R=Me or iPr, reacts with BX_2Y (X=halogen, Y=halogen or phenyl) to give the (metalla-β-diketonato)B(X)(Y),(23); 12 of these were reported. In addition, [cis-$(OC)_4Mn(CH_3CO)$]Li reacts with gaseous BF_3 to give (mangana-acetylacetonato)-BF_2.[125]



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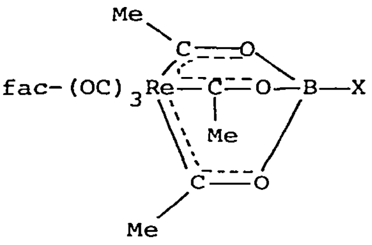


(24)

BX_3 reacts (in CH_2Cl_2 at -50° to $0^{\circ}C$) with the triacetyltricarbonylrhenate dianion according to equation (13). These have

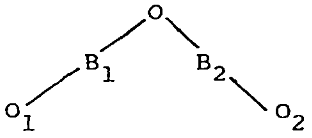
$$Li_2[fac\text{-}(OC)_3Re(CH_3CO)_3] + BX_3 \longrightarrow 2LiX + (\underline{24}) \quad \ldots (13)$$

(X=F,Cl,Br,I).

unusual electronic structures for neutral four-coordinate boron complexes. The boron atom is formally bonded to two anionic oxygen donors and an anionic halide atom, with the fourth coordination site occupied by a neutral oxygen atom acting as an adduct molecule. However, electron delocalisation renders all three oxygen atoms equivalent, while maintaining formal neutrality of the boron atom.[126]

The crystal structure of (24, X=Cl) has been determined; the crystals are monoclinic, space group $P2_1/m$. The results confirm that the triacetylrhenate ligand does act as a trioxygen, vicinal, bifurcated chelating ligand towards boron.[127]

The potential surface has been calculated for the B_2O_3 molecule using a restricted Hartree-Fock approximation with a minimal STO-3G basis set. The equilibrium geometry was calculated to be C_{2v} - with bond lengths in reasonable agreement with those found from electron diffraction: (25), $r(O_1-B_1)$ 1.241Å; $r(O-B_1)$ 1.341Å; B_1-O-B_2 142°, O_1-B_1-O 177°.[128]



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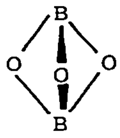


(26)

Raman data have been obtained for vitreous and molten B_2O_3 in the temperature range -196° to 1594°C. The vitreous material is largely composed of boroxol rings, but in the melt the boroxol ring concentration decreases with increasing temperature, and is small, near 1600°C.[129]

It had been proposed that the hypothetical bipyramidal B_2O_3, (26), could be a major component of B_2O_3 vapour. *Ab initio* SCF-MO calculations show that it is a highly strained structure - and could only be a very minor contributor to real systems.[130]

Phase studies have been reported for the following systems: B_2O_3-La_2O_3-V_2O_5;[131] B_2O_3-CoO-Li_2O;[132] B_2O_3-Cu_2O-Li_2O.[133]

$Sr_2B_2O_6$ crystallises, like $Ca_3B_2O_6$, in the space group R$\bar{3}$c - as deduced from X-ray powder diffraction studies.[134]

Thermochemical measurements have been reported on the CoO-B_2O_3 system. The enthalpies of formation (ΔH_f^o) of the cobalt borates (referred to solid CoO and liquid B_2O_3) were determined by oxide melt solution calorimetry in $2PbO.B_2O_3$ melts at 973 ± 2K. The values were as follows: $Co_3B_2O_6$, -81.4 ± 1.6kJ mol^{-1}; $Co_2B_2O_5$, -64.7 ± 1.3kJ mol^{-1}; CoB_4O_7, -20.7 ± 1.5kJ mol^{-1}.[135]

I.r. and Raman spectra were listed for solid H_3BO_3, $Na[B(OH)_4]$, $Na_2[B_4O_5(OH)_4].8H_2O$, $Na[B_5O_6(OH)_4].3H_2O$, $K[B_5O_6(OH)_4].2H_2O$, $(NH_4)_2[B_4O_5(OH)_4]2H_2O$, β-$NH_4[B_5O_6(OH)_4].2H_2O$, $NH_4[B_5O_6(OH)_4].0.67H_2O$, and $NH_4[B_5O_6(OH)_4]$. Data were also obtained for $H_3{}^{11}BO_3$, $H_3{}^{10}BO_3$, $Na[{}^{11}B(OH)_4]$, $Na[{}^{10}B(OH)_4]$, $Na_2[{}^{11}B_4O_5(OH)_4].8H_2O$, $Na_2[{}^{10}B_4O_5(OH)_4].8H_2O$, $(NH_4)_2[{}^{11}B_4O_5(OH)_4].2H_2O$, $(NH_4)_2[{}^{10}B_4O_5(OH)_4].2H_2O$, $K[{}^{11}B_5O_6(OH)_4].2H_2O$ and $K[{}^{10}B_5O_6(OH)_4].2H_2O$. The spectra were interpreted by comparison with known structures, by comparisons within these compounds, and from observed isotopic shifts.[136]

Both H_2O molecules and OH groups were found by ^1H n.m.r. in crystalline hydrated tetraborates. The ^{11}B n.m.r. spectrum of $Na_2B_4O_7.10H_2O$ contained an unsymmetrical broad line due to two boron atoms in trigonal coordination, and a symmetrical narrow line due to two boron atoms in tetragonal coordination (by water molecules).[137]

EuB_4O_7 is orthorhombic, with crystals belonging to the space group $Pnm2_1$. The structural framework is built up from a three-dimensional, $(B_4O_7)_\infty$ array of BO_4 tetrahedra. The Eu^{2+} is nine-coordinated, by oxygen atoms.[138]

Solubility, density, viscosity and refractive index measurements have been made on the liquid phases of the $(NH_4)_2B_4O_7$-$(H_2N)_2C{=}X$ - H_2O (where X=O,S) systems.[139] Phase equilibria were also studied in $(NH_4)_2B_4O_7$-$HCONR_2$-H_2O systems, for R=H or Me, at 25°C and 50°C.[140]

Phase studies revealed simple eutonic behaviour for all of the following systems: LiB_5O_8-LiX-H_2O (X=Cl,Br or I);[141] ($X=NO_2^-$, NO_3^-);[142] MB_5O_8-M_2SO_4-H_2O (M=Li,Na or K);[143] MB_5O_8-hexamethylenetetramine-H_2O (M=Li,Na or K).[144]

The crystal structure of the europium (II) bromoborate, $Eu_2B_5O_9Br$ has been determined. It is isostructural with the Ca(II)analogue, and belongs to the space group Pnn2 (orthorhombic). The structure consists of a three-dimensional $(B_5O_9)_\infty$ network, built up from B_5O_{12} units ($3BO_4$+$2BO_3$) sharing corner oxygens. The Eu and Br atoms are in tunnels of the $(B_5O_9)_\infty$ framework, extending along the *c*-axis.[145]

$YCo(BO_2)_5$ has been isolated from the Y_2O_3-CoO-B_2O_3 system. Its crystal structure reveals the presence of $B_5O_{10}^{5-}$ anions, consisting of $3BO_4$ and two BO_3 units. The Y and Co cations were situated between layers of the anions.[146]

An improved synthetic route has been reported for boracites, complex cage compounds of formula $M_3B_7O_{13}X$. The reaction is

$$7LiBO_2 + 3MX_2 + H_2O \rightarrow M_3B_7O_{13}X + 5LiX + 2LiOH \quad \ldots \; (14)$$

shown in equation (14), where M is a divalent metal and X a univalent anion. About 15% excess of H_2O was beneficial, and the reactions were complete in 50-60h., at 20-30 atm. pressure and 250-300°C. Yields were good, thus for M=Ni, X=I; M=Zn, X=Br and M=Mg, X=Cl yields in excess of 95% were achieved.[147]

3.1.8 Boron Halides

The BF_2 radical can be generated by the reaction of $SF_6(g)$ or $BF_3(g)$ with solid boron in an effusion cell at 1600-1800K. Thermochemical studies gave the standard enthalpy of formation, $\Delta H^o_{f,298}(BF_2) = -502 \pm 8$ kJ mol^{-1} (about 85 kJ mol^{-1} less stable than previously accepted values). The FB-F bond is weaker than either the B-F or the F_2B-F bond.[148]

The difluoroboron cations $DD'BF_2^+$, where D=H or F, D'=MeO or NO_2; D=MeO, D'=NO_2, were detected, by ^{19}F n.m.r. measurements, in benzoate ester/BF_3/BCl_3 systems.[149]

The reaction (15) occurs spontaneously in the system hexamethylphosphoramide-BF_3 (HMPA=hexamethylphosphoramide). The degree of ionisation for the reaction was 0.13 in $CDCl_3$ solution at 27°C.

$$2HMPA.BF_3 \rightleftharpoons BF_2(HMPA)_2^+ + BF_4^- \quad \ldots (15)$$

The crystal structure of BF_3 has been determined. It is surprising that this simple compound has a structure which is fundamentally different from the other boron trihalides. The crystals are monoclinic, space group $P2_1/c$. The boron has effectively trigonal bipyramidal coordination with three fluorines at 1.26-1.31Å, and two at 2.68 and 2.71Å. This linking to adjacent molecules gave a three-dimensional array.[151]

BF_3, but not B_2H_6, reacts with acyclic or cyclic polyethers to form Lewis acid-base adducts. The stoichiometries of these adducts are very variable, and appear to be sterically controlled, e.g. BF_3:L=3.9 for L=18-crown-6; 1.7 for L=dicyclohexano-18-crown-6.[152]

Adiabatic electron affinities were measured for several boron trihalides, from a determination of threshold kinetic energies for (16). A crossed molecular beam apparatus was used. For BF_3, BCl_3, BCl_2Br, $BClBr_2$ and BBr_3 respectively the electron affinities are 0.0; 0.33; 0.69; 0.92; 0.82 eV (all ± 0.02 eV). These values were used, via an ionic energy cycle, to give B-N bond energies for $BX_3.NMe_3$ adducts; these were in reasonable agreement with values deduced from n.m.r. measurements.[153]

$$Cs + BX_3 \rightarrow Cs^+ + BX_3^- \quad \ldots (16)$$

The formation and characterisation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}[C(=O)CH_3].MX_3$ (where M=B, X=F,Cl,Br; M=Al, X=Br or CH_3) were used to obtain a comparison of basicities and reactivities of the carbonyl function in ketones, a metal acetyl, and polynuclear metal carbonyls. Towards BF_3, the following order of basicity was deduced: $(CH_3)_2C{=}O > (\eta^5\text{-}C_5H_5)Fe(CO)_2[C(=O)CH_3] > (\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$.[154]

Ab initio calculations (using two-exponent Roos-Siegbahn and Huzinaga-Dunning basis sets) were used to give potential surfaces, equilibrium geometry and stability values for $LiBF_4$.[155]

The thermodynamic parameters of the thermal decomposition of $LiBF_4$ on sublimation, (17), have been determined:

$$LiBF_4(\text{solid}) \rightarrow LiF(\text{solid}) + BF_3(\text{gas}) \qquad \ldots\ (17)$$

$\Delta H^o_{298} = 20.7 \pm 0.6$ kcal. mol^{-1}, $\Delta S^o_{298} = 47.9 \pm 1.1$ e.u.
The enthalpy and entropy of solid $LiBF_4$ were also calculated: $\Delta H^o_{298} = 1439.4 \pm 0.7$ kcal. mol^{-1}; $S^o_{298} = 21.3 \pm 1.1$ e.u.[156]

$BH_2Cl.SMe_2$ is formed in almost quantitative yield by refluxing an equimolar mixture of $BH_3.SMe_2$ and CCl_4. It can be used to produce dialkylchloroboranes by the hydroboration of alkenes.[157]

High-resolution (ca. 0.035 cm^{-1}) infrared spectra of BCl_3 or BCl_2F have been obtained in solid argon or krypton. The narrowness of the lines enabled features due to different isotopic species to be resolved. For $BCl_3 \nu_2, \nu_3, \nu_1 + \nu_4$, $\nu_1 + \nu_3$ and $2\nu_3$ bands were seen.[158]

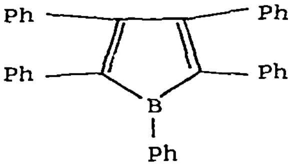
The infrared spectra of Ar/BX_3 (where X=Cl or Br) mixtures deposited on a CsI window at 10K and undergoing simultaneous proton radiolysis showed boron isotopic absorptions due to ν_4 and ν_5 of HBX_2 i.e. the $\nu_{as}BX_2$ and inplane deformation respectively. Irradiation of BX_3 with a windowless Ar resonance lamp gave bands assigned to ν_3 of BX_3^+. Radiolysis and vacuum u.v. photolysis both gave bands due to ν_3 of BX_2. The $^{10}B/^{11}B$ data suggested a bond angle of 125 ± 5^o for these species.[159]

The vibrational spectra of $AsR_3.^{10}BX_3$ ($R=CH_3$ or CD_3; X=Cl or Br) and $AsR_3.^nBX_3$ ($R=CH_3$ or CD_3; X=Cl, Br or I; n=10/11, natural abundance) have been reported. The νBAs modes were in the range 640-740 cm^{-1}. For X=I,Br and Cl, the k(B-As) force constants are 2.84 2.26 and 1.70 mdyn. $Å^{-1}$ respectively. The order of B-As bond strengths was the same as that determined previously by calorimetry.[160]

At about 430°C, $[Et_3NH]^+[B_{10}Br_{10}]^-$ forms the new compound MeB_9Br_8 (apparently via a radical mechanism). Varying the conditions produced the previously unknown boron subhalides: EtB_9Br_8, $Me_2B_9Br_7$, $Me(Et)B_9Br_7$, and smaller amounts of B_9Br_9. The boron chemical shifts of B_9Br_9(-60.4 p.p.m.) and MeB_9Br_8 (-62.2 p.p.m.) show that the boron atoms are very deshielded compared to similar nine-atom frameworks containing (2n+2) framework electrons.[161]

3.1.9 Boron-containing Heterocycles

Pure pentaphenylborole, (27; PPB), can be synthesised from 1,1-dibutyl-2,3,4,5-tetraphenylstannole and $PhBCl_2$ in toluene (yield 95%). Reduction of this with metallic potassium in THF gives



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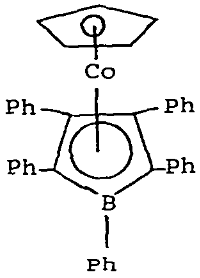
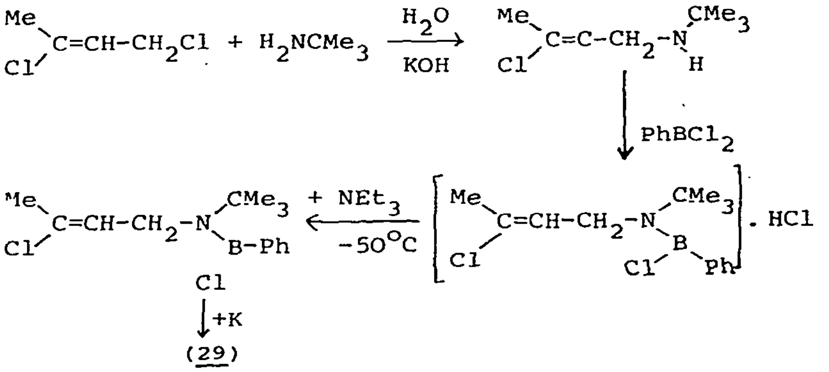


