Metalloboranes and Metal–Boron Bonding

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Introduction

Compounds in which a metal atom is directly bonded to a boron hydride group have been increasingly studied since the first examples were synthesized some ten years ago, and it is now clear that the field of metalloborane chemistry is potentially as large and diverse as the older field of organometallic chemistry. Boron is the element immediately preceding carbon in the Periodic Table and it therefore has one less electron available for bonding but the same number of orbitals (the 2*s* and the three 2*p* orbitals). The covalent radius, electronegativity, and ionization energies of the two atoms are very similar and this, coupled with the propensity of boron to form polyatomic clusters both with itself and with other elements, permits an extensive covalent chemistry to be developed.[1] Just as the numerous and novel types of structure and bonding that can be adopted by compounds between metals and hydrocarbons or their derivatives have been elucidated and exploited during the past 25 years, so it now appears that a similarly rich variety of structural and bonding types can be generated by compounds between metals and boron hydrides or their derivatives.

Metalloborane compounds can be divided into four broad categories:

(i) Ionic hydroborates, of which the simplest are the tetrahydroborates such as $NaBH_4$ and $Ba(BH_4)_2$; these have recently been reviewed by James and Wallbridge.[2] Also in this category are the ionic octahydrotriborates MB_3H_8 and a variety of *nido*- and *arachno*-polyhydroborates such as MB_5H_8,[3] MB_6H_9,[3] CsB_9H_{14},[4] and $NaB_{10}H_{13}$.[5] Ionic *closo*-polyhydroborates of general formula $M_2B_nH_n$ (n = 6—12) are likewise well known and adequately documented,[1,6] though the special case of $Cu_2B_{10}H_{10}$ will be considered further (on p. 255).

(ii) Metal hydroborates containing hydrogen-bridge bonds M—H—B, for example $Al(BH_4)_3$,[7] $(Ph_3P)_2CuBH_4$,[8] and $(Ph_3P)_2CuB_3H_8$.[9]

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[1] N. N. Greenwood, 'Boron', Chapter 11 in 'Comprehensive Inorganic Chemistry', ed. J. C. Bailar, H. J. Emeléus, R. S. Nyholm, and A. Trotman-Dickenson, Pergamon Press, Oxford, 1973.

[2] B. D. James and M. G. H. Wallbridge, *Progr. Inorg. Chem.*, 1970, **11**, 99.

[3] H. D. Johnson, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, 1970, **9**, 908.

[4] N. N. Greenwood, J. A. McGinnety, and J. D. Owen, *J.C.S. Dalton*, 1972, 986; N. N. Greenwood, H. J. Gysling, J. A. McGinnety, and J. D. Owen, *Chem. Comm.*, 1970, 505.

[5] L. G. Sneddon, J. C. Huffman, R. O. Schaeffer, and W. E. Streib, *J.C.S. Chem. Comm.*, 1972, 474.

[6] W. H. Knoth and E. L. Muetterties, 'Polyhedral Boranes', M. Dekker Inc., New York, 1968.

[7] A. Almenningen, G. Gunderson, and A. Haaland, *Acta Chem. Scand.*, 1968, **22**, 328.

[8] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 1967, **6**, 2223.

[9] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 1969, **8**, 2755.

(iii) Metal–carbaborane complexes including π-bonded 'sandwich' compounds; this is probably the most extensive class of metal–boron compound to date and several reviews are available.[10–13]

(iv) Compounds containing direct metal–boron bonds except those in the carbaborane category (iii) above. It is these compounds which form the subject of the present review. The sequence of presentation will be according to the various synthetic routes that have been developed for these compounds. The chemical reactions, physical properties, structure, and bonding will be incorporated within this framework, and a concluding section will summarize the types of bonding so far observed in these diverse structures.

Seven broadly distinguishable preparative routes have been devised; they overlap to some extent but form, nevertheless, a convenient framework for discussion. The routes are:*

1. borane plus metal hydride compound;
2. borane plus metal alkyl or aryl;
3. borane plus transition-metal complex;
4. borane anion plus transition-metal complex;
5. metathesis (*i.e.* mutual interchange of metal atoms);
6. borane anion plus metal halide (or alkylmetal halide);
7. borane (or borane anion) plus transition-metal carbonyl.

