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THE SYNTHESIS, STRUCTURE, AND CHEMICAL REACTIONS OF METALLOBORANES

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Abstract - Recent work on the synthesis, structure, and chemical reactions of metalloboranes is reviewed. In the decaborane series, single-crystal X-ray studies indicate that the metal atom can be (a) fully incorporated within the borane cluster, (b) joined to the cluster by an exopolyhedral B-M-B bond in which the metal replaces a bridging proton, or (c) joined by a normal σ B-M bond by replacement of a terminal hydrogen atom. Complexes of $B_{10}H_{12}^{2-}$ with Fe; Zn, Cd, Hg; Mg; Al, Ga, In, Tl; and Sn are specifically discussed. In the pentaborane series numerous complexes have been prepared for a wide variety of transition metals and main group metals (Ti; Fe; Co, Rh, Ir; Ni, Pd, Pt; Cu, Ag, Au; Cd, Hg; and Si) and details of the bonding are elucidated. Kinetic control of products frequently appears to be more important than the achievement of greatest thermodynamic stability. Replacement of bridge protons or terminal hydrogen atoms in the basal borons are the prevalent modes of attachment for B_5 and B_6 systems and no examples of B-H-M bonding have been detected. By contrast, B_3H_8 is found to bond exclusively *via* B-H-M bonds in its non-ionic derivatives (examples include complexes of Mn; Fe; Ir; Zn; Al, Ga, In; Si, Ge, Sn, and Pb). NMR spectroscopy proves to be valuable in elucidating the structure and in defining which complexes are fluxional and which have a rigid 'tetraborane-type' structure in which a coordinated metal centre formally replaces a BH_2 group in tetraborane(10). The results, taken as whole, establish the general ability of boron hydrides and their anions to act as electron-donating ligands to most, if not all, metals in the Periodic Table.

Ten years ago metalloboranes were virtually unknown. Coordination of metal atoms by carbaboranes was, of course, well established but the direct coordination of metals by boron hydrides or borane anions acting as ligands had yet to be established as a general mode of bonding. Now, several hundred such compounds have been prepared: the field has recently been extensively reviewed (1-3) and it is also well represented by papers at this conference. In this lecture I shall therefore concentrate mainly on work we have completed during the past two years since the second IMEBORON in Leeds, or which is at present still in progress. Some twenty metals spanning both the main groups and the transition elements have been studied, and the borane ligands are predominantly in the decaborane, pentaborane, and triborane series.

METALLODECABORANES

The earliest work in this area (4) was done in an attempt to parallel, with aluminium and gallium, the well known cluster expansion reactions of decaborane which occur under appropriate conditions with borane adducts, tetrahydroborates, or acetylenes:

$$B_{10}H_{14} \xrightarrow{LBH_3 \text{ or } BH_4^-} B_{11}H_{14}^-,\ B_{11}H_{11}^{2-},\ B_{12}H_{12}^{2-}$$

$$B_{10}H_{14} \xrightarrow{R_2C_2} B_{10}H_{10}(CR)_2$$

Decaborane was found to react smoothly with trimethylamine-alane in ether to give the novel anion $[AlB_{10}H_{14}]^-$ which could be formulated either as a $B_{11}H_{14}^-$ species in which one boron atom is replaced by aluminium, or as an AlH_2^+ unit coordinated by $B_{10}H_{12}^{2-}$ (5):

$$B_{10}H_{14} + [AlH_3(NMe_3)] \xrightarrow{OEt_2} [NHMe_3]^+[Al(B_{10}H_{12})H_2]^-.2OEt_2$$

The reaction was subsequently extended to give a variety of $B_{10}H_{12}^{2-}$ derivatives of Mg, Zn, Cd, and Hg (6) and the structures of $[PMePh_3]_2^+[Zn(B_{10}H_{12})_2]^{2-}$ and the dimer $[Cd(B_{10}H_{12})(OEt_2)_2]_2$ were established by single-crystal X-ray studies (7,8). These studies showed that the $B_{10}H_{12}^{2-}$ anion could act either as a tetrahapto-ligand thereby incorporating the metal centre fully within the polyhedral cluster (7), or as a bis-dihapto ligand in which bridge protons in $B_{10}H_{14}$ were replaced by the metal to give exopolyhedral 3-centre B-M-B μ-bonds (8). Compounds were also prepared in which the metal simply replaced a terminal hydrogen atom, thereby becoming bonded to the decaborane moiety via a normal σ two-centre bond, e.g. $[Fe(B_{10}H_{13}py)Br_2(py)]$ (9).

In our most recent work in this area we have prepared $B_{10}H_{12}^{2-}$ derivatives of Hg(II), In(III), Tl(III), Sn(II), and Sn(IV) and some interesting results emerge. Decaborane reacts smoothly with two moles of dimethylindium in benzene at room temperature to give a quantitative yield of the ionic compound $[InMe_2]^+[In(B_{10}H_{12})Me_2]^-$ as pale-yellow, air-sensitive crystals (10):

$$2InMe_3 + B_{10}H_{14} \xrightarrow{C_6H_6} [InMe_2]^+[In(B_{10}H_{12})Me_2]^- + 2CH_4$$

The complex is a 1:1 electrolyte in acetone and its infrared spectrum shows the presence of both ionic and coordinated $InMe_2$ groups. This is also confirmed by the proton n.m.r. spectrum. When the reaction is carried out using a 1:1 mole ratio of reactants, a 10% yield of the pale-yellow, non-electrolyte $[In(B_{10}H_{12})Me]$ is obtained by elimination of two moles of methane from the same indium atom:

$$InMe_3 + B_{10}H_{14} \xrightarrow{C_6H_6} [In(B_{10}H_{12})Me] + 2CH_4$$

In both these compounds the indium is fully incorporated within the borane cluster which acts as a tetrahapto four-electron ligand.