(28)

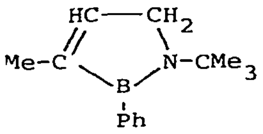
brownish-red $K_2[PPB]$, containing the 6-π-electron anion PPB^{2-}. In addition, PPB reacts with $CpCo(CO)_2$ to form (28).[162]

1-Tert-butyl-3-methyl-2-phenyl-Δ^3-1,2-azaboroline, (29) is prepared by the route shown in (18). The product is a colourless



... (18)

liquid, b.p. 52-53°C (1 torr.). It is soluble in inert solvents,



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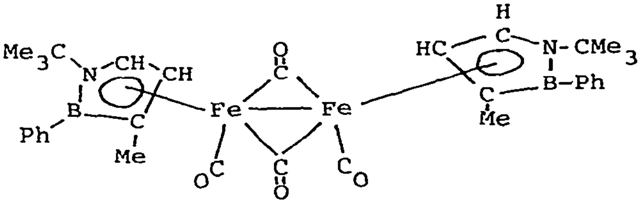
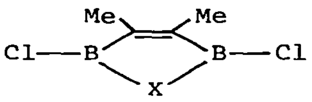


(30)

but moisture sensitive. With $Fe(CO)_5$ it forms (30), in which the η^5-bonding mode is confirmed by X-ray diffraction.[163]



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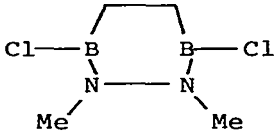
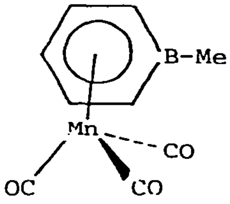


(32)

The bifunctional molecules $(Me_3Si)_2X$, where X=S, NMe or NMe-NMe, react with the diboryl compounds $Cl_2B\text{-}CR{=}CR\text{-}BCl_2$ (R=H or Me) or $Cl_2BCH_2CH_2BCl_2$ to give the new ring compounds (31; X=S, NMe or NMeNMe) and (32).[164]

Compound (33) is obtained in 67% yield by the ligand transfer reaction of $Co(C_5H_5BMe)_2$ with $Mn_2(CO)_{10}$. Treatment with $CH_3COCl/AlCl_3$ forms both (2-acetyl-1-methylborinato)tricarbonylmanganese and the tricarbonyl(toluene)manganese cation.[165]



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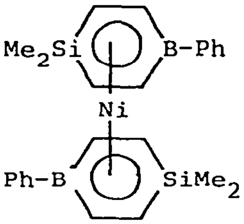
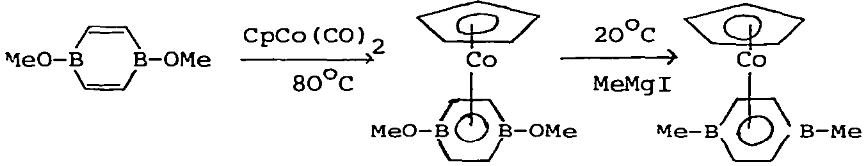


(34)

Cyclopentadienyl(1,4-dimethyl-1,4-dibora-2,5-cyclohexadiene)cobalt is prepared by equation (19). A crystal structure determination of the product showed that all six atoms of the cyclohexadiene ring are

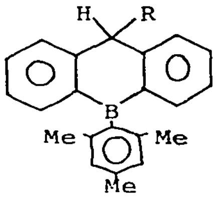


... (19)

within bonding distance of the cobalt, but that the boron atoms bend away from the metal atom.[166]

Nine new complexes of the type ML_2, where M=Ni, Pd or Pt; $L{=}X(CH{=}CH)_2B\text{-}Ph$, $X{=}Me_2C$, Me_2Si or $(CH_2)_2$, have been prepared. X-ray structure analysis of the compound with M=Ni, $X{=}Me_2Si$ shows that it is a sandwich-type bis(η^5-divinylborane)metal complex, with C_2 symmetry, (34). All of the complexes are much more stable thermally than the corresponding 1,5-cycloöctadienyl metal complexes.[167]

Free energies of rotation about the B-C(mesitylene) bond have been determined by ^{1}H n.m.r. for several 9-mesityl-9,10-dihydro-9-boranthracenes, (35, R=Me,CH_2OH, COOEt, $SiMe_3$, Ph or CH_2CMe_3). Both in solution and in the solid state they adopt a ground-state configuration in which the mesitylene and bora-anthracene rings are approximately perpendicular.[168]



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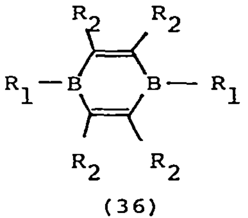

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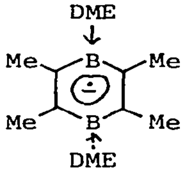
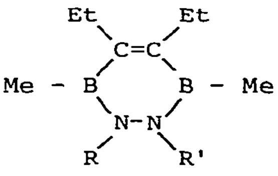


(37)

1,4-Dimethyl-2,3,5,6-tetra-*n*-butyl-1,4-diboracyclohexa-2,5-diene, (36,R_1=Me, R_2=*n*Bu), can be obtained by the addition of methylborylene, MeB: to 5-decyne. The methylborylene is generated *in situ* by the system $C_8K/MeBBr_2$.[169]

The photoelectron spectra and one-electron reduction behaviour of 1,4-difluoro-2,3,5,6-tetramethyl-1,4-diboracyclohexa-2,5-diene, (36, R_1=F, R_2=Me), and its isoelectronic analogue duroquinone, have been compared. The latter gives a very stable anion radical (durosemiquinone), but the former only a short-lived intermediate. Potassium metal, however, produces a secondary anion radical, which can be stabilised by dicyclohexyl-18-crown-6(which complexes the K^+ produced). This species is believed to be the radical anion of 2,3,5,6-tetramethyl-1,4-diborine, (37)where DME=dimethoxyethane), a hitherto unknown benzenoid heterocycle.[170,171]



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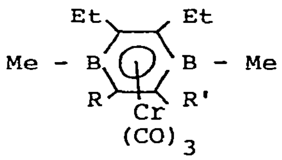
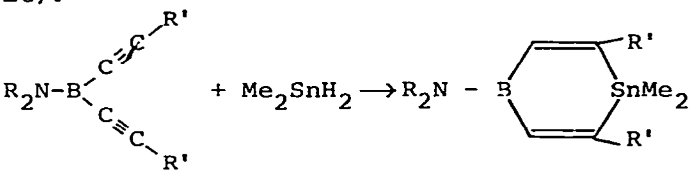


(39)

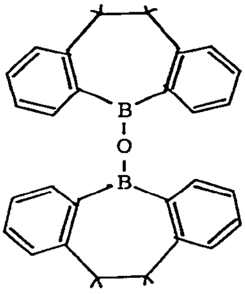
3,4-Diethyl-2,5-dimethyl-1,2,5-thiadiborolene reacts with hydrazines to give (38, R=R'=H or Me; R=H, R'=Me). X-ray diffraction shows that the ring is planar. These diazadiborins react with $(MeCN)_3Cr(CO)_3$ to form (39).[172]

Hydrostannation of (dialkylamino)dialkynylboranes by means of dimethylstannane gives reaction (20) (R=Me, R'=Me or Et; R=H, R'=Et).



... (20)

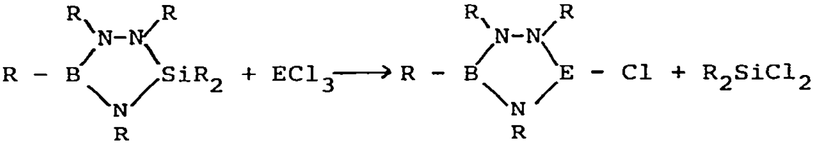
The products are 1,1-dimethyl-1-stanna-4-bora-2,5-cyclohexadienes, and they react with alcohols to give the analogous alkoxy-derivatives.[173]



(40)

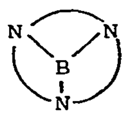
The crystal structure of bis(4-dibenzoborepinyl)ether, (40), has been determined. The crystals are orthorhombic, space group $Pca2_1$, and the B-O distances are 1.340 and 1.347Å, corresponding to partial double bond character.[174]

1,2,4-Triaza-3-sila-5-borolidines can be prepared from N,N'-dilithio-N,N'-dimethylhydrazine and $Br(Me)B-NMe-SiMe_2Br$ or by transsilylation of the permethyl derivative of this ring system. The silicon atom can be replaced by E(P or As) by reaction (21).[175]



... (21)

Four tris(amino)boranes, (41), with ethylene and/or trimethylene bridges, have been prepared. Predictions that the smallest member of the series, 10-bora-1,4,7-triazatricyclo-$[5.2.1.0^{4,10}]$decane, would be very strained were supported by the observation that this compound only exists as a tight dimer. 11-Bora-1,4,7-triazatricyclo$[5.3.1.0^{4,11}]$undecane exists as a dimer in solution, but as a monomer in the gas phase. X-ray studies of 13-bora-1,5,9-triazatricyclo $[7.3.1.0^{5,13}]$-tridecane show that it has a stable, planar BN_3 skeleton.[176]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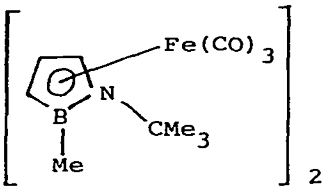
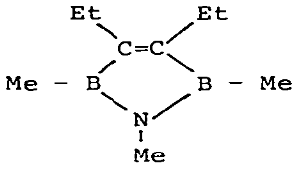

(42)

LiCH=CHCH$_2$NCMe$_3$Li and MeBBr$_2$ react to form Δ^3-1-*tert*-butyl-2-methyl-1,2-azaboroline. This is isoelectronic with $C_5H_5^-$, and a forms a complex with $Fe(CO)_5$, (42). This has bridging carbonyl groups and exists as *cis* and *trans* forms.[177]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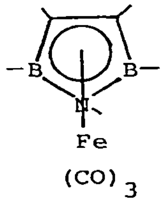
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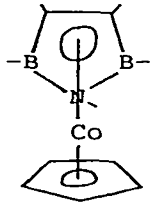
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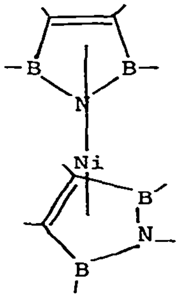
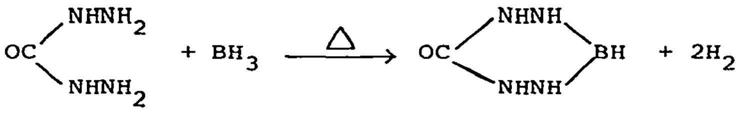
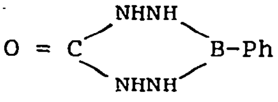

(46)

(43), (3,4-Diethyl-1,2,5-trimethyl-1,2,5-azadiborolene) is obtained by the reaction of the C_2B_2S analogue with heptamethyldistannazane. The new compound acts as a four-electron ligand in forming the complexes (44)-(46). Unlike the C_2B_2S ring system this does not favour the formation of "triple-decked" sandwich complexes.[178]

A cyclic derivative of carbohydrazide, containing boron, has been reported for the first time, equation (21). The νBH band is very


... (22)

broad, centred at 2395cm^{-1}, as is νNH (definite maximum at 3190cm^{-1}). Support for the proposed structure came from the preparation of the B-phenyl derivative, (47), characterised by mass spectrometry and n.m.r.[179]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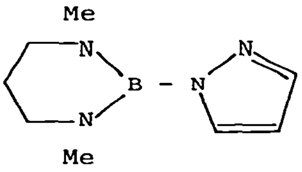
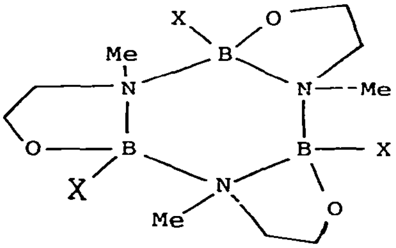
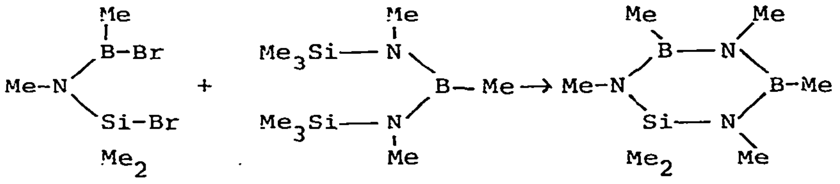

(48)

Thermolysis of a mixture of 1,3-dimethyl-1,3,2-diazaboracyclohexane with pyrazole produces 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclohexane, (48). Spectroscopic data confirm that it is a monomer, and therefore the first known example of a pyrazolyl-1-borane containing a trigonal boron atom.[180]


(49)

Derivatives of 1-aza-2-bora-3-oxacyclopentane are easily prepared by cleavage of N-Si and O-Si bonds in disilylated ethanolamines by halogenoboranes. The B-hydro- and B-halogeno compounds are associated in the solid state, and partially so in the liquid and gas phases also, e.g. (49, X=H,F,Cl or Br).[181]

Permethylated silaborazines are prepared from BrMeB-NMe-SiMe$_2$ or BrMeB-N(SiMe$_3$)-SiMe$_2$Br, as in (23). This type of ring can, in turn, be used to generate phosphaborazines, since phosphorus halides replace the SiMe$_2$ selectively, as in (24). The P-X bond is more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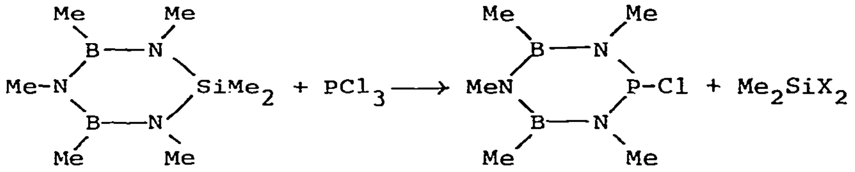
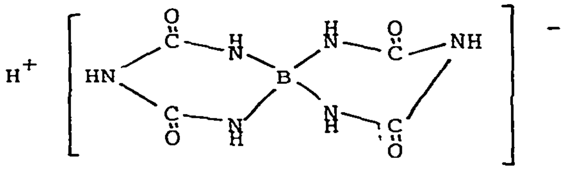
reactive than the P-N or B-N bonds of the ring, and this allows selective nucleophilic substitution reactions to occur at the phosphorus. N.m.r. data of the new compounds suggest that the rings are non-planar.[182]


...(24)

Bis(biureto)boric acid, (50), is prepared by the thermolysis of a mixture of biuret and boric acid. There is no change in the ν(C=O) of biuret on complexation, but $\nu(NH_2)$ of the free ligand disappears. νBN is seen at $1390 cm^{-1}$. All of these observations are consistent with the structure as shown.[183]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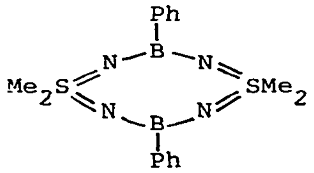
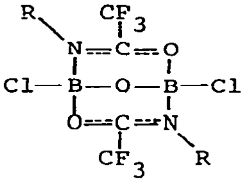