1 Borane plus Metal Hydride Compound

One of the first syntheses of a covalently bonded metal derivative of a polyhedral borane cluster was reported in 1965 by Greenwood and McGinnety.[14] Decaborane(14) was allowed to react in ethereal solution at room temperature with trimethylamine-alane to give a quantitative yield of the highly reactive colourless complex $[Me_3NH]^+[B_{10}H_{12}AlH_2]^-,n Et_2O$, where $n = 1.5$—2.0:

$$B_{10}H_{14} + Me_3NAlH_3 \xrightarrow{Et_2O} [Me_3NH]^+[B_{10}H_{12}AlH_2]^-,nEt_2O + H_2 \qquad (1)$$

The structure of the metalloborane anion has not been established with certainty

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**Note added in proof:* An important additional route has recently been published by O. Hollander and S. G. Shore, 167th Natl. Meeting Amer. Chem. Soc., Los Angeles, April 1974, Abstract INORG 184; this involves skeletal build-up by insertion of BH_3 into a preformed metalloborane complex [see equation (62)]:

$$\mu\text{-}B_6H_{10}Fe(CO)_4 + KH \longrightarrow K^+[\mu\text{-}B_6H_9Fe(CO)_4]^- + H_2$$
$$K^+[\mu\text{-}B_6H_9Fe(CO)_4]^- + \tfrac{1}{2}B_2H_6 \longrightarrow K^+[B_7H_{12}Fe(CO)_4]^-$$
$$K^+[B_7H_{12}Fe(CO)_4]^- + HCl \longrightarrow [B_7H_{11}Fe(CO)_4] + KCl + H_2$$

The product is stable at −78 °C, decomposes over several hours at 0 °C, and is the first example of a previously unknown neutral borane (B_7H_{11}) to be stabilized by co-ordination to an electron-withdrawing group.

[10] R. Snaith and K. Wade, 'International Review of Science, Inorganic Chemistry, Series I', M.T.P., Butterworths, 1972, Vol. 1, Ch. 4.

[11] M. F. Hawthorne, *Endeavour*, 1966, **25**, 146

[12] M. F. Hawthorne, *Pure Appl. Chem.*, 1968, **17**, 195.

[13] M. F. Hawthorne, *Pure Appl. Chem.*, 1972, **29**, 547.

[14] N. N. Greenwood and J. A. McGinnety, *Chem. Comm.*, 1965, 331.

but its reactions and i.r. spectrum are consistent with its formulation as the 6,9-*dihapto*-derivative of $B_{10}H_{14}^{2-}$ shown in Figure 1. Thus,[14,15]

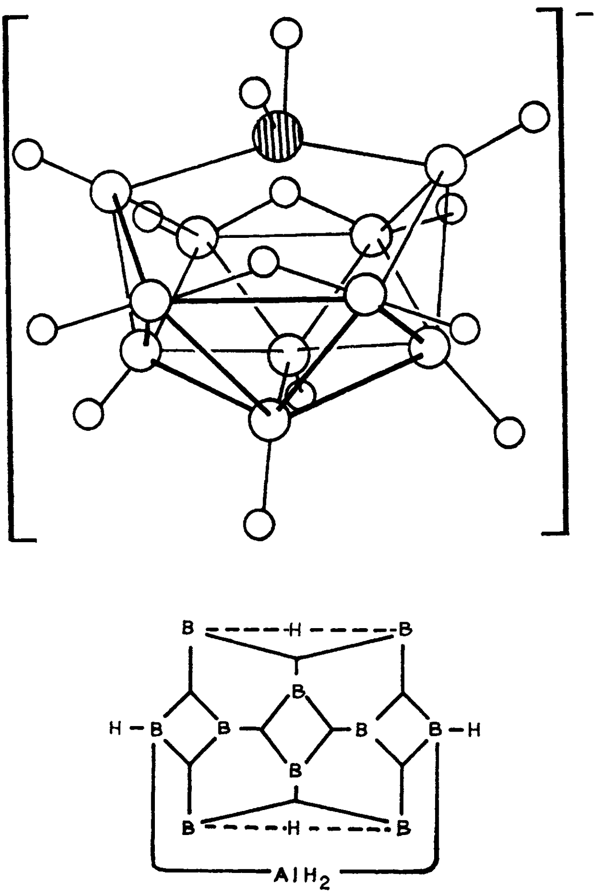

Figure 1 *Possible structure and topology of* $[B_{10}H_{12}AlH_2]^-$

$$B_{10}H_{14} + Me_3NAlH_2Cl + nEt_2O \rightarrow [Me_3NH]^+[B_{10}H_{12}AlH_2]^-,nEt_2O + HCl \qquad (2)$$