Decaborane reacts similarly with two moles of trimethylthallium in ether at room temperature to give an 85% yield of the pale-yellow complex $[TlMe_2]^+[Tl(B_{10}H_{12})Me_2]^-$, but with 1:1 stoichiometry $[TlMe_2]^+[B_{10}H_{13}]^-$ is obtained (10). Evidently the inherent stability of the $[TlMe_2]^+$ cation precludes further elimination of methane to give the thallium analogue of $[In(B_{10}H_{12})Me]$ and attack by a second molecule of trimethylthallium is necessary for the reaction to proceed further. The ^{11}B n.m.r. spectrum of the $[Tl(B_{10}H_{12})Me_2]^-$ anion at 28.87 MHz (with and without broad-band proton decoupling) was more complex than that of the indium analogue and the spectrum at 80.53 MHz also implied the absence of a mirror plane in the anion when dissolved in a donor solvent such as deutero-acetone. To check whether $B_{10}H_{12}^{2-}$ was acting as a dihapto rather than a tetrahapto ligand, single crystals of the compound $[PMePh_3]^+[Tl(B_{10}H_{12})Me_2]^-$ were prepared by metathesis with $[PMePh_3]Br$ and subjected to X-ray structural analysis (11). The results confirmed tetrahapticity in the solid, as shown in Fig.1. The anion has a mirror plane

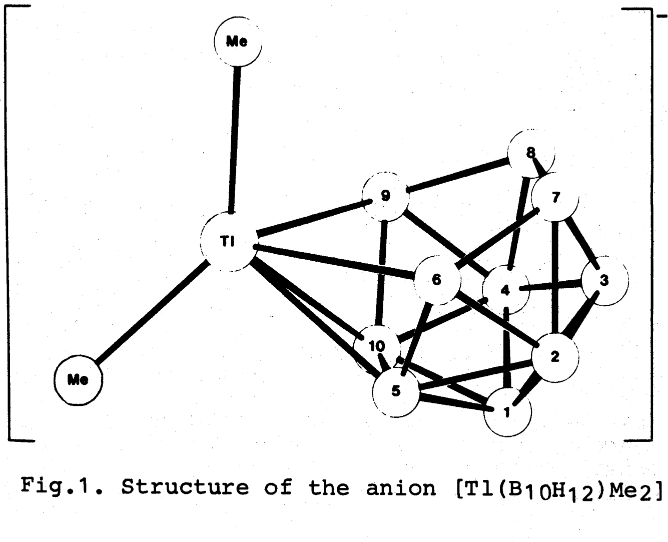

Fig.1. Structure of the anion $[Tl(B_{10}H_{12})Me_2]^-$

through $C_2TlB(1)B(3)$ and the distances from thallium to the four nearest boron atoms are 251, 261, 276, and 277 pm respectively. The dihedral angle subtended at thallium by the bonding B(5)B(6)Tl and B(9)B(10)Tl planes is 66.2°, which can be compared with the value of 77.3° found at the smaller zinc atom in $[Zn(B_{10}H_{12})_2]^{2-}$ (7). The other bond angles at thallium are all close to tetrahedral except for Me-Tl-Me which opens up to 134.1° to compensate for the smaller angle subtended by the two three-centre bonds to the borane fragment.

When $[TlMe_2]^+[Tl(B_{10}H_{12})Me_2]^-$ is allowed to react with methylmercury chloride in tetrahydrofuran at room temperature, quantitative subrogation of the cluster-coordinated $TlMe_2$ by HgMe occurs and Me_2TlCl is precipitated. Metathesis of the product with $[PMePh_3]Br$ leads to the isolation of orange crystals of the air-stable compound $[PMePh_3]^+[Hg(B_{10}H_{12})Me]^-$ (10). The compound is readily soluble in chlorinated hydrocarbons and polar organic solvents but not in hexane or diethyl ether. The ^{11}B n.m.r. spectra at 28.87 and 80.53 MHz show a series of doublets of intensity 2:1:2:3(unresolved 2+1):2 and are therefore consistent with the structure shown in Fig.2. A bis(decaborato)-complex of mercury has also been prepared (12).

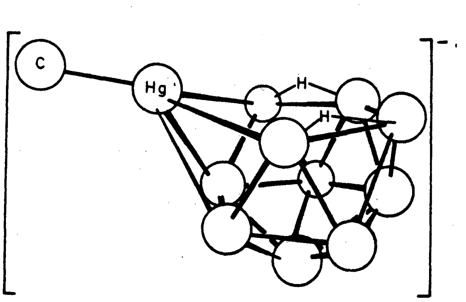

Fig.2. Proposed structure of the anion $[Hg(B_{10}H_{12})Me]^-$

Moving on from Groups IIB and IIIB to Group IVB the reactions of various tin(II) and tin(IV) compounds were studied (13). Anhydrous tin(II) chloride undergoes two concurrent reactions with the nido-anion $B_{10}H_{12}^{2-}$ in mixed thf/dichloromethane solution at room temperature. In the first, the <u>closo</u>-anion $B_{10}H_{10}^{2-}$ is formed and metallic tin is precipitated; in the second, $SnCl_2$ becomes coordinated by $B_{10}H_{12}^{2-}$ to give a 40% yield of the pale yellow crystalline complex $[AsPh_4]_2^+[Sn(B_{10}H_{12})Cl_2]^{2-}$:

$$SnCl_2 + [AsPh_4]_2^+[B_{10}H_{12}]^{2-} \longrightarrow [AsPh_4]_2^+[B_{10}H_{10}]^{2-} + Sn + 2HCl$$

$$SnCl_2 + [AsPh_4]_2^+[B_{10}H_{12}]^{2-} \longrightarrow [AsPh_4]_2^+[Sn(B_{10}H_{12})Cl_2]^{2-}$$

Spectroscopic information indicates that the anion has the same tetrahapto-structure as shown in Fig.1 for $[Tl(B_{10}H_{12})Me_2]^-$, but this leaves unresolved the subtle bonding problem as to whether the compound should be considered as a tin(II) complex coordinated by $B_{10}H_{12}^{2-}$ or as a tin(IV) derivative of $B_{10}H_{14}^{2-}$ formed by substitution of two terminal hydrogen atoms. The problem was resolved by ^{119}Sn Mössbauer spectroscopy at liquid nitrogen temperature which showed that the compound had a chemical isomer shift $\delta + 3.17$ mm s^{-1} relative to $BaSnO_3$, typical of Sn(II) and incompatible with Sn(IV) for which $\delta < 2.0$ mm s^{-1}. The quadrupole splitting Δ 1.26 mm s^{-1} was also close to values previously obtained for authentic tin(II) complexes (14).