(51)

The eight-membered ring compound (51), i.e. 1,1,5,5-tetramethyl-3,7-diphenyl-$1\lambda^6$, $5\lambda^6$, 2,4,6,8,3,7-dithiatetra-azadiborocin, was prepared by the reaction of dichlorophenylborane with S,S-dimethyl-N,N-bis(trimethylsilyl)sulphodi-imide. The crystal structure was determined - the compound forms orthorhombic crystals (space group Pbca). The eight-membered ring departs significantly from planarity.[184]

1,5-Dichloro-3,7-bis(trifluoromethyl)-4,8-bis(2',6'-dimethylphenyl)-2,6,9-trioxa-4,8-diaza-1,5-diborabicyclo-[3.3.1]nonadiene (52), forms monoclinic crystals, space group $P2_1/e$. The molecule is structurally analogous to $B_4O_7^{2-}$. The eight-membered ring was folded by 104° about the B-B vector. The boron was bonded more strongly to the bridge oxygen (139pm) than to the other atoms i.e. B-O(C) (155pm), B-N(160pm), B-Cl(182pm).[185]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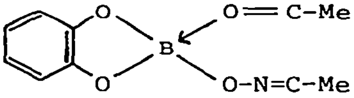
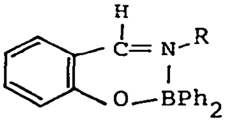

(53)

2-Alkoxy-1,3,2-benzodioxaboroles react with various monofunctional bidentate oximes, e.g. furfuraldoxime, pyridine-2-aldoxime, diacetylmonoxime, salicylaldoxime and α-benzoinoxime to give new complexes, in all of which the boron is four-coordinate, e.g. (53).[186]

Infrared, u.v., ^{1}H, ^{13}C and ^{11}B n.m.r. spectra have been reported for disubstituted diphenylboron chelates derived from salicylaldehyde azomethines, (54, where R=H, Me, Et, OH, NH_2, NHPh, NMe_2, Ph etc.).[187]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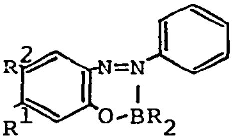
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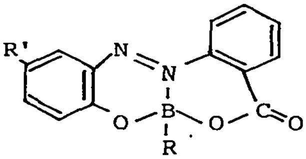
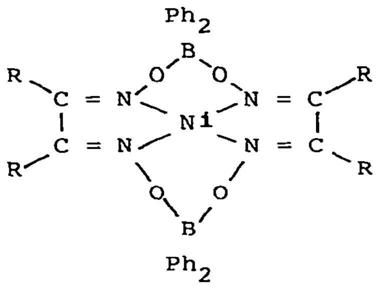

(56)

Diphenylboronic acid anhydride or boron trihalides (F or Cl) react with bidentate chelate reagents, e.g. (55, where R=Ph, R^1 = OH, R^2 = H; R=F, R^1=H, R^2=CH_3 etc.). Tridentate chelates react similarly (at high temperatures) to form (56, where R=Ph, R'=Me or OMe; R=F, R'=Me). All were characterised by elemental analysis, infrared, ^{1}H, ^{11}B and ^{19}F n.m.r. spectra.[188] Mass spectral fragmentation patterns of these chelates were also reported.[189]

The bis(diphenylboron) chelates (57, R=H,Ph; R_2=$(CH_2)_4$, $(CH_2)_5$) are prepared from diphenylboronic anhydride and the boron free nickel complex.[190]



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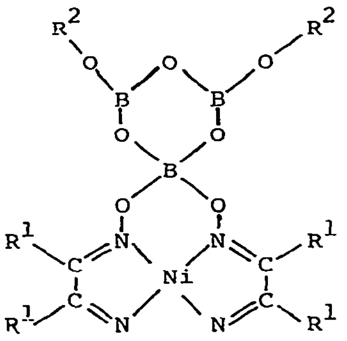
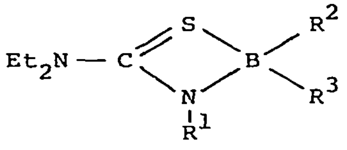


(58)

Trimethoxyboroxine or dimethylammonium pentaborate dihydrate react with nickel glyoximates to form monoboroxino-chelates: (58, where $(R^1)_2=(CH_2)_5$, R^2 = Me; R^1 = Me or Ph, R^2=H). The B:Ni ratio was 3:1.[191]

N,N'-N'-Triorganyl-N-trimethylsilylthioureas react with XBR_2 (X=halide) to form N,N'N'-organyl-thioureidoboranes, (59, R^1=Ph, $R^2=R^3$=Et,nBu,Me or Ph) and isothioureidoboranes, (60, R^1=Me, $R^2=R^3$= Et; R^1=Et, $R^2=R^3$=Et or Ph; $R^1=R^2$=Ph, $R^3=NMe_2$, etc.).[192]



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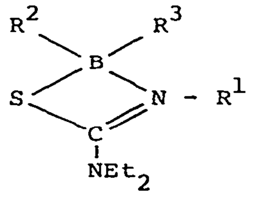
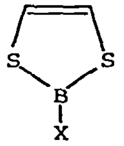
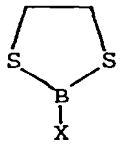


(60)

A series of boron-substituted 1,3,2-dithiaborols, (61a, where X=Me,Ph,Cl,Br,OMe,$OCMe_3$,SMe,$SCMe_3$, NMe_2, NEt_2, $N/SiMe_3)_2$), has been prepared by various routes. N.m.r. results suggest that this type of compound can be regarded as a 6π-electron system. Nevertheless, mass spectral behaviour shows considerable similarity to that of the saturated analogues (61b).[193]

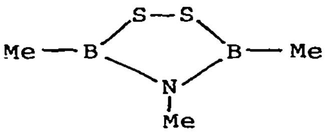


(61a)



(61b)

Crystal structures have been determined for (62) and (63); both contain planar ring structures, and can therefore be described



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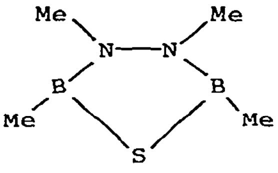

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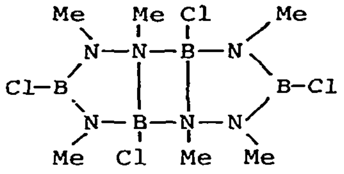
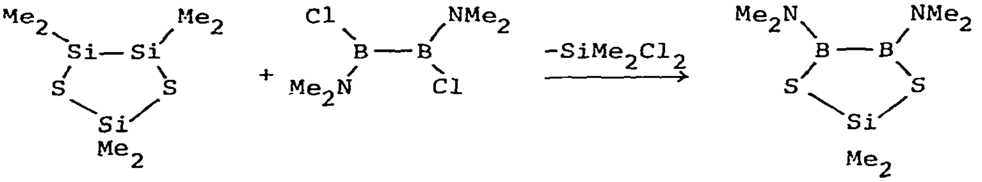


(64)

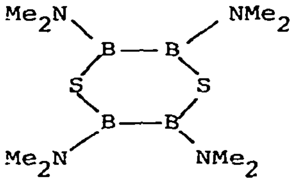
as five-membered 6π-electron systems. 3,5-Dichloro-1,2,4-trimethyl-1,2,4,3,5-triazaborolidine, however, is a tricyclic dimer in the solid state, (64).[194]

A new boron/sulphur/silicon heterocycle has been obtained by reaction (25). The product reacts with excess ClB(NMe$_2$)-B(NMe$_2$)Cl



...(25)

to form (65). An S$_2$Si$_4$ ring system, on reaction with PhBCl$_2$ gives (66).[195]



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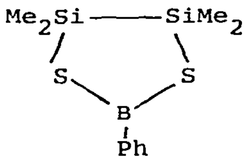
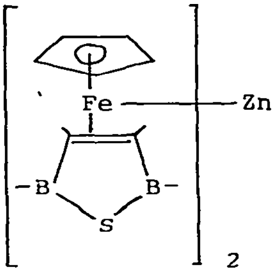


(66)

Reaction of [CpFe(C$_8$H$_{12}$)]$_2$Zn with 1,2,5-thiadiborolene gives (67). This in turn reacts with excess potassium metal to form (68), and this new anion reacts with MCl$_2$ (M=Fe or Co) yielding four-decker sandwich complexes.[196]



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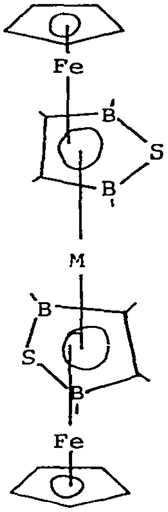

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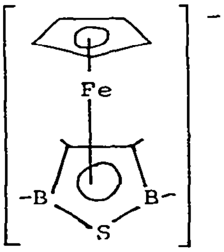
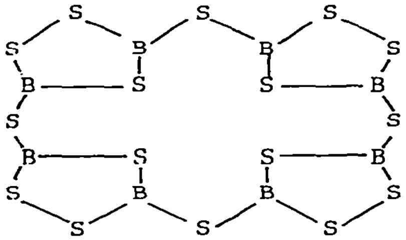


(68)

$(BS_2)_8$ is formed by fusion of a mixture of B_2S_3 and S_8 *in vacuo* at 100-300°C. X-ray analysis shows that it is a planar porphin-analogue, (70).[197]



(70)

3.1.10 Boron Carbides and Nitrides; Metal Borides

A detailed study of the crystal structure of $B_{13}C_2$ (which had revealed the presence of linear C-B-C units and distorted B_{12} icosahedra) has been followed by a determination of static deformation density maps for regions of interest in both units.[198]

$(B_{12})_4C_2Ti_{1.86}$ and $(B_{12})_4C_2V_{1.29}$ both form tetragonal crystals; space group $P4_2/nnm$.[199]

Boron nitride films have been obtained by pyrolysis of a variety of boron/nitrogen compounds (e.g. $i\text{-}Pr_2NBBr_2$, $(ClBNH)_3$ and Me_3NBF_3). Infrared results show that both hexagonal and cubic forms of BN are present, and that a lower pyrolysis temperature produces more of the cubic modification.[200]

Infrared spectra (200-1500cm^{-1}) have been reported for "$B_{12}P_2$" and "$B_{12}As_2$", and their ^{10}B-enriched analogues. The structures are in fact disordered, and about 10% the P or As atoms replaced by boron, compared to the ideal stoichiometry. A normal coordinate analysis was carried out, using the idealised atomic arrangement and a simple valence force field. The results were in reasonable agreement with experiment, including $^{10}B/^{11}B$ and P/As shifts.[201]

Electron spectra (i.e. ESCA; X-ray-excited Auger, or XAES; and electron-excited Auger, or EAES) have been reported for the iron borides FeB and Fe_2B. The surface compositions were the same as those for the bulk specimens. There are no significant binding energy shifts of the Fe or B ESCA core levels, compared to the free elements. There had therefore been no major charge transfers between Fe and B. This was confirmed by XAES and EAES. There was evidence for B-B bonding (covalent) in FeB, but the boron atoms appeared to be isolated in Fe_2B.[202]

It has been possible to rationalise the observed heats of formation of MB_2 (M=Sm,Gd,Lu,U or Al) in terms of the energy contributions from electron populations in various levels.[203]

A self-consistent band structure has been calculated for ZrB_2, using the Korringa-Kohn-Rostoker method. Extensive charge transfer was not needed to explain the observed properties of the compound, and considerable similarities were found with intercalated graphite.[204]

The ternary metal borides MRu_3B_2, where M=Ce,Pr,Nd,Sm,Gd,Tb,Dy, Ho,Er,Tm,Yb,Lu,Y,Th or U, crystallise with the $CeCo_3B_2$ type of structure. Above 300K typical M^{3+} paramagnetic Curie-Weiss behaviour was found for most systems.[205]

A crystal structure determination has been reported for LaB_2C_2. It forms tetragonal crystals, belonging to the space group $P\bar{4}2c$. The structure consists of two planar, infinite layers. Within the ordered B-C network, each atom is bonded to three other atoms giving aromatic-like, fused 4- and 8-membered rings. Each 4-

membered ring contains two borons and two carbons, in opposite positions. Each 8-membered ring contains (alternately) 4 borons and 4-carbons.[206]

ErB_4 has been studied by single-crystal neutron diffraction. At room temperature it crystallises with a UB_4 type of structure (space group P4/mbm).[207]

$SmFeB_4$ crystallises in the space group Pbam. It is a new ternary boride, of the $YCrB_4$ type. It is the first time that the positions of the boron atoms have been established crystallographically in such a structure.[208]

The crystal structure of $LaIr_4B_4$ has also been determined. It is tetragonal (space group $P4_2/n$) and isotypic with $NdCo_4B_4$. $ThIr_4B_4$ and $ThOs_4B_4$ are also isotypic with this, but URu_4B_4 and $UOsB_4$ crystallise with $LuRu_4B_4$-type structures.[209]

3.2. ALUMINIUM

3.2.1 Aluminium Hydrides

Theoretical calculations suggest that insertion of Al into H_2O to give HAlOH is exothermic by 38kcal mol^{-1} or more. Further, there exist reaction paths leading to HAlOH which are fully attractive, i.e. with no energy barrier.[210]

The electronic structure of the AlH_2Al bridge of the $(Me_2AlH)_2$ dimer has been calculated using an *ab initio* SCF procedure. Compared to diborane, the ionic, $Al^+ H_2^{2-} Al^+$ structures are more significant, in addition to the usual covalent, three-centre bonds.[211]

Ab initio molecular orbital calculations have been reported for $LiAlH_4$, in which the AlH_4^- anion is connected to the lithium by one, two or three hydrogen atoms. It was suggested that it is a structurally non-rigid molecule, with respect to the relative motion of the anion and cation.[212]

^{27}Al and ^7Li n.m.r. studies (in the concentration range 0.0075 to 3.75 molar) have been carried out on ether solutions of $LiAlH_4$. The aluminium signal only gives fine structure due to Al-H coupling at concentrations less than 0.15M. The chemical shift $\delta^{27}Al$ is only slightly concentration dependent, however. The results were consistent with multiple-ion formation at higher concentrations, with ion-pairs at lower concentrations.[213]

Electron diffraction experiments on gaseous $Al(BH_4)_2Me$ show that it is monomeric, with a planar $CAlB_2$ skeleton. The aluminium is five-coordinate, with bidentate BH_4 groups. The planes containing the Al(μ-H)$_2$B units depart from being normal to the CAlB$_2$ plane by approx. 5^o, i.e. the overall symmetry is C_2, not C_{2v}. The following structural parameters were determined: Al-C, 194.1(0.9)pm; Al-B, 215.2(1.6)pm; Al-H$_b$, 182.0(0.9)pm; B-H$_b$124pm; B-H$_t$, 120pm; B-Al-B, 121.5(0.7)^o; H$_b$-Al-H$_b$, 70.3 (0.4)^o.[214]