$$B_{10}H_{14} + Me_3NAlD_3 + nEt_2O \rightarrow [Me_3NH]^+[B_{10}H_{12}AlD_2]^-,nEt_2O + HD \qquad (3)$$

$$[Me_3NH]^+[B_{10}H_{12}AlH_2]^-,nEt_2O + 3H_2O \rightarrow [Me_3NH]^+[B_{10}H_{15}]^- + Al(OH)_3 + H_2 + nEt_2O \qquad (4)$$

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[15] N. N. Greenwood and J. A. McGinnety, *J. Chem. Soc. (A)*, 1966, 1090.

In these reactions it is noteworthy that the HCl liberated in reaction (2) does not react with the co-ordinated AlH_2 moiety, and that in reaction (3) almost pure HD and co-ordinated AlD_2 are produced. When μ^4-bridge-deuteriated decaborane was used, a partially deuteriated product was obtained plus one molar equivalent of composition H_2 26%, HD 74%, $D_2 < 0.1\%$. This indicates that it is the bridge hydrogens which are involved in the reaction. The hydrolysis of the complex with water or alcohols was explosively violent unless moderated by a very large excess of ether; under these conditions the aluminium was quantitatively eliminated but only one mole of hydrogen was evolved, due to the formation of $B_{10}H_{15}^-$ ion. The i.r. spectrum of the original complex indicates that the ether molecules are co-ordinated (presumably to the aluminium) rather than free; for this reason the *dihapto*-structure shown in Figure 1 is preferred rather than the 6,7,8,9-*tetrahapto*-structure, though this structure, which is known in other metallo-boranes (see later), is not rigorously excluded.

The reaction of decaborane with trimethylaminegallane in ether at room temperature proceeds rather differently, according to equation (5).

$$B_{10}H_{14} + Me_3NGaH_3 \xrightarrow{Et_2O} [Me_3NH]^+[B_{10}GaH_{16}]^- \qquad (5)$$

No hydrogen is evolved and the product is a fine, white, solvent-free powder, stable under dry nitrogen, and soluble as a 1:1 electrolyte in ethanol.[14] In view of the violent reactivity of $[B_{10}H_{12}AlH_2]^-,nEt_2O$ to water it is remarkable that the anion $[B_{10}GaH_{16}]^-$ can be recovered unchanged even from 1M-hydrochloric acid; it is, in fact, the only known gallium hydride derivative which is hydrolytically stable.

Few other direct reactions of boranes with metal hydride compounds have been exploited to yield metalloboranes but one example is the reaction of diborane with germylpotassium in 1,2-dimethoxyethane at low temperatures to give the *monohapto* anionic derivative potassium germyltrihydroborate(1 –):[16]

$$\tfrac{1}{2}B_2H_6 + KGeH_3 \xrightarrow{(MeOCH_2)_2} K^+[H_3GeBH_3]^- \qquad (6)$$

This anion can be regarded either as a germyl-substituted BH_4^- ion or as an adduct between the germyl anion GeH_3^- and BH_3. The salt KH_3GeBH_3 melts at 99 °C and decomposes at 200 °C to germanium, germanium hydrides, hydrogen, and potassium tetrahydroborate(1 –). It is fairly stable in alkaline aqueous solutions but hydrolyses completely in acids to germane, hydrogen, and boric acid.

2 Borane plus Metal Alkyl or Aryl

A. Group II Metals.—The first reaction of this type to be reported concerned decaborane and diethylcadmium;[17,18] these reacted slowly in equimolar propor-

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[16] D. S. Rustad and W. J. Jolly, *Inorg. Chem.*, 1968, **7**, 213.