Reaction of $B_{10}H_{12}^{2-}$ with tin(IV) compounds under similar conditions also resulted in concurrent processes in which the tin was reduced to tin(II) with the formation of <u>closo</u>-$B_{10}H_{10}^{2-}$ and in which tin(IV) complexes of <u>nido</u>-$B_{10}H_{12}^{2-}$ were formed as pale yellow crystals (13):

$$SnCl_2Me_2 + [AsPh_4]_2^+[B_{10}H_{12}]^{2-} \longrightarrow [B_{10}H_{10}]^{2-} + [Sn^{II}Cl_2Me_2]^{2-} + \ldots\ldots$$

$$SnCl_2Me_2 + [AsPh_4]_2^+[B_{10}H_{12}]^{2-} \longrightarrow [AsPh_4]_2^+[Sn^{IV}(B_{10}H_{12})Cl_2Me_2]^{2-}$$

Mössbauer spectroscopy of this latter complex at liquid nitrogen temperature established the presence of tin(IV) in an essentially octahedral environment with <u>trans</u>methyl groups: chemical isomer shift δ 1.75 mm s^{-1} relative to $BaSnO_3$, quadrupole splitting Δ 3.13 mm s^{-1}. The corresponding diethyl derivative $[AsPh_4]_2^+[Sn(B_{10}H_{12})Cl_2Et_2]^{2-}$ was also prepared by a similar reaction, starting with $[SnCl_2Et_2]$. An important feature of all these reactions is their sensitivity to the co-cation used: $[AsPh_4]^+$ and $[PMePh_3]^+$ salts of nido-$B_{10}H_{12}^{2-}$ reacted smoothly but $Na_2B_{10}H_{12}$ failed to react at all, perhaps because the $B_{10}H_{12}^{2-}$ ion may already be involved in coordination i.e. $Na^+[Na(B_{10}H_{12})]^-$.

METALLOHEXABORANES

Hexaborane was recently shown (15) to behave as an electron-pair donor which could displace carbon monoxide from $[Fe_2(CO)_9]$, to give the yellow crystalline complex $[Fe(\eta^2\text{-}B_6H_{10})(CO)_4]$. Complexes of the corresponding anion $B_6H_9^-$ with magnesium, zinc, and cadmium have also recently been prepared, principally by deprotonation of hexaborane with metal alkyls (16), and the complex $[Cu(\eta^2\text{-}B_6H_9)(PPh_3)_2]$ is also known (17). As part of a more extensive investigation of pentaborane complexes to be reported in the next section, we have deprotonated hexaborane with potassium hydride and allowed the resulting anion to react with the four-coordinate nickel(II) complex $[NiBr_2(dppe)]$, where dppe is the chelating ligand $Ph_2PCH_2CH_2PPh_2$ (18):

$$[NiBr_2(dppe)] + K^+[B_6H_9]^- \xrightarrow{thf/CH_2Cl_2} [Ni(\eta^2\text{-}B_6H_9)Br(dppe)] + KBr$$

The red complex $[Ni(\eta^2\text{-}B_6H_9)Br(dppe)]$ melts with decomposition at 200° and is stable at room temperature for short periods. The ^{11}B n.m.r. shows two doublets of relative area 1:5, implying that each boron is still bonded to one terminal hydrogen atom. The equivalence of the five basal boron atoms indicates fluxional behaviour of the dihapto nickel bridge bond and the three remaining B-H-B bridge bonds around the five available positions. The ease of these preparative reactions augers well for the extensive development of metallohexaborane chemistry with a wide variety of transition metals and main-group metals.

METALLOPENTABORANES

Pentaborane is known to form direct metal-bonded derivatives in which the B_5 moiety acts as a mono-, di-, or tetra-hapto ligand (1). Examples of each class are:

monohapto:	$[Mn(2\text{-}B_5H_8)(CO)_5]$, $[Re(2\text{-}B_5H_8)(CO)_5]$		(19)
dihapto:	$[Mn(2,3\text{-}\mu\text{-}B_5H_8)R_3]$	M = Si, Ge, Sn, Pb	(20)
	$[Cu(2,3\text{-}\mu\text{-}B_5H_7X)(PPh_3)_2]$	X = H, Me	(21)
tetrahapto:	$[Mn(2,3,4,5\text{-}B_5H_5)(CO)_3]$		(22)

Zero-hapto ionic compounds such as $M^+[B_5H_8]^-$ are, of course, also known. Definitive single-crystal structures have been completed for the monohapto iridium(III) complex $[Ir(2\text{-}B_5H_8)Br_2(CO)(PMe_3)_2]$ (23) and the dihapto silicon complex $[Si(1\text{-}Br\text{-}2,3\text{-}\mu\text{-}B_5H_7)Me_3]$ (24) but few metals have been studied from either the synthetic or structural point of view and there is no general understanding of the factors which determine the type of bonding to be adopted. Accordingly, we embarked on a broadly-based preparative programme, supplemented by single-crystal X-ray determination of structure in the solid state and n.m.r. studies of potential fluxional behaviour in solution. The metals so far studied include Ti; Fe; Co, Rh, Ir; Ni, Pd, Pt; Cu, Ag, Au; Cd, Hg; and Si, though the order of presentation below will be somewhat different from this because of the particular chemistry involved.