The crystal structure of Al, Zr-μ-hydrido-(triethylalumino)-[tri-(cyclopentadienyl)zirconium(IV)], Cp$_3$Zr-H-AlEt$_3$, has been determined. The crystals belong to the space group Pcmn, and the Zr-H$_\mu$ and Al-H$_\mu$ distances are 188,177pm. respectively.[215]

^{1}H, ^{7}Li, ^{13}C and ^{27}Al n.m.r. studies of lithium tert-butoxy-aluminates in THF solution have been carried out. The ^{7}Li results

$$3Li(\underline{t}BuO)_2AlH_2 \rightleftharpoons 2Li(\underline{t}BuO)_3AlH + LiAlH_4 \qquad \ldots (26)$$

were not very informative, but the others showed that Li($\underline{t}$BuO)AlH$_3$ does not exist in high enough concentration to be detected. The equilibrium (26) is set up, for which $K_{eq}=2.2 \times 10^{-2}$.[216]

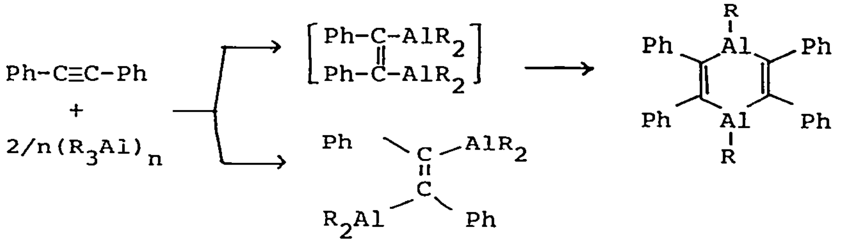
3.2.2 Compounds containing Al-C or Al-Si Bonds

Non-empirical quantum mechanical calculations have been carried out on AlCH$_3$, AlCH$_2$ and AlCH, thought to represent the simplest aluminium-carbon single, double and triple bonds. For AlCH$_3$ the Al-C single bond length is predicted to be 2.013Å (cf. 1.96Å in AlMe$_3$). For AlCH$_2$ and AlCH, however, the ground states do not contain Al=C or Al≡C bonds, but a simple single bond (AlCH$_2$) or a bond with only slight "multiple" character (AlCH). The Al=CH$_2$ and Al≡CH states were calculated to be 21kcal mol^{-1}, 86kcal mol^{-1} above these respective ground states. Dissociation energies were calculated as 68(AlCH$_3$), 77(AlCH$_2$) and 88(AlCH)kcal mol^{-1}.[217]

The crystal structure of [NMe$_4$][AlMe$_3$I] has been determined. The crystals belong to the space group Iba2, with bond distances: Al-C(1), 1.96(4)Å; Al-C(2), Al-C(3), 2.04(3)Å; Al-I 2.66(1)Å. The last is very close to the value found in AlMe$_2$I$_2^-$, and both are longer than in neutral Me$_3$N.AlMe$_2$I:2.58Å.[218]

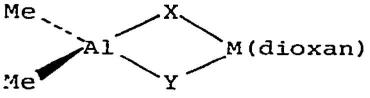
Triethylaluminium reacts with potassium in hexane at 20^{o}C to give the radical species Et$_3$AlK. At higher temperatures this forms an aluminate complex K[AlEt$_4$], via a radical dimer, [Et$_3$AlK]$^{\bullet}_2$.[219]

Trialkylaluminium compounds undergo photoreaction with dephenyl-acetylene, according to equation (27), where R=Et, iPr or iBu.[220]



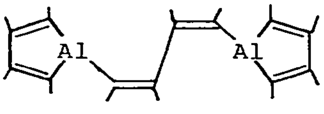
... (27)

Tricyclopropylaluminium dimer forms monoclinic crystals, space group $P2_1/c$. The $Al-C_t$ and $Al-C_{br}$ distances are as expected (1.944Å, 2.074Å respectively). The terminal and bridging cyclopropyl groups all have rather long $C_\alpha-C_\beta$, and short $C_\beta-C_\beta$ distances.[221]



(71)

The compounds $Me_2(MeC{\equiv}C)_2AlM$ (where M=Li or Na) and $Me_2(Me_3CC{\equiv}C)_2AlLi$ have been synthesised, which form stable 1:1 complexes with 1,4-dioxan. The latter are monomeric, with a strong covalent interaction between the alkali metal and the alkynyl groups (71, X,Y= same or different C≡CR groups), even in polar solvents.[222]



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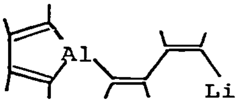

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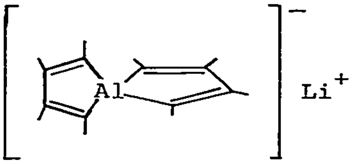
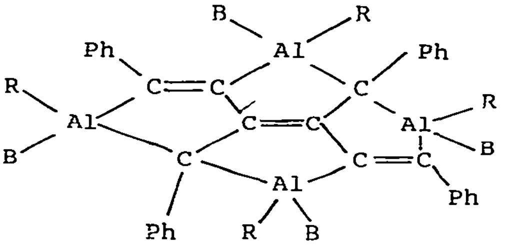


(73b)

Depending on the stoichiometry and the reaction conditions 1,2,3,4-tetraphenyl-1,4-dilithiumbutadiene reacts with aluminium trichloride to form (72) and (73). The latter is mainly present in the *spiro*-form, (73b).[223]

The new polycyclic aluminium compound (74), where B=THF or Et_2O; R=Me or Et, has been prepared by a series of reactions starting from 1,4-diphenylbutadiyne, dialkylaluminium halides and lithium.[224]



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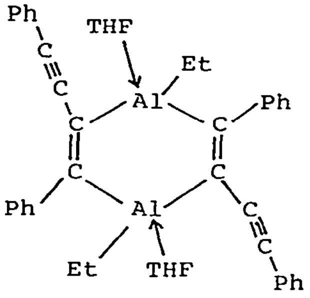
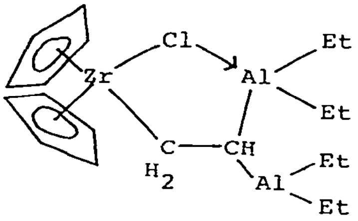


(75)

1,4-Diethylaluminyl-1,4-diphenyl-3-cumulene cyclises on u.v. irradiation to give the 1,4-dialuminacyclohexane derivative, (75).[225]

The complex (76) forms crystals belonging to the space group $P2_12_12_1$. The results confirmed the structure, which had been suggested on the basis of ^1H n.m.r. results.[226] It was possible to confirm the structure of di-(η^5-cyclopentadienyl)-2,2-bis(diethylalumino)-ethylzirconium cyclopentadienide, (77), by X-ray diffraction.[227]



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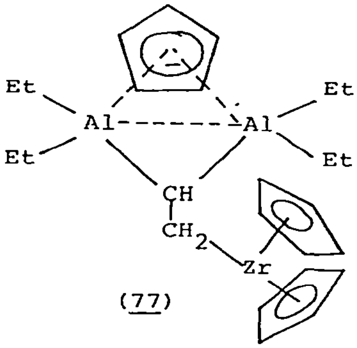


(77)

Tris(trimethylsilyl)aluminium, coordinated with Et_2O or THF, is formed by the treatment of chlorotrimethylsilane with aluminium and

$$Al + 3Me_3SiCl + 3Li \xrightarrow[65^\circ C,\ 7d]{THF/benzene} Al(SiMe_3)_3.THF + 3LiCl \quad ...(28)$$

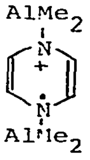
lithium in THF/benzene or Et_2O, in the presence of mercury, e.g. (28). The unsolvated compound can only be formed by the reaction of tetrakis(trimethylsilyl)-aluminate with aluminium chloride in pentane.[228]

The sodium or potassium salt of tetrakis(trimethylsilyl)-aluminate is formed by the reaction of M(=Na or K) with $Hg(SiMe_3)_2$ and $Al(SiMe_3)_3.Et_2O$, equation (29). The vibrational (infrared and Raman) and n.m.r. (^1H, ^{13}C) spectra were reported and discussed.[229]

$$2M + Hg(SiMe_3)_2 + Al(SiMe_3)_3Et_2O \xrightarrow[\text{pentane}]{Et_2O} M[Al(SiMe_3)_4] \quad \ldots(29)$$

3.2.3 Compounds containing Al-N or Al-P Bonds

Alkylaluminium compounds react with certain aza-aromatics and alkali metals to give persistent paramagnetic species, such as (78), which could be characterised by e.p.r.[230]



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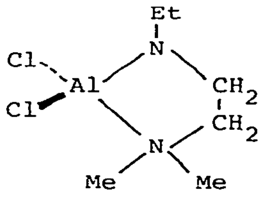
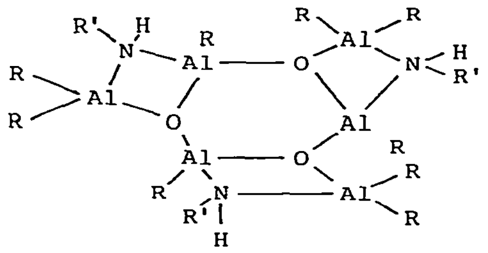


(79)

The crystal and molecular structures of (79), a neutral, chelated, four-coordinate aluminium compound, have been determined. Two types of Al-N bond were shown to be present; the $Al-N(Me_2)$ distance was 1.963Å (a typical single bond value), while the Al-N(Et) distance was 1.770Å. The latter showed that there is a significant π-interaction between the lone pair on the (planar) nitrogen and the aluminium.[231]

The stable new N-alkyliminoalanes, $[Me_2N(CH_2)_3N(AlH_2)_2]_2.THF$ and $[Me_2NCH_2(CH_3)CHN(AlH_2)_2]_2.THF$, have been prepared from $AlH_3.THF$ or $NaAlH_4$ and the corresponding amine (or its hydrochloride).[232]

3-Dimethylamino-n-propylamine, 2-dimethylamino-iso-propylamine and 3-methoxy-n-propylamine can be used to synthesis poly(*N*-alkyl-iminoalanes) by a variety of routes. They gave products with open cage structures even under drastic conditions involving direct reaction of hydrogen, the amine and aluminium metal.[233]



(80)

^1H, ^{13}C n.m.r. and i.r. spectroscopy and cryoscopy were used to study the organoaluminium amides, (80; R=Et, R'=CH_2Ph or Me; R=Me, R'=CH_2Ph), formed by the thermal decomposition of complexes of tetraalkylaluminoxanes with benzylamine or methylamine.[234]

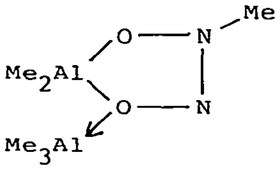
Aluminium, gallium and indium trimethyls react with equimolar amounts of phosphoric or phosphinic acid amides, $HN(Me)P(=Y)X_2$, where Y=O or S; X=F, Cl or Me, to give dimeric or monomeric dimethylmetal derivatives of the acids. The monomers were $Me_2M(S)PN(Me)Me_2$ - the others were dimeric. For the dimers $Me_2Al(Y=)PN(Me)Me_2$, the ^1H n.m.r. spectra could only be interpreted by assuming the presence of two structural isomers.[235]

3.2.4 Compounds containing Al-O or Al-S Bonds

Reaction between M(=Al,Ga or In) and N_2O in an argon matrix leads to the formation of MO species. The electronic spectra of these have been reported. The matrix shifts ($\nu_{gas}-\nu_{matrix}$) were determined in each case, and they decreased in the sequence Al>Ga>In. For the O-O transition ($B^2\Sigma \leftarrow X^2\Sigma$) the figures were $-1168cm^{-1}$ (M=Al), $-617cm^{-1}$(Ga), $-532cm^{-1}$(In).[236]

The Raman spectra of polycrystalline boehmite, γ-AlOOH, and its deuteriated analogue, together with previous infrared data, were said to be consistent with the recently discarded space group D_{2h}^{17} (Amam).[237] A separate report, however, comes down in favour of the space groups D_{2h}^{16} or C_{2h}^{5}.[238]

Al_2Me_6 and nitric oxide react to form (81), with triclinic crystals, space group $P\bar{1}$. The ONN(Me)O unit gives rise to a five-membered chelate ring, as shown, with the Me_3Al coordinated to the nitroso-oxygen. The position of maximum basicity at this position in the ring is confirmed by ab initio calculations. In the presence of bases, (81) rearranges to {AlMe[ONN(Me)O]$_2$}, with five-coordinate aluminium, and {Al[ONN(Me)O]$_3$}, with six-coordinate aluminium.[239]



(81)

Solubility was investigated in the $Al(OEt)_3$-$Ba(OEt)_2$-EtOH system at 20°C. Two congruently soluble complexes were found: $Ba[Al(OEt)_4]_2$, and crystalline $Ba_3[Al(OEt)_6]_2$.[240]

Tetra-alkylaluminoxanes, R_4Al_2O, where R=Me, Et or iBu, react with acetylacetone (Hacac) to form a variety of acetylacetonate derivatives. The acac ligand has a destabilising effect on the aluminoxanes (as the mixed derivatives disproportionate to $Al(acac)_3$) and so the stabilities lie in the sequence:

$R_4Al_2O > R_3(acac)Al_2O > R_2(acac)_2Al_2O \gg (acac)_4Al_2O$

The nature of R also affects the stability: i-Bu>Et>Me.[241]

Addition of tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)lanthanide(III), $Ln(fod)_3$, where Ln=La,Pr,Nd,Sm or Eu, to a benzene solution of tris(acetylacetonato)aluminium III, $Al(acac)_3$, enables ^{27}Al nuclear magnetic resonances due to free and complexed $Al(acac)_3$ to be seen at 25°C. Chemical exchange is slow on the n.m.r. time-scale, and the separation of the paramagnetic shifts into contact (CS) and pseudocontact (PCS) contributions implies a fairly large CS contribution, and that the hyperfine splitting constant of the aluminium is positive.[242]

A ^{13}C n.m.r. study of trans-tris(trifluoropentanedionato)-aluminium(III) was used to follow the fluxional behaviour of the β-diketonate complex. Free energies of activation ($\Delta G^{\ddagger}$) were calculated for the exchange of all the units in the molecule. All were very similar, suggesting that all the exchanges occur at comparable rates.[243]

The effects of temperature and concentration changes on the nuclear magnetic relaxation times of ^1H and ^{27}Al in the aluminium nitrate-hexamethylenetetramine system have been reported.[244]

Phase relationships were studied in the $Al(NO_3)_3$-$CsNO_3$-HNO_3-H_2O system at 25°C and HNO_3 concentrations of 10,20,30 and 40 mass %.[245] In addition, solubility measurements have been made on $Al(NO_3)_3$-$CsNO_3$-H_2O and $Al(NO_3)_3$-$CsNO_3$-HNO_3-H_2O systems at 50°C.[246]

$MAl(HPO_4)_2,H_2O$ (where M=K or Ag) have been synthesised. The structures and thermal changes (in the range 20-1000°C) were studied by infrared and ^1H n.m.r. spectroscopy. The decomposition products are $MAlP_2O_7$.[247] The compositions and properties of aluminium fluoride phosphates, $AlH_x(PO_4)F_x.nH_2O$ (from the H_3PO_4-$Al_2(SO_4)_3$-NH_4F-H_2O system at 80°C) have been determined. I.r. spectra were reported for the species with x=1, n=2 or 3.[248]

$M(PO_2F_2)_3$, where M=Al or Ga, can be prepared from the corresponding trihalides and difluorophosphoric acid. Infrared spectra and their physical properties show that both are polymeric.[249]

Stopped-flow Fourier-transform n.m.r. and conventional n.m.r. line-broadening experiments were used to determine rate data for DMSO exchange with the $[M(DMSO)_6]^{3+}$ (where M=Al or Ga) ions in nitromethane-d_3 solutions. Dissociative mechanisms were proposed in each case. When M=In, the exchange rate is too fast to follow, even at low temperatures.[250]

The reactions of $Na[Al(SO_3Cl)_4]$ with Lewis bases such as H_2O, NO_3^-, NO_2^- and F^- have been studied. In the first 3 cases, there is an analogy with the reaction of $Na(SO_3Cl)$, suggesting nucleophilic attack on the sulphur. In the last case the aluminium seems to act as an acceptor, to give AlF_4^- and SO_3Cl^-.[251]

Improved syntheses have been reported for $Al(ClO_4)_n^{(n-3)-}$, where n=4,5, or 6, i.e. reactions of anhydrous $HClO_4$ with stoichiometric mixtures of $AlCl_3$ and NH_4ClO_4 or $AlCl_3$ and NH_4Cl. The infrared and Raman spectra of $Al(ClO_4)_6^{3-}$ show only unidentate ClO_4^- groups. The other species have more complex spectra, and both uni- and bidentate ligands are present in each case. For $Al(ClO_4)_5^{2-}$ the structure is probably analogous to that of $Al(NO_3)_5^{2-}$, with one bi- and four unidentate ligands.[252]

Another review of methods for preparing aluminium perchlorato-complexes has appeared. The formation of $[AlCl_3(ClO_4)]^-$, $[AlCl_2(ClO_4)_2]^-$ and $[AlCl(ClO_4)_3]^-$ was detected by ^{27}Al n.m.r. in solutions containing Al^{3+}, Cl^- and ClO_4^-, in $CHCl_3$ or CH_2Cl_2. The infrared spectra of $[Al(ClO_4)_6]^{3-}$, $[Al(ClO_4)_5]^{2-}$ (as Li, Na or Ca salts) and $Al(ClO_4)_3.3L$ (where L=H_2O, THF or $MeNO_2$) were all interpreted in terms of the presence of only unidentate ClO_4^- groups. $Al(ClO_4)_3$ contained only bidentate ligands, while $[Al(ClO_4)_4]^-$ and $[Al(ClO_4)_5]^{2-}$ (as K,Rb or NH_4 salts) contain uni- and bidentate perchlorates.[253]

$Al(ClO_4)_3$ dissolves in CH_3COOH, $(CH_3CO)_2O$, CH_3OH or C_2H_5OH with complete replacement of ClO_4^- by solvent molecules. NOCl or N_2O_4 on the other hand, give nitrosyl perchlorate and an aluminium chloro- or nitrato-complex. In MeCN,THF and $MeNO_2$, the ClO_4^- groups remain coordinated to the aluminium, but are now unidentate. All three ClO_4^- groups are also unidentate in $Al(ClO_4)_3.3H_2O$. The complexes $(^nBu_4N)[Al(ClO_4)_4]$ and $(^nBu_4N)_2[Al(ClO_4)_5]$ were both prepared - both were soluble in $CHCl_3$ and CH_2Cl_2.[254]

Lithium tetrakis(thiocarbamato)aluminates were prepared as in equation (30), where X=O or S; Y=S; R=n-Pr, iPr, nBu, iBu, cyclo-

$$LiAlH_4 + 4\left[RNH_3{}^+RNCXY^-\right] \rightarrow Li\left[Al(XYCNHR)_4\right] + 4H_2 + 4RNH_2 \qquad \ldots(30)$$

C_6H_{11}, in dry Et_2O as solvent. Their infrared spectra contained bands as expected for metal monothio- and dithiocarbamates.[255]

Single crystals of $BaAl_{1.88}Mn_{0.12}O_4$ are hexagonal (space group $P6_3$-$C_6{}^6$), with a large unit cell (a=1043.4pm, c=879.4pm). The parent $BaAl_2O_4$ structure resembles that of $BaGa_2O_4$, but differs from it in having a unique tetrahedron orientation.[256]

The crystal structure of α-Al_2O_3 has been determined at 300K and 2170K. There are significant changes with temperature in the positional parameters of the aluminium atoms, but only slight changes in those of the oxygen atoms. At 2170K the aluminium atom moves towards the vacant octahedral hole between oxygen layers, and the distorted hcp plane of oxygen atoms becomes more regular.[257]

An X-ray powder diffraction examination of $Rb_2[M_2O(OH)_6]$, where M=Al or Ga, showed that both are orthorhombic, with probable space group Aba2.[258] $NaAl_3(OH)_6(CrO_4)_2$ forms rhombohedral crystals, belonging to the space group $R\bar{3}m$. It is isomorphous with the Fe(III) analogue - i.e. it possesses the alunite structure.[259]

The crystal structure of $(H_3O)[Al_3(H_2PO_4)_6(HPO_4)_2].4H_2O$ contains layers consisting of AlO_6 octahedra sharing vertices with $O_2P(OH)_2$ and $O_3P(OH)$ tetrahedra. The spaces between the layers are occupied by H_3O^+ ions, while the H_2O molecules are held between neighbouring layers (by hydrogen bonds).[260]

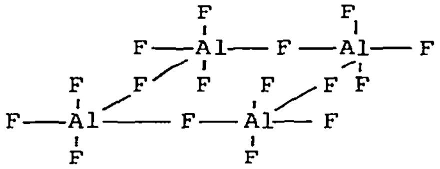
The formation of sodium polyaluminate (β-alumina) in $Al(OH)_3$/Na_2CO_3/NaF mixtures was studied by X-ray diffraction, DTA-TG and mass spectrometry. Replacement of $CO_3{}^{2-}$ by F^- leads to the disappearance of monoaluminate and the β'' phase from the reaction products rich in sodium.[261]

3.2.5 Aluminium Halides

Mass and i.r. spectra and X-ray data suggest that the phthalocyanines AlPcF and GaPcF are polymeric, with $(M$-$F)_x$ backbones. AlPcCl, AlPcBr, AlPcI, GaPcCl and InPcCl are all monomeric.[262]

A fluoride-sensitive electrode has been used to study complex formation in the $Al(EDTA)$-F^--H_2O system. The mixed complex $AlF(EDTA)^{2-}$ was identified, and shown to have a stability constant of $(5.5\pm0.6)\times10^4$ at 25°C and I=0.2.[263]

Single crystals (tetragonal, $I\bar{4}c2$) of β-$RbAlF_4$ have been prepared by hydrothermal synthesis. The structure is closely related to that of tetragonal tungsten bronze, being built up from two $[AlF_{4/2}F_2^{-}]_\infty$ layers of AlF_6 octahedra connected by 4 corners. At 588K the crystals undergo an irreversible transformation to the stable α-form. This involves concerted $\pi/4$ rotation of four-octahedra groups about the c axis.[264]



(82)

"$Ba_3Al_2F_{12}$" turns out to be $Ba_6[(F_4AlF_{2/2})_4]F_4$, where the tetrameric anion has the structure (82). This is the first example of such a structure in an aluminium-containing species.[265]

$AlX_3.2MeCN$ (where X=Cl or Br) are isomorphous and can be formulated as $[Al(MeCN)_5X]^{2+}[AlX_4]_2^{2-}.MeCN$. Skeletal vibrational assignments were proposed for the cations, based on analogy with $Al(MeCN)_6^{3+}$, and from data obtained by H/D substitution. The compounds $AlX_3.1.66MeCN$ (X=Cl or Br) were also prepared; their spectra suggest they are simply non-solvated analogues of the above.[266]

The e.m.f.'s of concentration cells with chloroaluminate melts have been estimated. There remains a great need for experimental measurements of transport numbers in such melts, especially those with organic cations.[267]

Raman studies on LiCl-CsCl and $CsCl$-$AlCl_3$ melts show that chloroaluminate and sulphide ions react at about 400°C at a 1:1 ratio to form clear solutions. The glassy compound $(CsAlSCl_2)_\infty$ was isolated. The possible existence of homologous chain-like ions $Al_nS_{n-1}Cl_{2n+2}{}^{n-}$ $(n>3)$ was proposed, together with $[AlSCl_2]_n^{n-}$ (for large n only). The ions give a strong, polarised Raman band near 325cm^{-1}, assigned to stretching of $AlCl_2$-S-$AlCl_2$ units. In neutral and acidic chloroaluminate melts the ions dissociate to form dissolved species $[Al_nS_{n-1}Cl_{2n+2-m}]^{(n-m)-}$, and solid AlSCl. The solutions give a polarised Raman band at 292cm^{-1}, due to the doubly-bridged $>\mathrm{Al}<^{\mathrm{S}}_{\mathrm{Cl}}>\mathrm{Al}<$ unit.[268]

Raman spectra were obtained for nine molten $SbCl_3/AlCl_3$ mixtures (and the pure components), together with three $AlCl_3/NaCl/SbCl_3$ mixtures. The $AlCl_3$ melt contains Al_2Cl_6 (D_{2h}) units. There was no evidence for $SbCl_2^+$ or $AlCl_4^-$ in the mixed melts.[269]

Infrared spectra have been reported for acidic and basic aluminium chloride/1-butylpyridinium chloride melts at room temperature. $AlCl_4^-$ modes show a splitting of ν_3, i.e. the T_d ions are distorted in the melt. In a 2:1 molar ratio melt $Al_2Cl_7^-$ bands are seen, and they are consistent with the presence of a bent Al-Cl-Al bridge.[270]

A(I)M(III)Cl_4 (where A(I)=Cs,Rb,In,Tl,NH_4; M(III)=Al or Ga) are prepared by heating 1:1 mixtures of ACl and MCl_3 in glass ampoules. All crystallise with the barytes structure.[271]

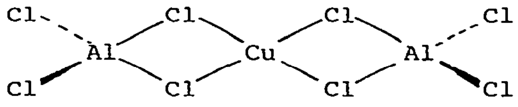
Single crystals of $LiAlCl_4.3SO_2$ are orthorhombic (space group Pnam). The structure is built up of parallel $Li(SO_2)_{6/2}$ chains, with almost ideal tetrahedral $AlCl_4^-$ in the intervening spaces. The structure is closely related to that of $LiClO_4.3H_2O$.[272] The crystal structure of $NaAlCl_4$ (space group $P2_12_12_1$) has been further refined, to give improved R values. The data were used to assign Raman spectra of polycrystalline and single crystal samples of this compound.[273]

The equilibrium (31) has been studied. Measurements on

$$CuCl_2(s) + Al_2Cl_6(g) \rightleftharpoons CuAl_2Cl_8 \qquad \ldots \ (31)$$

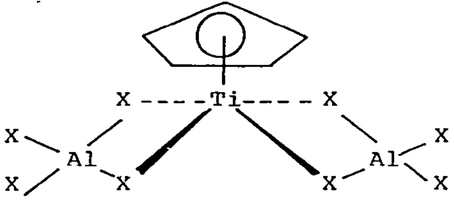
$CuAl_2Cl_8$ as a solid-phase confirmed this formula for the gaseous molecule. However, small amounts of $CuAlCl_5$ and $CuAl_3Cl_{11}$ were also present in the gas phase.[274]

Crystals of $CuAl_2Cl_8$ have been prepared. They are monoclinic (space group $P2_1/c$), and contain square planar Cu(II), as shown in (82), although there are two more distant chlorines, giving a distorted octahedral arrangement. The coordination at Al is approximately tetrahedral ($Al-Cl_t$=2.08Å; $Al-Cl_{br}$=2.20Å).[275]



(83)

Electronic absorption spectra have been reported for the vapour phase complexes formed by $ErCl_3$ and MCl_3 (where M=Al, Ga or In). They gave no conclusive results as to the identities or the structures of the complexes.[276]



(84)

$CpTiCl_3$ reacted with two equivalents of ethylaluminium compounds to form trinuclear complexes $CpTiAl_2Cl_{8-x}Et_x$ (x=1-4). These were characterised by their e.p.r. and visible (d-d) spectra. All had the general form (84).[277]

A mass-spectrometric study of the equilibrium (32) in the gas

$$2Al_3Cl_9 \rightleftharpoons 3Al_2Cl_6 \qquad \ldots (32)$$

phase gave the following results: $\Delta H^o(298)=10.1$ kcal.mol^{-1}; $DS^o(298)=40.8$ cal.mol^{-1}K^{-1}. The gas phase above Al_2Cl_6 at its sublimation point contains 1 mol.% of Al_3Cl_9.[278]

$CoAl_3Cl_{11}$ (as its molecular ion) has been directly observed for the first time by mass spectrometry. Measurements of the

$$CoCl_2(S) + 1.5Al_2Cl_6(g) \rightleftharpoons CoAl_3Cl_{11} \qquad \ldots (33)$$

equilibrium (33) gave the following thermodynamic data: $\Delta H^o(556)=+2.9$ kcal.mol^{-1}; $\Delta S^o(556) = -4.8$cal.mol.$^{-1}$K^{-1}.[279]

Conductivity studies on the $AlBr_3$-CH_3CN system (at 25°C,

$$2AlBr_3 + 4CH_3CN \rightleftharpoons AlBr_2(CH_3CN)_4^{2+} + AlBr_4^- \qquad \ldots (34)$$

and H_2O concentrations in the range $4x10^{-3}$ to 10^{-2}mole/l.) have been carried out. The dissociation mechanism (34) was able to rationalise the observations.[280]

3.2.6 Intermetallic Phases containing Aluminium

Mn_4Al_{11} is triclinic (space group $P\bar{1}$), and its structure contains layers of Mn and Al atoms. The Mn-Al and Al-Al distances were very short - both within and between the layers.[281]

The new phases $Pd_{2.4-2.9}Al$, $Pd_{2.99-3.3}Al$, $Pd_{3.8-4.15}Al$ were prepared from molten mixtures, with subsequent annealing at 600°C, or by reaction of the elements in the presence of I_2 at 600°C.