The copper(I) complex $[Cu(B_5H_8)(PPh_3)_2]$ is thought to be nonfluxional in solution and was believed from spectroscopic evidence to feature a three-centre B-Cu-B bond in which copper bridges two basal boron atoms (21,25). We have prepared single crystals of this compound and have determined its structure from X-ray diffraction data (26). The compound crystallizes as colourless needles in the monoclinic space group $P2_1/c$ and the structure is illustrated in Fig.3. The copper(I) atom is essentially trigonal planar with bond angles P(1)-Cu-P(2) 123.4°, P(1)-Cu-$\bar{B}$ 114.0°, P(2)-Cu-$\bar{B}$ 122.3°, where $\bar{B}$ is the mid point between B(2) and B(3). This is the first example of a 16-electron copper(I)-borane complex involving a three-centre B-Cu-B bond. All borane hydrogen atoms were located (see Fig. 3b) and the absence of Cu-H-B bonds was established, thus distinguishing the bonding in this complex from that in all other (18-electron) copper-borane complexes whose structures had been determined. The refinement was continued to a final R value of 0.0547. Inter-atomic distances of interest include: Cu-P 228.5 pm, Cu-B(2) 220.9 pm, Cu-B(3) 223.6 pm, B(2)-B(3) 170 pm, average B-H(terminal) 114 pm, B-H(bridge) 121-148 pm 1 pm = 0.01Å. The angle B(2)-Cu-B(3) is 45.0° and the dihedral angle between the planes B(1)B(2)B(3) and CuB(2)B(3) is 178.4°, which means that the four atoms are essentially coplanar.

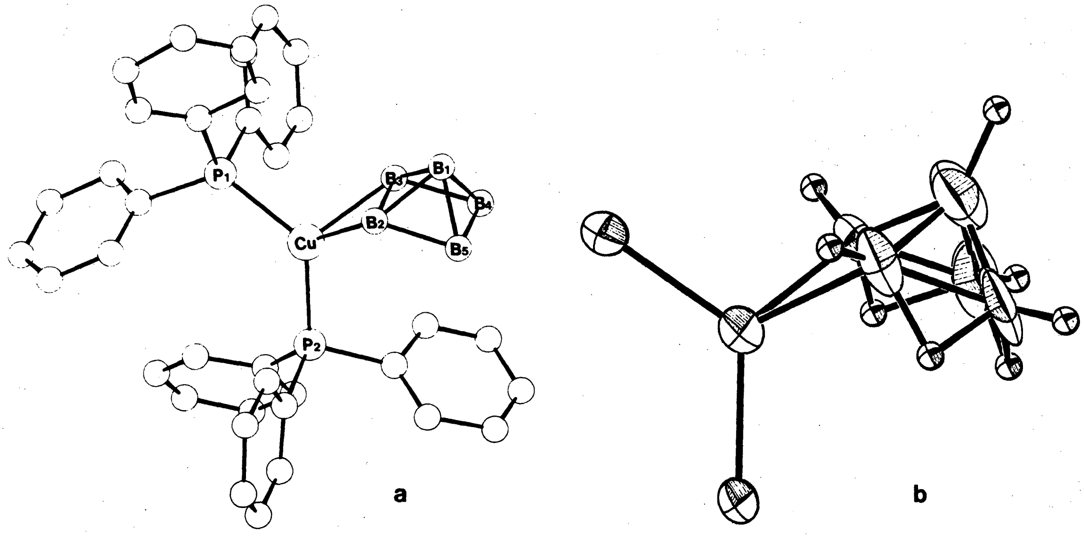

Fig.3. Structure of $[Cu(2,3\text{-}\mu\text{-}B_5H_8)(PPh_3)_2]$ showing (a) the position of all atoms except hydrogen, (b) the detailed structure of the central $\{P_2Cu(B_5H_8)\}$ portion of the molecule

In seeking to extend the chemistry of this group, $[Cu(1\text{-}Br\text{-}2,3\text{-}\mu\text{-}B_5H_7)(PPh_3)_2]$ was obtained as white needles d.110° and $[Cu(2,3\text{-}\mu\text{-}B_5H_8)(dppe)]$ was prepared by ligand displacement as an off-white solid m.p. 114°(d). Silver(I) complexes could be prepared by reaction of phosphine halogeno-silver complexes with KB_5H_8 (18). For example, $[Ag(2,3\text{-}\mu\text{-}B_5H_8)(PPh_3)_2]$ was obtained as an off-white photosensitive solid which appeared to be non-fluxional on the ^{11}B n.m.r. timescale: the spectrum comprised a high-field apical doublet area 1 (δ 48.0 ppm from BF_3OEt_2, J 140 Hz) and a pair of overlapping doublets each of area 2 due to the two sets of basal boron atoms (δ 14.0 and 8.0 ppm, J $\sim$ 130 Hz). This is the first silver-pentaborane complex to be prepared. Analogous gold complexes were too unstable to be isolated (18).

Reaction of $[CdCl_2(PPh_3)_2]$ with KB_5H_8 in thf/dichloromethane solution at -40° gave a 60% yield of $[Cd(2,3\text{-}\mu\text{-}B_5H_8)Cl(PPh_3)]$ as a white powder, m.p. 85° and the 1-bromo derivative was obtained similarly (m.p. 98°) (18). Both these novel compounds when treated with hydrogen chloride gas in diethyl ether regenerated the parent borane in good yield.

Moving back into the transition metals, a wide variety of compounds have been studied. There are indications that $[Ti(C_5H_5)_2Cl_2]$ reacts with KB_5H_8 to give unstable compounds of the type $[Ti_2(B_5H_n)(C_5H_5)_3]$ for which ^{11}B n.m.r. indicates both terminal and bridging basal substitution by titanium (27). Cyclopentadienyliron derivatives proved more tractible. Reaction of $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ with KB_5H_8 in dimethyl ether afforded an 84% yield of $[Fe(2\text{-}B_5H_8)(\eta\text{-}C_5H_5)(CO)_2]$ as a moderately stable, yellow-orange oil. Again, the yield was strongly dependent on the alkali metal salt chosen and the particular ethereal solvent used. ^{11}B n.m.r. at 28.87 MHz with and without proton decoupling revealed four resonances of relative area 1:2:1:1 consistent with a basal boron bonded to iron (singlet), two basal borons cis to the B-Fe bond, a basal boron trans to the B-Fe bond and the apical boron (all doublets). Deprotonation of the complex with KH in monoglyme gave the corresponding anion $[Fe(2\text{-}B_5H_7)(\eta\text{-}C_5H_5)(CO)_2]^-$ which reacted with a further mole of $[Fe(\eta\text{-}C_5H_5)(CO)I]$ to give several products of which the main one (20% yield) was the diferraborane $B_5H_7[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$. The composition was established by high-resolution mass spectrometry coupled with a full assignment of the fragmentation products at unit-mass resolution. The ^{11}B

n.m.r. spectrum shows the expected 2:2:1 area ratios and multiplet structure for bis-basal substitution of terminal hydrogen atoms but does not allow a decision between <u>cis</u> and <u>trans</u> substitution geometries (28).

A σ-bonded rhodium(I)-pentaborane derivative was isolated in 35% yield from an analogous reaction (18).

$$[Rh(CO)Cl(PPh_3)_2] + KB_5H_8 \xrightarrow[\text{room temp.}]{\text{thf/CH}_2\text{Cl}_2} [Rh(2\text{-}B_5H_8)(CO)(PPh_3)_2] + KCl$$

The complex forms bright yellow crystals, m.p. 123° and the ^{31}P n.m.r. is consistent with mutually <u>trans</u>-phosphines about the square planar rhodium(I). The ^{11}B n.m.r. features a low-field singlet due to the unique basal B(2) carrying the rhodium residue, an asymmetric mid-field resonance which collapses to two singlets of area 2 (<u>cis</u> basal borons) and 1 (<u>trans</u> basal boron) and a high-field doublet due to the apical boron atom. It is notable that this 16-electron rhodium(I) complex is σ-bonded to the B_5H_8 cluster whereas the isoelectronic copper(I) complex shown in Fig.3 is μ-bonded. It was therefore of interest to see whether the iridium(I) analogue could be prepared and if so, which structure it adopted.

Reaction of $[Ir(CO)Cl(PPh_3)_2]$ with KB_5H_8 in thf/benzene solution at -40° results in the loss of one phosphine and the formation of $[Ir(B_5H_8)(CO)(PPh_3)]$ as a golden brown solid (28). Initial results indicate that this may be a unique three-coordinate 14-electron iridium(I) species and its chemistry is at present under investigation. The 16-electron species $[Ir(B_5H_8)(CO)(PPh_3)_2]$ is probably also formed.

The preparation of a series of isoelectronic 16-electron complexes of nickel(II), palladium(II), and platinum(II) proved to be much more straightforward and a large number of such compounds have now been characterized by John Staves (18). The compounds are essentially square planar at the metal centre which, in turn, is μ-bonded to the borane cluster as in the copper(I) complex. This deduction is at present based mainly on n.m.r. and other spectroscopic evidence but single-crystal structure analyses of representative members of the series will shortly be determined to elucidate fine details of the bonding. The compounds are monomeric and non-conducting in chloroform solution and treatment with hydrogen chloride in diethyl ether regenerates the parent borane in moderate yield. Typical examples are listed below (dppe = $Ph_2PCH_2CH_2PPh_2$):

Compound	Colour	m.p.(decomp)
$[Ni(2,3\text{-}\mu\text{-}B_5H_8)Cl(dppe)]$	orange	190°
$[Ni(2,3\text{-}\mu\text{-}B_5H_8)Br(dppe)]$	bright red	220°
$[Ni(2,3\text{-}\mu\text{-}B_5H_8)I(dppe)]$	dark red	210°
$[Ni(1\text{-}Br\text{-}2,3\text{-}\mu\text{-}B_5H_7)Cl(dppe)]$	orange-red	210°
$[Ni(1\text{-}Br\text{-}2,3\text{-}\mu\text{-}B_5H_7)Br(dppe)]$	brick red	240°
$[Ni(1\text{-}Br\text{-}2,3\text{-}\mu\text{-}B_5H_7)I(dppe)]$	dark red	260°

The metal-bromo complexes are the most stable (at least 14 months at room temperature) and the iodo complexes the least stable (2-4 months at room temperature).

Analogous <u>cis</u>-phosphine complexes of palladium and platinum with μ-bonded $B_5H_8^-$ can be prepared in 60% yield by a similar reaction (18):

$$\underline{cis}\text{-}[MX_2L_2] + KB_5H_8 \xrightarrow[\text{low temp.}]{\text{thf/CH}_2\text{Cl}_2} \underline{cis}\text{-}[M(2,3\text{-}\mu\text{-}B_5H_8)XL_2] + KX$$

M = Pd; X = Cl; L = ½dppe
M = Pt; X = Cl; L = ½dppe, PPh_3, PMe_2Ph, PMe_3
X = Br; L = ½dppe, PPh_3, PMe_2Ph
X = I; L = ½dppe, PPh_3, PMe_2Ph
X = Me; L = PMe_2Ph

The triphenylarsine complex <u>cis</u>-$[Pt(2,3\text{-}\mu\text{-}B_5H_8)Cl(AsPh_3)_2]$ has also been prepared. The compounds are all off-white or pale beige-coloured powders which can be handled in air at room temperature. The platinum complexes are more stable than the palladium and the stability also apparently decreases in the sequence dppe ∿ PPh_3 > PMe_2Ph ∿ PMe_3 >> $PMePh_2$. The compounds are monomeric and non-conducting in chloroform and regenerate B_5H_9 in high yield on treatment with HCl/Et_2O.