They were identified by X-ray powder diagrams. The existence of Pd_5Al_3 was confirmed, and the new compound Pd_5AlI_2 also prepared. The latter had a tetragonal layer structure (space group I4/mmm), and was a metallic conductor, with preferred conductivity parallel to the layers.[282]

$Al_xCu_2Mg_{12-x}Si_7$ (or h-AlCuMgSi) forms crystals with a disordered structure. The probable idealised space group is $P6_3/m$, but the data could be explained by the space group $P\bar{6}$.[283]

X-ray investigations of several samples in the U-Cu-Al system showed the presence of two new disordered ternary phases: U_2Cu_3Al (hexagonal; $P6_3/nmc$; $MgZn_2$ type); and $UCuAl_2$ (tetragonal; I4/mmm; variant of $TiAl_3$ type).[284]

3.3 GALLIUM

3.3.1 Compounds containing Ga-C or Ga-Si Bonds

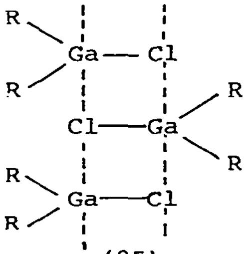
Raman, infrared, ^1H and ^{13}C n.m.r. spectra have been reported for $Ga(CH=CH_2)_3$, $In(CH=CH_2)_3$ and related species. Molecular association *via* vinyl bridges, using a π-complex type of linkage can be ruled out. In $(CH_2=CH)_2MX$, (X=Cl, OMe or C≡CMe), only terminal vinyl ligands are present.[285]

Various base adducts of $EtGaFe(CO)_4$, i.e. $B_n(Et)GaFe(CO)_4$, have been prepared. Where n=1, B=THF, the compound is dimeric, but for n=1, B=bipy or TMEDA, n=2, B=py, they are monomers. All contain four-coordinate gallium and 5- or 6- coordinate iron.[286]

$Ga(CH_2SiMe_3)_3$ can be prepared from $GaCl_3$ and Me_3SiCH_2MgCl in ether solution. It is a monomer in benzene solution, and acts as a weak Lewis acid. Et_2GaI and CH_2N_2 react together with Me_3SiCH_2MgCl in ether to produce $Et_2Ga(CH_2SiMe_3)$.[287]

A new series of neutral organogallium(III) compounds has been prepared: $Ga(CH_2SiMe_3)_nX_{3-n}$, where X=Cl or Br, n=3,2, or 1. All were characterised by various analytical and spectroscopic techniques. The parent compound (n=3) was made as described in the previous reference; the halo-derivatives were made from it by elimination reactions with HCl or HBr and by exchange reactions with $GaCl_3$ or $GaBr_3$. The compounds with n=2, X=Br or n=1, X=Cl or Br are dimers; that with n=2, X=Cl is a polymer. Apparently the structure of the last is unusual. Two possibilities are a "ladder" polymer, (85), and a linear arrangement, (86).[288]

(Trimethylsilyl)methyl gallium(I) compounds have also been reported: $MGa(CH_2SiMe_3)_2$ (where M=Na or K) and $MGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$ (where M=Li or Na). They were characterised by elemental



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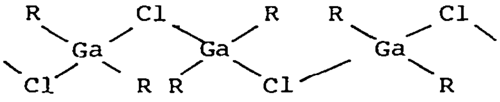


(86)

analysis, cryoscopy, infrared, ^{1}H and ^{13}C n.m.r. spectroscopy. They are of a novel type, incorporating low-oxidation-state main group metal anions. The reactions to give them seem to involve a reductive elimination between $Ga(CH_2SiMe_3)_3$ and alkali metal hydrides. They appear to contain covalent units: $[KGa(CH_2SiMe_3)_2]_2$, $[NaGa(CH_2SiMe_3)_2]_3$ and $[LiGa(CH_2SiMe_3)_2.MeOC_2H_4OMe]_x$.[289]

Another new compound to be reported is $Ga(SiMe_3)_3$. This is made by the thermal decomposition (on sublimation) of $Li[Ga(SiMe_3)_4].xEt_2O$, which is in turn made by reaction (35). The Raman spectrum of $Ga(SiMe_3)_3$ contains bands at 312 cm^{-1} ($\nu_s GaSi_3$) and 349 cm^{-1}

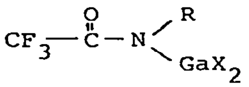
$$5Li + 4Me_3SiCl + Ga \xrightarrow[-4LiCl]{Hg/Et_2O;14d} Li[Ga(SiMe_3)_4].xEt_2O \quad ...(35)$$

($\nu_{as} GaSi_3$). Only the latter has an infrared counterpart - consistent with the presence of a planar $GaSi_3$ skeleton.[290]

3.3.2 Compounds containing Ga-N Bonds

A detailed study has been made of the microwave spectrum of trimethylaminegallane, using the following isotopic variants: $(CH_3)_3{}^{14}N^{69}GaH_3$, $(CH_3)_3{}^{14}N^{71}GaH_3$, $(CH_3)_3{}^{15}N^{69}GaH_3$, $(CH_3)_3{}^{15}N^{71}GaH_3$, $(CH_3)_3N^{14}N^{69}GaD_3$ and $(CH_3)_3{}^{14}N^{71}GaD_3$. r_s was found to be 2.111 ± 0.002Å for the Ga-N bond. Infrared and Raman spectra were also recorded for $(CH_3)_3NGaH_3$, $(CH_3)_3NGaD_3$ and $(CH_3)_3{}^{15}NGaH_3$ in the solid state at low temperatures. These could be interpreted satisfactorily by assuming C_{3v} symmetry. A normal coordinate analysis showed that the Ga-N stretch and the NC_3 symmetric deformation were extensively mixed, and that the Ga-N stretching force constant was 2.44 mdyn.Å^{-1}.[291]

Gallium trichloride or tribromide reacts with 2,6-dimethyl- or 2,4,6-trimethyl-N-trimethylsilyltrifluoroacetonilide to form (87), where X=Cl or Br; R=$2,6-Me_2C_6H_3$ or $2,4,6-Me_3C_6H_2$. Interesting by-products are (88). The formation and reactions of a number of other aminogallanes were described.[292]



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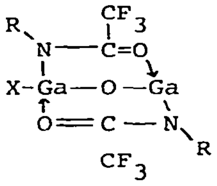

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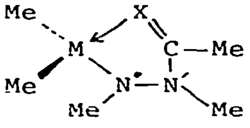
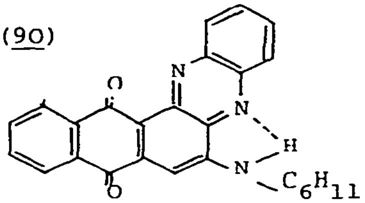


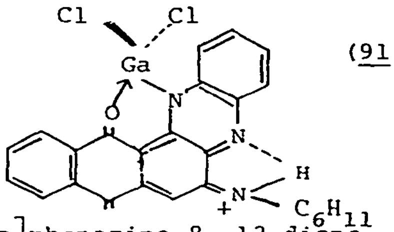
(89)

Trimethylgallium and -indium react with N',N"-dimethylacethydrazide and N',N",N'"-trimethylacetimido hydrazine respectively, to give (as a first step) monomeric dimethylmetal compounds, with five-membered skeletons, (89, M=Ga or In; X=O or N'"Me). These immediately add a further alkyl-metal molecule. ^{1}H n.m.r., infrared and Raman spectra were presented and discussed, and the structures were confirmed by X-ray diffraction.[293]

N.m.r. studies of interactions of Ga(III) with the antibiotic bleomycin showed that the metal displaces a proton from the α-amino group of the diaminopropionamide fragment of the drug.[294]

(90)

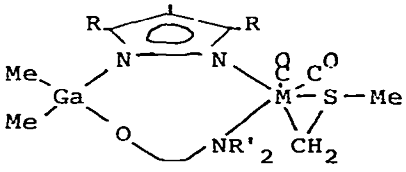




(91)

6-Cyclohexylaminonaphtho[2,3-a]phenazine-8, 13-dione, (90, =L) forms a complex (GaCl$_3$)$_2$L. Infrared and electronic spectra, and conductivity measurements show that it is ionic in type, and the possible structure of the cation is (91).[295]

Molybdenum and tungsten carbonyl complexes containing the bidentate chelating thiomethoxymethyl group and tridentate chelate gallate ligands have been prepared and characterised, (92, M=Mo or W; R,R'=H,Me). The crystal structures of the complexes where R=H or Me, R'=Me were determined; the metal atoms are seven-coordinate, as shown.[296]



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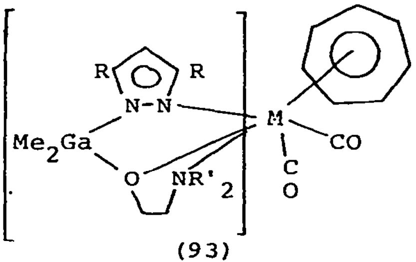
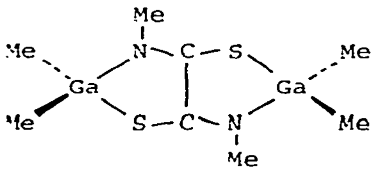


(93)

The preparation and physical properties of octahedral and trigonal bipyramidal complexes containing tris-chelating ligands $[Me_2Ga(N_2C_5H_7)(OCH_2CH_2NR'_2)]$ where R'=H or Me have been described. Thus, [dimethylbis(3,5-dimethyl-1-pyrazo gallato-(N(2),N'(2))]-[dimethyl-(3,5-dimethyl-1-pyrazolyl)(N,N-dimethylethanolamino-(gallato(N(2),O,N(3))]nickel(II) forms triclinic crystals, space group P$\bar{1}$. The coordination about the nickel is distorted trigonal bipyramidal, with two nitrogens from the $Me_2Ga(N_2C_5H_7)_2$ ligand in equatorial positions.[297]

Cycloheptatrienyl molybdenum and -tungsten dicarbonyl complexes including dimethyl(1-pyrazolyl)(ethanolamine)gallate ligands have been prepared, (93, M=Mo or W). They are monomeric, and pseudo-octahedral at the metal. The organogallate ligand is so arranged as to give *fac*-bonding, while the C_7H_7 ring is η^3-coordinated and fluxional.[298]

Trimethylgallium and N,N-dimethyldithio-oxamide react to give a 2:1 complex, as two configurational isomers. ^1H n.m.r. and vibrational spectra were used to characterise these as (94), the E-form, and (95), the Z-form. Both contain planar, fused five-membered ring systems.[299]



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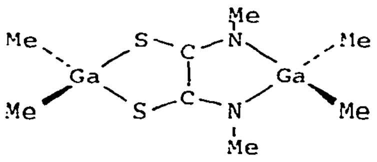


(95)

3.3.3 Compounds containing Bonds between Gallium and Elements of Group 6

Infrared spectra have been obtained for alkali metal metagallates, $MGaO_2$(M=alkali metal), together with those for the lower gallates $Li_2O.5Ga_2O_3$ and $M_2O.6Ga_2O_3$ (M=Na,K,Rb or Cs). Some assignments were proposed.[300]

$Ba[Ga(OH_2)_2O]_2$ forms monoclinic crystals; thermography shows that its thermal stability is less than that of the corresponding aluminium compound. νGaO infrared bands were assigned.[301]

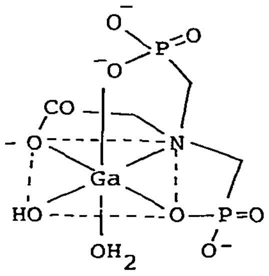
Crystals of V_2GaO_5 (i.e. V(III)V(IV)GaO_5) are monoclinic, space group C2/m. The structure is built up of β-Ga_2O_3-like columns of GaO_4 tetrahedra (containing all of the gallium atoms) and VO_6

octahedra parallel to the c axis.[302]

The Ga_2O_3-Li_2O-SiO_2-H_2O system has been studied, revealing the existence of a lithium gallium hydroxide silicate with a 2:1 layer structure. This was described by the crystal chemical formula: $Li_{2x+y}\{Ga_{2-x}Li_x[Si_{4-y}Ga_yO_{10}](OH)_2\}.nH_2O$, where x=0.6 to 0.8; y=0.3 to 0.1.[303]

It is possible to carry out an estimation of gallium, as the salicylato-complex $[Ga(C_6H_4OCOO)_3]^{3-}$, by means of square-wave polarography.[304]

Stability constants, chelate protonation constants, hydrolysis constants and formation constants have been determined by potentiometric measurements on aqueous solutions containing gallium(III) and one of ten multidentate ligands containing combinations of phosphonate, acetate, phenolate and tertiary amine donor groups. In some cases it was possible to infer probable coordination sites and the stereochemistry of metal-ligand interactions, e.g. with glycine-N,N-bis(methylenephosphonic acid), $(=H_5L)$, the species formed appears to be (96).[305]



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Equilibria between Ga(III) and the 5-nitrososalicylate anion (HA^-) have been investigated by spectrophotometry in acid solutions (pH 1 to 2.5). Two complexes were identified, with formation constants: $K_1 = \frac{[GaA^+][H^+]}{[Ga^{3+}][HA^-]} = 49 \pm 2\ dm^3\ mol^{-1}$, $K_1' = \frac{[Ga(HA)^{2+}]}{[Ga^{3+}][HA^-]} = 500 \pm 55\ dm^3 mol^{-1}$. both at 25°C and I=0.1 mol. dm^{-3}. The kinetics of formation and decomposition were determined by a temperature jump method.[306]

Sodium and mixed ammonium/sodium salts of cupro(II)- and mangano (II) undecatungstogallate(III) have been prepared e.g. $(NH_4)_{6.5}Na_{0.7}[H_{1.8}CuO_6GaO_4W_{11}O_{30}]$. X-ray structural studies are in agreement with a Keggin-type structure for both of the heteropolytungsten anions.[307] Several salts have been isolated which contain the nickel(II) undecatungstogallate(III) anion, $[H_{2.1}NiO_6GaO_4W_{11}O_3]^{6.9-}$. Single-crystal X-ray structural studies for the NH_4/Na salt shows that this anion also possesses a Keggin-type structure.[308]

The crystal structure of $Ba_xTi_{8-2x}Ga_{10+2x}O_{31}$ has been studied by high-resolution (3Å) electron microscopy. The tunnel structure contains elements of the hollandite, rutile and β-gallia structures, intergrown coherently to give a tetragonal unit cell.[309]

MGa_2S_4 (where M=Ca,Sr or Ba) are formed by heating the corresponding oxogallates with H_2S. The calcium and strontium compounds from orthorhombic, the barium cubic crystals. It is also possible to form $M_3Ga_2S_6$.[310]

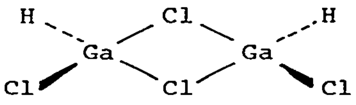
$Pb_2Ga_2S_5$ forms orthorhombic crystals (space group Pbca). The sulphur atoms are in positions of four- and five-fold, the Pb in eightfold, and the Ga in four-fold coordination. The structure is built up of alternate sheets: one built up of GaS_4 tetrahedra, the other with the formula $(PbS)_n$.[311]

The Cd-Ga-Se system has been studied - the CdSe-GaSe, $CdGa_2Se_4$-GaSe and CdSe-Ga sections. The last is not quasibinary (due to the formation of GaSe and Cd).[312] The phase diagram of the Cl-Ga-Te system has been constructed: the compound $GaCl_3.TeCl_4$ was identified.[313]

3.3.4 Gallium Halides

M.O. calculations on third-row main group compounds, including GaF_3 and GaH_3 show that an STO-3G basis set gives good agreement with experimental equilibrium geometries. The smaller STO-2G set was not nearly so good.[314]

Infrared and Raman spectra of "$HGaCl_2$" (and the deuterio-analogue) show that it is a dimer, with all the hydrogens terminal. The number of bands suggests that the arrangement is cis-, i.e. (97). νGaH is seen at 2047cm^{-1} (1465cm^{-1} for νGaD), compared to bridging νBH near 1600 cm^{-1} - showing the absence of bridging hydrogens.[315]



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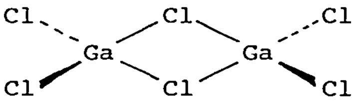