Trans-phosphine complexes of platinum(II) are less common than their cis analogues but two have been shown to react with KB_5H_8 to yield platinum-pentaborane complexes with retention of trans-geometry, as indicated by ^{31}P n.m.r. spectroscopy (29):

$$\text{trans-}[PtXI(PMe_2Ph)_2] + KB_5H_8 \longrightarrow \text{trans-}[Pt(2,3\text{-}\mu\text{-}B_5H_8X(PMe_2Ph)] + KI$$

The compounds with X = I or Me were obtained as white powders in ∿ 30% yield and found to be much less stable than the cis-analogues.

One advantage of studying cis-phosphine complexes of platinum is that the ^{195}Pt-^{31}P n.m.r. coupling constant gives a measure of the 'trans-influence' of groups attached to the platinum and trans to the phosphine. Typical results for the compounds mentioned above are (29):

Group trans to P	Cl	Br	I	B_5H_8	Me
$J(^{195}Pt-^{31}P)$/Hz	3993	3860	3695	2328	1915

Increase of 'trans-influence' Cl < Br < I << B_5H_8 < Me

It can be seen that the trans-influence of the μ-bonded B_5H_8 group is substantially greater than those for the halogens but is significantly less than that for the methyl group.

The work on metalloborane compounds described in this section extends our knowledge of these compounds to many more metals than had previously been studied, but no clear picture has yet emerged as to the crucial factors dictating whether σ- or μ-bonding is adopted. As expected from the molecular dimensions of $B_5H_8^-$ however, there is no indication of M-H-B bonding such as is prevalent in the triborane complexes to be described in the final section of this review. Before proceeding to these, however, it is convenient to interpolate a brief section on metalloboranes containing four boron atoms.

METALLOTETRABORANES

Several groups working independently, simultaneously prepared the novel compound $[Fe(\eta^4\text{-}B_4H_8)(CO)_3]$ in which the apical {BH} group in B_5H_9 has been replaced by the 'isoelectronic' group $\{Fe(CO)_3\}$ (30). The preferred synthetic route is the co-pyrolysis of B_5H_9 and $Fe(CO)_5$ in a hot/cold reactor at 220°/20° for three days; this affords a 20% yield of the compound which is an orange liquid melting at ∿5°. Decaborane was another major product of the reaction. The proposed structure shown in Fig.4 is consistent with the high-resolution mass spectrum, the mass-spectral fragmentation pattern, and the infrared spectrum.

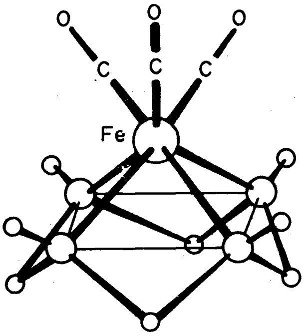

Fig.4. Structure of $[Fe(\eta^4\text{-}B_4H_8)(CO)_3]$

The ^{11}B n.m.r. spectrum exhibits a simple doublet (δ 4.69 ppm relative to BF_3OEt_2, J 162 Hz) due to the four equivalent basal boron atoms. This collapses to a singlet on proton decoupling. The proton n.m.r. spectrum shows a quartet (τ 7.56 J 158 Hz) due to the terminal hydrogen atoms and a broad multiplet of the same area τ 13.65 due to the bridging hydrogen atoms.

It will be noted that $[Fe(\eta^4\text{-}B_4H_8)(CO)_3]$ obeys the electron-count rules formulated by several workers (31) and is a new member of the series which includes the end members B_5H_9, $[Fe(\eta^4\text{-}C_4H_4)(CO)_3]$, and $[Fe_5C(CO)_{15}]$. It is also noteworthy that B_5H_9 reacts with $Fe(CO)_5$ by loss of a BH group whereas *nido*-$B_4C_2H_8$ reacts by loss of two bridge hydrogen atoms to give *closo*-$[Fe(B_4C_2H_6)(CO)_3]$ (32) and B_6H_{10} forms the simple adduct $[Fe(\eta^2\text{-}B_6H_{10})(CO)_4]$ (15).

The chemistry of $[Fe(\eta^4\text{-}B_4H_8)(CO)_3]$ awaits detailed development but its Brønsted acidity has been well defined (27). Deprotonation with KH or LiMe generates the alkali metal salt of the conjugate base $[Fe(B_4H_7)(CO)_3]^-$ which can be reprotonated to the parent compound by HCl. Use of deuterium chloride affords the bridge deuterated complex $[Fe(\eta^4\text{-}B_4H_7D_\mu)(CO)_3]$. Likewise, $[Fe(\eta^4\text{-}B_4H_8)(CO)_3]$ can be deprotonated by $B_5H_8^-$ and $B_6H_9^-$ to yield the conjugate base and the appropriate borane (B_5H_9 or B_6H_{10}), whereas decaborane is able to reprotonate the conjugate base with simultaneous formation of $B_{10}H_{13}^-$. This indicates that the acidity of these boranes decreases in the sequence:

$$B_{10}H_{14} > [Fe(\eta^4\text{-}B_4H_8)(CO)_3] > B_6H_{10} > B_5H_9$$

Other metallotetraboranes have recently been synthesized. Special interest attaches to those in which a {BH} group in pentaborane is subrogated by $\{Co(\eta^5\text{-}C_5H_5)\}$, which is isolectronic with $\{Fe(CO)_3\}$, since it has been shown (33,34) that the metal can occupy either the apical position or a basal position in the molecule. A detailed review of such compounds would however be inappropriate here.

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Published work in this area up to 1974 has been adequately reviewed (1,2,3) and the work to be presented in this final section is as yet unpublished. Metal derivatives of the octahydrotriborate(1-) anion fall broadly into three classes which can be distinguished by their n.m.r. spectra:

(a) ionic compounds $[ML_x]^+[B_3H_8]^-$ which feature an essentially free $[B_3H_8]^-$ anion in solution;

(b) compounds with a 'tetraborane-like' structure in which the metal residue replaces a BH_2 group in B_4H_{10} and is thus joined to the B_3H_8 fragment by two M-H-B bonds;

(c) compounds in which all three boron atoms are bonded to the metal via M-H-B bonds.

There appear to be no authenticated examples of direct M-B σ-bonded complexes, or complexes joined by a single M-H-B bond, though π-allylic complexes of $B_3H_7^{2-}$ have been reported (35). It can be seen that triborane clusters can act formally as zero-, three-, four-, or six-electron donors to metals but that examples of one-, two-, or five-electron donation are as yet unknown.

We have found that the reaction of TlB_3H_8 with complex metal halides affords a versatile high-yield route to a wide variety of metallotriborane complexes (37) and the results can be conveniently presented according to the groups in the Periodic Table. Our starting point was the reaction of TlB_3H_8 with $[MnBr(CO)_5]$ in dichloromethane at room temperature to give the yellow-brown liquid complex $[Mn(B_3H_8)(CO)_4]$. The ^{11}B and ^1H n.m.r. spectra showed that the complex was non-fluxional and the results confirmed independent work published during the course of our own experiments (36). Likewise, $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ under the same conditions gave a 75% yield of the air-stable, diamagnetic complex $[Fe(B_3H_8)(\eta\text{-}C_5H_5)(CO)]$ as dark red, sublimable crystals (37). The ^{11}B n.m.r. spectrum at 28.87 MHz showed a broad, low-field triplet (δ 7.39 ppm from BF_3OEt_2, J 140 Hz) due to the BH_2 group, and a broad high-field doublet (δ 54.06 ppm, H 132 Hz) due to the two boron atoms bonded to iron via B-H-Fe bonds. On being proton-decoupled the spectrum collapsed to two singlets of relative area 1:2 as expected, and the results establish the rigid bonding of the $\{Fe(\eta\text{-}C_5H_5)(CO)_3\}^+$ group to the $B_3H_8^-$ in a 'tetraborane-like' structure.

The isoelectronic complex $[FeBr_2(CO)\}^+$ also reacted smoothly with one mole of TlB_3H_8 in dichloromethane at 0°C to give golden hexagonal plates of $[Fe(B_3H_8)Br(CO)_3]$ and the ^{11}B n.m.r. spectrum in CCl_2D_2 again indicated a non-fluxional situation (37): the spectrum comprised a 4:5:2:1 multiplet due to the overlap of a low-field 4:4 doublet and a higher-field 1:2:1 triplet, the overall 2:1 area ratio of the two component multiplets being confirmed by proton decoupling. It is noteworthy that the relative positions of the

BH and BH_2 resonances are reversed from those found in the cyclopentadienyl-iron derivative mentioned in the preceding paragraph.

Under more forcing conditions (two moles of TlB_3H_8 in refluxing dichloromethane) both bromine atoms in $[FeBr_2(CO)_4]$ could be replaced to give a 20% yield of $[Fe(B_3H_8)_2(CO)_2]$ as a red-brown, moderately volatile, viscous liquid (37). The iron is seen to be essentially octahedrally coordinated, the bidentate $B_3H_8^-$ ligands each acting as four-electron donors via two B-H-Fe bonds. The n.m.r. spectra are complex and may indicate the presence of more than one of the four possible geometrical isomers.

Reaction of Vaska's 16-electron compound $[Ir(CO)Cl(PPh_3)_2]$ with TlB_3H_8 in benzene at room temperature gives golden yellow crystals of $[Ir(B_3H_8)(CO)(PPh_3)_2]$ in high yield (37). The compound is monomeric and non-conducting in solution and appears to be an 18-electron iridium(I) complex, taking $B_3H_8^-$ to be a 4-electron donor. The ^{11}B n.m.r. spectrum is very broad and rather uninformative, a feature which has previously been observed by others working with iridium-borane complexes. Rather surprisingly, the complex appears to take up one mole of CO or PPh_3 in benzene solution to give $[Ir(B_3H_8)(CO)_2(PPh_3)_2]$ and $[Ir(B_3H_8)(CO)(PPh_3)_3]$ as yellow-brown powders. The detailed formulation of these compounds is not immediately evident on the basis of ^1H, ^{11}B, and ^{31}P n.m.r. spectra, particularly if the implication of a 20-electron iridium species is to be avoided. Several alternatives present themselves and are the subject of further current investigations (38). Another curious reaction of $[Ir(B_3H_8)(CO)(PPh_3)_2$ is its oxidation with hydrogen chloride to give an iridium(III) complex which analyses as $[Ir(B_3H_8)(CO)(Cl)_2(PPh_3)_2]$ and which has the B_3H_8 group rigidly bound to the iridium as evidenced by ^{11}B resonances at 16.1 ppm (area 1) and 38.1 ppm (area 2). Again, further work is required before a convincing formulation can be advanced.

Anhydrous zinc bromide reacts with two moles of TlB_3H_8 in methanol at -50^o to give white crystals of $[Zn(B_3H_8)_2]$ (37). The compound decomposes above -30^o and is clearly less stable than the recently reported compound $[Be(B_3H_8)_2]$ (39). Similar reactions with $CdCl_2$ and $HgCl_2$ in methanol at low temperatures indicate that the triboranates of these elements are even less stable, the overall stability sequence being Be > Zn > Cd > Hg.