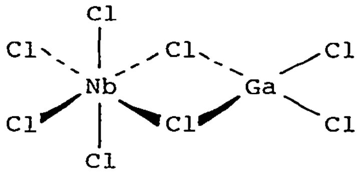
(98)

N.q.r. spectra have been reported for $GaCl_3$. ^{35}Cl and ^{37}Cl each give three lines, ^{69}Ga and ^{71}Ga one line each, confirming the symmetrical dimer structure (98).[316]

Electrochemical studies of the chloride donor-acceptor properties of $GaCl_3$ and $InCl_3$ have been made. Both formed $HECl_4$(E=Ga or In) in THF or 1,2-dimethoxyethane - they reacted as strong acids in both solvents.[317]

$KGaCl_4$ exists in three enantiotropic forms: $KGaCl_4$-I - stable below -25°C; -II, stable from -25°C to 130°C ($KAlCl_4$ type of structure); -III, stable from 130°C to 259°C (m.pt.).[318]

Tensimetric studies have been made of the $GaCl_3$-PCl_5 system. There was no evidence for $GaCl_3.PCl_5$ in the gas phase. The thermodynamic characteristics of dissociation of crystalline $GaCl_3.PCl_5$ into gaseous $GaCl_3$, PCl_3 and Cl_2 are: $\Delta H^o_T = 73.5$ kcal.mol^{-1}; $\Delta S^o_T = 99.6$ e.u.[319]



(99)

The Raman spectra of molten and solid $NbCl_5.GaCl_3$ show that it is present as a discrete molecule in the solid and in the melt just above the melting point. The structure appears to be (99), i.e. an octahedron and a tetrahedron sharing an edge. Increased temperature lead to dissociation into the components (Nb_2Cl_{10} and Ga_2Cl_6).[320]

3.3.5 Intermetallic Phases containing Gallium

The new intermetallic compound K_3Ga_{13} is orthorhombic (space group Cmcm). The structure can be described in terms of a packing of two types of polyhedron (one with 11, the other with 12 gallium atoms), linked in a non-compact fashion, with the potassium atoms in the resulting holes.[321]

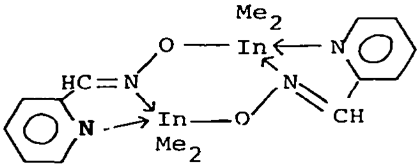
A new metastable phase, $MgGa_2$-m, is formed by solidification of a supercooled Mg/Ga liquid alloy; it is isotypic with $CaIn_2$. The phase diagram of the Mg-Ga system was corrected.[322]

A study of the gallium-rich sides of the systems Nd-Ga and Ce-Ga revealed new compounds MGa_6 (where M=Nd or Ce). Both are tetragonal, with lattice parameters: (M=N'd) a=5.996Å, c=7.620Å; (M=Cl) a=6.03Å, c=7.632Å.[323]

3.4. INDIUM

3.4.1 Compounds containing In-N Bonds

Dimethylindium-pyridine-2-carbaldehyde oximate forms orthorhombic crystals, space group Pbcn. The molecular structure is (100) i.e. a dimer, consisting of five fused rings, of which the central one is an InONInON unit. The indium is five-coordinate, with a distorted trigonal bipyramidal form.[324]



(100)

Electrochemical oxidation of anodic indium in non-aqueous media containing a halogen can give either InX_3 (X=Cl,Br or I) or the adducts of the trihalides with neutral ligands (depending on the solute present). Details for the preparation of the MeCN, py, 2,2'-bipy and PPh_3 adducts were given. The vibrational spectra of $InX_3.3MeCN$ (where X=Cl or Br) were consistent with the presence of the fac-InX_3N_3 isomers. For $InI_3.2MeCN$, the data indicated the probable formation of $[InI_2(MeCN)_4]^+[InI_4]^-$.[325]

The first crystal and molecular structure determination of an indium pophyrin has been reported, for (5,10,15,20-tetraphenylporphinato)indium(III) chloride. It forms monoclinic crystals, space group $P2_1/n$. The In is five-coordinate, square pyramidal, with the chlorine as the axial ligand. Bond distances are: In-N(mean); 2.156(6)Å; In-Cl, 2.369(2)Å. The porphinato-core is somewhat expanded (average radius 2.067(3)Å). The macrocycle is non-planar, with the amount of "doming" similar to that for the Fe(III) high-spin porphyrins.[326]

A potentiometric study of equilibria in the systems $In(NTA)_2^-$-$In(EDTA)X_2$ ($X=SCN^-$, $S_2O_3^{2-}$, SO_3^{2-}, NO_3^-, NH_3), and NTA=nitrilotriacetate ion, established that the mixed dinuclear complexes $[In(EDTA)X_2](EDTA)$ are formed.[327]

Methyl(tetraphenylporphinato)indium(III), In(Me)(tpp), is monoclinic (space group $P2_1/c$ or $P2_1/a$). The indium forms a square based pyramid, with In-N, 2.06(1)Å, In-Cl, 2.13(1)Å. The In atom lies 0.78(2)Å and 0.92(2)Å from the plane of the four nitrogens and from the porphinato plane respectively. These are the highest values found in metalloporphyrin chemistry.[328]

Indium(III) complexes have been prepared with salicylidene aromatic Schiff bases. The large molar absorbance of the 1:2 In(III) complex with salicylidene-o-hydroxyquinoline can be used to determine micro-amounts of In (down to 0.57 g ml^{-1}).[329]

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

The equilibrium between In_2O_3 and gaseous Cl_2 has been studied at temperatures from 500°C to 700°C. The temperature dependence of the equilibrium constant is given by the expression: $\ln K_e = 2.34 - (2550/T)$.[330]

The vibrational spectra of the double oxides $^{40}CaIn_2O_4$ and $^{44}CaIn_2O_4$ have been studied. The isotopic shifts enabled νInO and νCaO modes to be differentiated.[331] A number of barium indates were isolated from the BaO-In_2O_3 system: $Ba_5In_2O_8$, $Ba_3In_2O_6$, $Ba_2In_2O_5$, $Ba_4In_6O_{13}$ and $BaIn_2O_4$. Their vibrational spectra were reported, and for $BaIn_2O_4$ it was suggested that the indium was five-coordinate.[332]

$In(acac)_3$ forms orthorhombic crystals (space group Pbca). They are isomorphous with $Fe(acac)_3$, with an average In-O distance of 2.132(8)Å, and an O---O ligand "bite" distance of 2.905(8)Å.[333]

Solubility has been investigated in the $In(NO_3)_3$-HNO_3-H_2O system at 20°C, 30°C, 40°C and 50°C. The heat of solution of $In(NO_3)_3$

$$In(NO_3)_3.4.5H_2O \xrightarrow{119^{\circ}C} In(NO_3)_3.3,25H_2O \xrightarrow{160^{\circ}C} (In_2O(NO_3)_4.H_2O$$
$$\xrightarrow{188^{\circ}C} In_2O(NO_3)_4 \xrightarrow{220^{\circ}} InO(NO_3) \xrightarrow{>243^{\circ}C} In_2O_3 \quad ...(36)$$

in water is : $\Delta H_d^{298} = -7.15 \pm 0.21 kJ\ mol^{-1}$, while the thermal decomposition of hydrated indium nitrate follows the scheme (36).[334]

The low-temperature form of $(NH_4)_3In(SO_4)_3$ is monoclinic, space group $P2_1/c$. The indium atoms have distorted octahedral coordination, with an average In-O distance of 2.125Å. These units are linked to give $In(SO_4)^{3-}$ columns of pseudo-trigonal symmetry.[335]

In_2O_3 or $In(NO_3)_3.5H_2O$ both react with V_2O_5 to form only one indium vanadate, $InVO_4$. This was found to have three crystalline modifications, with transformation temperatures: $InVO_4$(amorphous)

$\xrightarrow{541^{o}C}$ $InVO_4$(I) $\xrightarrow{682^{o}C}$ $InVO_4$(II) $\xrightarrow{716^{o}C}$ $InVO_4$(III). The last melts incongruently at 1134°C. Thallium(III) gives $TlVO_4$ in only one form, isotypic with $InVO_4$(III).[336]

The low-temperature form of $InVO_4$ forms orthorhombic crystals (space group Cmcm). The structure is built up of chains of InO_6 octahedra, linked by VO_4 groups. The 6 oxygen atoms are all at 2.160Å from the indium, but the InO_6 is not a regular octahedra having a symmetry approximating to D_{2h}.[337]

The equilibrium diagram for the FeS-In_2S_3 system has been constructed by DTA, microstructural examinations, X-ray diffraction and microhardness measurements. The spinel-type compound $FeIn_2S_4$ is formed.[338] Phase diagrams have also been determined for the CoS-In_2S_3 and NiS-In_2S_3 systems. The previously known congruent compounds MIn_2S_4(M=Co or Ni) are formed most rapidly by solid phase reactions.[339]

The hitherto unknown compounds $Rb_6In_2S_6$ and $Rb_4In_2S_5$ are formed by a disproportionation reaction, starting from Rb and InS. The $Rb_4In_2S_5$ forms triclinic crystals (space group $P\bar{1}$), while $Rb_6In_2S_6$ forms monoclinic crystals (C2/m). The $In_2S_6^{6-}$ unit is the basis of both structures (i.e. two edge-sharing InS_4 tetrahedra).[340]

The space group of crystalline In_5S_4 is Pa3. It possesses a three-dimensional network structure, built up from corner-sharing In_2S_3 tetrahedra (one In at the centre, and the second In at the common corner of 4 tetrahedra).[341]

$CuIn_5S_8$ forms cubic crystals, space group $F\bar{4}3m$, with a spinel-type structure. This paper confirms earlier, preliminary conclusions.[342] $Bi_3In_5S_{12}$ crystals are monoclinic; with space group C2/m. The structure is built up of irregular In/S tetrahedra, with mono- and bicapped trigonal Bi/S prisms, forming chains along the y axis.[343]

The As_2S_3-InSe system has been investigated, and the phase diagram constructed. Two compounds - $InAs_2S_3Se$ and $In_3As_2S_3Se_3$ - were observed.[344]

Equilibrium diagrams were constructed for the $PbIn_2Se_4$-Se and InSe-$PbIn_2Se_4$ sections of the In-Pb-Se system. The InSe primary crystallisation field occupies the largest area.[345]

3.4.3 Indium Halides

Raman spectra have been obtained (at up to 1200K) from the vapours over liquid indium halides, $InAlX_4$ and "InX_2" (X=Cl or Br). InX vapours give O,Q and S vibration/rotation contours, with maxima at 305 cm^{-1} (X=Cl), or 213 cm^{-1} (X=Br). Pure rotational contours were also seen. Over InX_2 and $InAlX_4$, the results show that the complexes exist in the vapour, but that some dissociation,

$$InEX_4(g) \rightleftharpoons InX(g) + EX_3(g) \qquad \ldots (37)$$

$$(X=Cl \text{ or } Br)$$

equation (37), also occurs.[346]

L_2InCl (where L=2-[(dimethylamino)methyl]phenyl) is formed from LiL and $InCl_3$ in ether solution. The complex forms orthorhombic crystals (space group $P2_12_12_1$). The indium has distorted trigonal-bipyramidal geometry, with an InC_2Cl equatorial plane (In-Cl= 2.465(1)Å; In-C(1)=2.144(3)Å; In-C(2)=2.154(3)Å), and apical In-N bonds (In-N(1)=2.442Å, In-N(2)=2.482Å).[347]

Phase diagrams have been constructed for the systems $InCl_3$-MCl_2-H_2O, where M=Be, Mg, Ca, Sr, Ba, Zn, Cd or Hg. In many cases it was not possible to confirm the existence of previously reported double salts. The only double salts definitely detected were $2BeCl_2.InCl_3.(4-5)H_2O$; $MgCl_2.InCl_3.(6-8)H_2O$ and $CaCl_2.InCl_3.7H_2O$.[348]

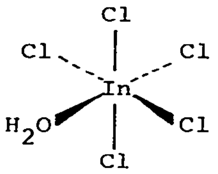
Electrochemical oxidation of indium metal in cells of the type: $Pt_-/RX + CH_3CN/In_+$ produces $RInX_2$ compounds. If 2,2'-bipy is present, then the products are the adducts $RInX_2$.bipy (R=Me,Et,Ph, CH_2Ph; X=Cl,Br or I - but not in all combinations).[349]

Investigation of the extraction systems $TOAH^+X^-$/benzene-InX_3-HX (where X=Br or I) showed that $TOAH^+InX_4^-$ and $TOAH^+InX_4^-.TOAH^+X^-$ were present in the organic phase (TOA=tri-n-octylamine).[350]

The indium(II) compounds $In_2X_6^{2-}$ (where X=Cl,Br or I) and halogen (Y_2;where Y=Cl,Br or I) give anionic mixed halogeno-complexes, InX_3Y^-. In(I) ions are oxidised similarly, to give $InX_2Y_2^-$. Infrared and Raman data confirm that all are monomeric mixed-ligand species. Typical figures are: $[InCl_3Br]^-$, C_{3v} symmetry: (A_1) ν_1,320; ν_2,226; ν_3,103 cm^{-1}; (E)ν_4, 330; ν_5,113; ν_6, 80 cm^{-1}; $[InBr_2I_2]^-$ C_{2v} symmetry: $(A_1)\nu_1$, 215; ν_2, 149; ν_3, 77; ν_4 (60 - calculated); ν_5, 48 cm^{-1}; (B_1/B_2) ν_6, 229; ν_7, 187; ν_8, 65; ν_9, 51 cm^{-1}.[351]

Ether, pyridine and aniline adducts of the mixed halogen complex acids $HInX_3I$ (X=Cl or Br) have been reported. They were characterised by analytical, conductometric, spectroscopic (infrared, ultraviolet) and X-ray powder diffraction data.[352]

^{115}In n.m.r. results have been reported for InX_4^-; $In_2X_6^{2-}$; $InX_4^- + X^-$; InX_3Y^-; $InX_2Y_2^-$, where X≠Y=Cl,Br or I, in various non-aqueous solvents. The results confirmed and extended previous work.[353]



(<u>101</u>)

Raman and infrared spectra have been reported for $K_2InCl_5.H_2O$. The symmetry of the $[InCl_5(H_2O)]^-$ anion is C_{2v}, and a complete assignment of the skeletal modes was proposed, by comparison with $K_3InCl_6.H_2O$, K_2InCl_5 and $K_2InCl_5.D_2O$. The crystal structure shows the anion to be (<u>101</u>), with In-O=2.210(5)Å and In-Cl in the range 2.465Å to 2.486Å.[354]

$K[InBr_4(H_2O)_2]$ forms monoclinic crystals, space group $P2_1/c$. Discrete $[InBr_4(H_2O)_2]^-$ ions are present; the H_2O molecules lie <u>trans</u>, and the In-O distance is 2.261Å, with In-Br distances of 2.606 and 2.621Å.[355]

Interactions in the In-I-Te system have been studied by DTA, X-ray diffraction etc. The phase diagram was constructed, and the compound InTeI identified.[356]

3.4.4 <u>Other Indium Compounds</u>

$InCl_3$ and $GaCl_3$ react with $Li[CH(SiMe_3)_2]$ (=LiR) to form white, crystalline MR_3 (M=Ga or In). InBr or InCl (in diethyl ether) react with $Li[N(SiMe_3)_2]$ or InBr (in diethyl ether) with LiR give only metallic indium, together with organic derivatives. The crystal structure of $In[CH(SiMe_3)_2]_3$ has been determined. Discrete monomers are present, and thus this is the first crystallographically authenticated example of a monomeric heavy Group 3 metal trialkyl.[357]