In Group III, boron, aluminium, and gallium derivatives of B_3H_8 are known, the compounds $[B_4H_8Me_2]$, $[Al(B_3H_8)Me_2]$, and $[Ga(B_3H_8)Me_2]$ all being liquids with the 'tetraborane-like' structure (40). As the aluminium and gallium complexes showed fluxional behaviour of the bound B_3H_8 group and were of only marginal stability at room temperature, it was of interest to study the heavier analogues with indium and thallium. Dimethylindium chloride was found to react with TlB_3H_8 in monoglyme to give brilliant white crystals of $[In(B_3H_8)Me_2]$ which decompose rapidly at room temperature (37). The ^{11}B n.m.r. spectrum in CCl_2D_2 over a range of temperatures shows that the B_3H_8 group is bound but fluxional: at -43^o there was a broad absorption with a full-width-at-half-maximum of 157 Hz and centred 29.6 ppm upfield from BF_3OEt_2; at -30^o the resonance sharpened (124 Hz) and individual peaks began to emerge; at -14^o the spectrum had the appearance of that for free $B_3H_8^-$, seven peaks of the nonet being resolved (δ = 30.8 ppm, J = 31 Hz). This is very reminiscent of the behaviour of the aluminium and gallium analogues, though the changes in the spectrum of $[In(B_3H_8)Me_2]$ occur at a lower-temperature which implies less rigid bonding.

The dimethylthallium compound was quite different. Me_2TlI reacts rapidly and quantitatively with TlB_3H_8 in methanol at room temperature to give the air-stable, white, crystalline compound $[TlMe_2]^+[B_3H_8]^-$. The compound is soluble in water, methanol, and acetone, conducts electricity as a 1:1 electrolyte in methanol, and has a low 'molecular weight' compatible with extensive ionic dissociation (37). The diagnostic infrared and proton n.m.r. spectrum of the linear $[TlMe_2]^+$ cation and the characteristic ^{11}B nonet of ionic $[B_3H_8]^-$ (δ 30.3 ppm, J 32 Hz, collapsing to a singlet on proton decoupling) establish the ionic nature of the compound and rule out a 'tetraborane-like' structure. The series of Group III complexes $[M(B_3H_8)Me_2]$ thus show a steady gradation in properties from purely covalent (M = B) through increasingly fluxional bonding (M = Al, Ga, In) to purely ionic (M = Tl).

In Group IV, reaction of Ph_3MCl with TlB_3H_8 in ethereal solvents affords products of steadily decreasing stability as indicated below (37):

$[Si(B_3H_8)Ph_3]$ - white solid, d. > 0°

$[Ge(B_3H_8)Ph_3]$ - white solid, d. > -20°

$[Sn(B_3H_8)Ph_3]$ - white solid, d. > -30°

$[Pb(B_3H_8)Ph_3]$ - yellow crystals, d. > -60°

The ^{11}B n.m.r. spectra were, understandably, of rather poor quality but probably indicate a structure in which a BH_2 group in B_4H_{10} has been replaced by an MPh_3 group. The compounds $[Si(B_3H_8)Me_3]$ and $[Si(B_3H_8)_2Me_2]$ were also prepared from the corresponding chloride and had similar properties.

CONCLUSIONS

The general ability of boron hydrides and their anions to act as electron-donating ligands is now firmly established. A wide variety of coordination geometries and modes of bonding have been revealed but it is not always possible to predict in advance the type of structure and bonding to be adopted. Indeed, there are clear indications of kinetic control in many of the reactions, and the reaction conditions employed are frequently more decisive in determining the product obtained than is the relative thermodynamic stability of the compound with respect to other possible products.

In the decaborane systems, full incorporation of the metal heteroatom within the borane cluster frequently occurs, and the complexes can be formally represented as involving donation of two electron pairs from $B_{10}H_{12}^{2-}$ to the metal centre. Less frequently exopolyhedral three-centre B-M-B bridge bonding occurs by formal donation of a bonding pair of electrons from the borane cluster (i.e. the metal replaces the proton in a B-H-B bridge bond). Examples of single σ B-M bonds are also known by means of which the decaborane cluster is directly attached to a pendant metal carrying other coordinated groups (i.e. the coordinated metal substitutes the terminal hydrogen atom of a BH group).

Numerous examples of bridge-bonding of B_5 and B_6 clusters to metals have been presented. Isoelectronic rules and electron-counting procedures are of some value in indicating systems worthy of study but not infrequently formally isoelectronic systems adopt different modes of attachment, the most common being electron-pair donation from a B-B bond to form a B-M-B three-centre bond, and simple σ B-M bonding by substitution of a terminal hydrogen atom. No examples of B-H-M bonding have been so far encountered with these boranes of intermediate size though a few examples are known for the higher boranes and this type of bonding is exclusively adopted with triborane.

Many new metallotriborane complexes have been prepared and interest at present centres on whether the B_3 unit is fluxional on the n.m.r. timescale or is rigid. Metals or groupings which readily form cationic compounds result in essentially ionic compounds with free B_3H_8 anions in solution. No clearly established examples of B-M σ bonding or B-M-B bridge bonding have been detected in the triborane complexes which thus differ fundamentally from the $B_5H_8^-$ complexes. Details of molecular geometry and precise values of interatomic distances in the individual borane ligands are clearly of importance here.

Just as multinuclear n.m.r. experiments are proving invaluable for elucidating the solution structures of metalloborane complexes over a range of temperatures, so single-crystal X-ray studies are beginning to provide definitive structural data on these novel and versatile systems. The wide range of stoichiometries, stereochemistries and bond types which is emerging indicates an extensive and fruitful area for synthetic, structural, and theoretical studies in the future.

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