Cu_7In_3 forms triclinic crystals (space group $P\bar{1}$). The indium atoms form an approximate layer arrangement (also containing some Cu atoms). The remaining copper atoms are situated roughly halfway between these layers.[358]

$InMo_6Se_8$ and $In_2M_{15}Se_{19}$ are both rhombohedral (space groups $R\bar{3}$, $R\bar{3}c$ respectively. The former is isostructural with $PbMo_6S_8$, while the latter is a stacking variant of the hexagonal $In_{\sim 3}Mo_{15}Se_{19}$ phase.[359]

3.5 THALLIUM

3.5.1 Thallium(I) Compounds

Cyclopentadienylthallium(I) reacts with several electrophilic olefins to give new organothallium(I) derivatives. Thus, with tetracyanoethylene, $Tl^+[C_5H_5C(CN)C(CN)_2]^-$ is formed, while 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene gives $Tl^+[C_5H_4C(CF_3)_2CH(CN)_2]^-$ Both products are useful synthetic reagents in the field of metallocene chemistry.[360]

A germylmercury complex of thallium(I) can be prepared according

$$2\left[(C_6F_5)_3Ge\right]_2Hg + Tl \xrightarrow[95^oC,5h]{DME} Hg + 2\left[(C_6F_5)_3Ge\right]_2Hg.Tl\left[Ge(C_6F_5)_3\right] \quad ... (38)$$

to equation (38). The product is actually present as a DME (= dimethoxyethane) adduct.[361]

The formation of soluble complexes of Tl(I) with carbonate ions, in solutions containing 0.5 to 1.0M Na_2CO_3 at 20.00 ± 0.01°C, I=3.4 and pH = 12.5 ± 0.1, has been studied. $Tl(CO_3)^-$ and $Tl(CO_3)_2{}^{3-}$ are both formed, with (average) values of the cumulative stability constants: 3.23 ± 0.33 and 1.30 ± 0.38 respectively.[362]

$(NH_4)_{0.67}Tl_{0.33}H_2PO_4$ forms tetragonal crystals, space group $I\bar{4}2d$. They are isostructural with $(NH_4)H_2PO_4$.[363]

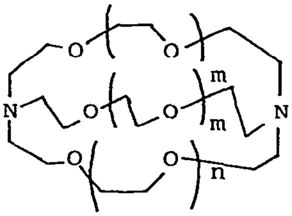
Thallium(I) tetra-acetatothallate(III), $Tl[Tl(C_2H_3O_2)_4]$, crystals are monoclinic, space group $P2_1/c$. The anions $Tl^{III}(CH_3CO_2)_4{}^-$ contain bidentate acetato-groups, and they are linked together by seven-coordinate Tl^+ ions (Tl^I-O = 2.88 to 3.15Å). The Tl^+ lone pair shows no stereoactivity. This is consistent with a hypothesis which suggests that Tl^I will form short bonds, have a small coordination number and a stereoactive lone pair when the counter-ion is a strong base. Otherwise, the bonds will be long, the coordination number >6, and the lone pair will show no stereoactivity.[364]

The crystal structure of thallium(I) tellurite(IV) has been determined. It is orthorhombic, space group Pban, and the lone pair of Tl^+ is stereochemically significant. There are two types of Tl^+ in the structure: $Tl_{(1)}O_3L$ and $Tl_{(2)}O_4L$ (where L represents a lone pair).[365]

$Tl_2Cr_2O_8$ is formed by the reaction of $Tl_2Cr_2O_7$ with a large excess of CrO_3. It is formulated as $Tl^ITl^{III}(CrO_4)_2$.[366]

Multinuclear n.m.r. experiments have been carried out on 1,10-diaza-18-crown-6 macrocyclic complexes with Tl^+ (also Li^+, Na^+ and Cs^+). Tl^+ forms the most stable complexes of the series.[367]

The kinetics of dissociation have been measured for the thallium cryptates $(221Tl)^+$, and $(222Tl)^+$ in water and in $MeOH/H_2O$(90/10) mixtures, in the temperature range 5°C to 35°C. Their behaviour was compared with that of $(222K)^+$. The ligands are (102,m=1,n=0): 221, and (102, m=n=1):222.[368]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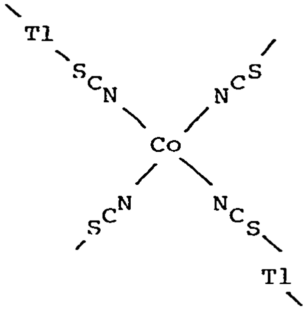
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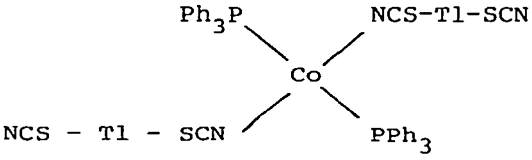
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^{205}Tl n.m.r. spectra have been reported for toluene solutions of eleven Tl^I alkoxides (including 5 previously unreported compounds), Tl(OR), where R=Et,n-Pr,n-Bu, n-C_5H_{11}, n-C_6H_{13}, $CHMe_2$, $CH(Me)(CH_2)_2Me$, $CH(Me)(CH_2)_3Me$, CH_2CHMe_2, CMe_2CH_2Me or CH_2Ph. All of the spectra were consistent with a predominance of tetramers $[\{Tl(OR)\}_4]$ in solution. Three-line spectra resulted from $^{203}Tl-^{205}Tl$ spin-spin coupling. The coupling constant $J(^{203}Tl-^{205}Tl)$ was in the range 2170-2769Hz.[369]

$Co[Tl(SCN)_2]_2$ has been prepared from $Co(NCS)_2$ and TlSCN in CH_2Cl_2 solution. Its infrared spectrum shows that only bridging NCS groups are present, suggesting the polymeric structure (103), analogous to $Co[Ag(SCN)_2]$. Evidence was presented for the formation of adducts with a number of Lewis bases e.g. monomeric

$Co[Tl(SCN)_2]_2.2PPh_3$, (104).[370]

Fusion of a stoichiometric mixture of Tl_2S,PbS and GeS_2 produces monoclinic crystals of Tl_2PbGeS_4 (space group $P2_1/a$). The structure is built up of GeS_4^{2-} tetrahedra, held together by Tl^+ and Pb^{2+} cations. The thallium ions are eight-coordinated by sulphurs, at distances between 3.085 and 4.055Å, to give a very irregular coordination polyhedron.[371]

$Tl_2Mo_9S_{11}$ belongs to the space group $R\bar{3}$, and its structure consists of chains: Mo_6S_8-Tl-Tl-$Mo_{12}S_{14}$. There are 2 different types of Tl atoms, one 7- and the other 8-coordinate (by sulphur atoms). The Tl-Tl distance is 3.572(2)Å.[372] $Tl_2Fe_3S_4$ can be prepared from a TlS/Fe/S mixture. The crystals are orthorhombic (space group Ibam). The coordination polyhedra about Tl^I is a distorted cube of sulphur atoms.[373] Monoclinic (C2/m)$TlCu_3S_2$ crystallises with the $CsAg_3S_2$-type of structure. Cu_4S_4 "tubes" are present, with the Tl^+ ions between the resultant sheets. The Tl^+ ions are irregularly 7-coordinate (by sulphur atoms).[374]

Tl(I)U(IV)F_5 forms monoclinic crystals (space group $P2_1/c$). The structure contains sheets in which the uranium is nine-coordinate (a tricapped trigonal prism). The Tl^+ ions also have nine nearest neighbour fluorine atoms.[375]

X-ray photoelectron spectra have been reported for TlX (X=Cl or Br) in their simple cubic and face-centred cubic crystallographic modifications. The two forms give distinctly different spectra.[376]

$TlHg_5Cl_{11}$ (one of a series of MHg_5X_{11}, where M=Tl,K,Rb,Cs,NH_4; X=Cl or Br; phases) forms monoclinic crystals, belonging to the space group C2/m (C_{2h}^3). It is best formulated as a double salt: $TlX.5HgCl_2$.[377] $Tl_{10}Hg_3Cl_{16}$, on the other hand, forms tetragonal crystals (I4/m). It consists of $HgCl_4$ tetrahedra and linear $HgCl_2$ units (with four longer Hg-Cl bonds to give a distorted octahedron). The structure is closely related to that of Tl_4HgX_6 (where X=Br or I).[378]

Rhombic "α-Tl_2Cl_3" has been shown by X-ray diffraction to be the mixed valence species $Tl_3^I\ Tl^{III}Cl_6$. The Tl^I is 7-9 coordinated by Cl atoms (at 306-383 pm); the Tl^{III} has octahedral 6-coordination by Cl's (250-265pm).[379]

Phase equilibria have been studied in the MI_2-TlI (where M=Sn or Pb) systems. A number of compounds were identified, including $TlMI_3$, which are isostructural, belonging to the space group Cmcm.[380]

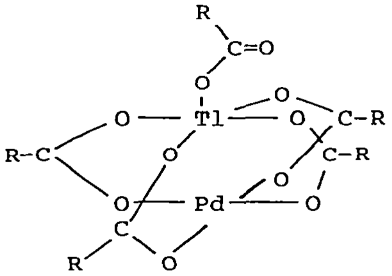
3.5.2 Thallium(III) Compounds

^{1}H and ^{13}C n.m.r. parameters have been reported for the organothallium(III) derivatives $RTlX_2$ and R_2TlX, where $R=Me_3CCH_2$ or Me_3SiCH_2; X=Cl, Br or O_2CCHMe_2. The crystal structure of $[Me_3SiCH_2]_2TlCl$ was also determined; the molecule is dimeric, with each four-coordinate Tl bonded unequally to two bridging Cl atoms.[381]

An X-ray diffraction study shows that $(pHC_6F_4)_2TlCl(OPPh_3)$ is dimeric, again with unsymmetrical chlorine bridging, i.e. Tl-Cl= 2.541Å, Tl-Cl'=2.936Å. The thallium atoms are approximately trigonal bipyramidal, the equatorial positions being filled by two carbon atoms and the more tightly bound chlorine.[382]

The hydrolysis constants of Tl(III) in aqueous acetonitrile have been determined over a range of CH_3CN concentrations. The rate of hydrolysis increases with increased $[CH_3CN]$.[383] The kinetics of reduction of Tl(III) by acetamide, formamide and N-methyl formamide have been studied at 70°C, in acidic perchlorate media. All rates are first order in each reactant, but independent of the concentrations of Tl^{I} or $NaClO_4$. A free radical mechanism was proposed.[384]

Crystal and molecular structures have been determined for diethyldithiocarbamatodiphenylthallium(III) and diphenyltropolonatothallium(III). The former is orthorhombic, space group $Pca2_1$, and contains monomers. The thallium is four-coordinate, with a C-Tl-C angle of 148°. The latter compound is triclinic ($P\bar{1}$), containing dimers, with five-coordinate thallium, bridging oxygen atoms, and a C-Tl-C angle of 163°.[385]



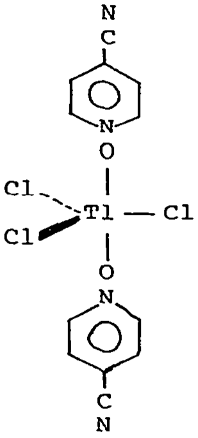
(105)

Palladium(II) and thallium(III) carboxylates react to give $PdTl(O_2CR)_5$, where R=Me,Et or i-Pr, or $PdTl(O_2CR)_2(O_2CR')_3$, where R=Me, Et, i-Pr, Ph; R'=Me, Et or i-Pr. These are the first examples of heterobinuclear palladium compounds lacking CO or phosphine ligands. The ^1H and ^{13}C n.m.r. data suggested that the $PdTl(O_2CR)_5$ species had the structure (105).[386]

$TlCl_3$ reacts with RLi to form TlR_2Cl (where $R=C_6F_5$, m- or p-C_6F_4H, 2,4,6-$C_6F_3H_2$, p-C_6FH_4 or m-$CF_3C_6H_4$).[387] TlR_2X, TlX_3 and $(TlX_4)^-$ react with RLi (where $R=C_6F_5$ or C_6Cl_5) to give anions of the types: $(TlR_4)^-$, $(TlR_2R'_2)^-$ or $(TlR_6)^{3-}$. $TlCl_3$ and $(TlR_4)^-$ give $(\mu\text{-}Cl)TlR_2Cl)_2{}^-$ (where $R=C_6F_5$) or $(TlRCl_3)^-$ (where $R=C_6Cl_5$). Addition of X^- (X=Br or SCN) to $Tl(C_6Cl_5)_3$ produces $[Tl(C_6Cl_5)_3X]^-$.[388]

A separate report has been made of the preparations and properties of R_2TlX and R_2LTlX, where $R=C_6F_5$, o- or p-C_6F_4H; X=Br or Cl; $L=Ph_3PO$, bipy or Ph_3P. R_2TlX are monomeric in acetone, and in this solvent R_2LTlX undergo partial dissociation, with loss of L. R_2TlX are dimeric in benzene, while R_2LTlX ($L=Ph_3PO$ or bipy) show slight association. Solid R_2TlX are polymeric, with five-coordinate thallium. Solid R_2TlX are dimeric, with 5-($L=Ph_3PO$) or 6-(L=bipy) coordinate thallium. These are inconsistent with previous reports of structures for the pentafluorophenyl derivatives.[389]

The structure of (106) was revealed by X-ray crystallography. The Tl-Cl distances are in the range 2.364-2.452Å, with Tl-O 2.36 and 2.40Å.[390]



(106)

$KTlCl_4$ forms tetragonal crystals, space group $I4_1/a$. The coordination at the thallium gives a distorted tetrahedron, with a Tl-Cl distance (average) of 2.433(3)Å, and Cl-Tl-Cl angles of 106.9(1)° and 114.8(1)°.[391] $Na_3TlCl_6.12H_2O$ forms trigonal crystals, space group $R\bar{3}m$. The thallium is coordinated by six chlorines, to give a slightly distorted octahedron (average Tl-Cl distance 2.593(3)Å).[392]

A previously reported preparation of $(pyH)_2TlCl_5$ has now been shown to give instead the well-known species $(pyH)_3Tl_2Cl_9$.[393]

Crystals of $KTlBr_4.2H_2O$ are cubic, space group Fm3c. Discrete $TlBr_4^-$ ions are present, with a Tl-Br distance of 2.554(3)Å. They are very close to being regular tetrahedral.[394]

3.5.3 Other Thallium Compounds

The gaseous Tl_2 molecule has been identified by Knudsen cell mass spectral experiments. Its dissociation energy was measured, and found to be $D_o^o(Tl_2)=60.7\text{kJ mol}^{-1}$, with an overall uncertainty of not more than 16 kJ mol^{-1}.[395]

The Pb-S-Tl phase diagram has been studied by D.T.A., X-ray diffraction, microhardness and e.m.f. measurements. Equilibrium diagrams of the Tl_4S_3-PbS, TlS-PbS, Tl_2S-Pb and TlPb-S sections were constructed.[396]

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