[17] N. N. Greenwood and N. F. Travers, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 169.

[18] N. N. Greenwood and N. F. Travers, *J. Chem. Soc.* (*A*), 1967, 880.

tions in diethyl ether at room temperature to give a white, crystalline product which was subsequently shown to be dimeric:[19]

$$2B_{10}H_{14} + 2Et_2Cd \xrightarrow{Et_2O} [(Et_2O)_2CdB_{10}H_{12}]_2 + 2EtH \tag{7}$$

The reaction is more rapid in THF and the corresponding product is pale yellow. No reaction occurred in benzene solution unless a co-ordinating ether was added.

Organozinc reagents, R_2Zn (R = Me, Et, or Ph), reacted similarly to give air-sensitive, yellow crystalline solids in yields which depended both on the nature of R and the solvent S.[17,20]

$$2B_{10}H_{14} + 2R_2Zn \xrightarrow[S]{\text{ethereal solvent}} [S_xZnB_{10}H_{12}]_2 + 2RH \tag{8}$$

A stoicheiometric complex could be obtained in the presence of a stronger ligand; *e.g.* decaborane reacted with the bipyridyl adduct of diethylzinc in diethyl ether solution at room temperature according to the stoicheiometry indicated in equation (9).[21]

$$B_{10}H_{14} + (\text{bipy})ZnEt_2 \xrightarrow{Et_2O} (\text{bipy})ZnB_{10}H_{12} + 2EtH \tag{9}$$

Diethylmagnesium reacted rapidly with an ethereal solution of decaborane even at -78 °C to give high yields of the cream-coloured complex $(Et_2O)_2MgB_{10}H_{12}$.[20] By contrast, organomercury compounds did not react even at elevated temperatures, thereby indicating the influence of metal–carbon bond polarity on reactivity.

The crystal and molecular structure of $[(Et_2O)_2CdB_{10}H_{12}]_2$ has been determined by single-crystal *X*-ray diffraction techniques.[19] The compound comprises two $B_{10}H_{12}^{2-}$ icosahedral fragments each acting as a bis-*dihapto*-ligand to the two cadmium atoms (Figure 2). Each cadmium atom is bonded by three-centre bonds so as to bridge the two borane clusters and is also co-ordinated by two oxygen atoms from the ether molecules to give an overall distorted tetrahedral bonding environment. The hydrogen atoms were not located but the structure clearly indicates that two bridge protons in each of the decaborane clusters have been replaced by the cadmium atoms to give the topology shown in Figure 3. This structure immediately rationalizes the chemical properties of the compound.[18] Thus, it dissolves as a non-electrolyte in methylene chloride and reacts smoothly and quantitatively with dry hydrogen chloride in ether to regenerate decaborane:

$$[(Et_2O)_2CdB_{10}H_{12}]_2 + 4HCl \longrightarrow 2B_{10}H_{14} + 2CdCl_2 + 4Et_2O \tag{10}$$

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[19] N. N. Greenwood, J. A. McGinnety, and J. D. Owen, *J.C.S. Dalton*, 1972, 989.
[20] N. N. Greenwood and N. F. Travers, *J. Chem. Soc.* (*A*), 1968, 15.
[21] D. W. Waite, Ph.D. thesis, 1973, Univ. Newcastle upon Tyne, England.

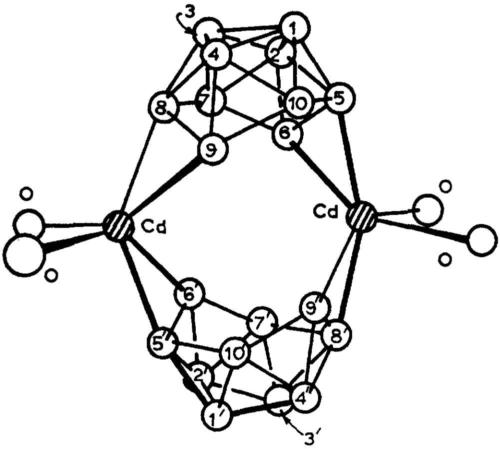

Figure 2 *Structure of* $[(Et_2O)_2Cd(B_{10}H_{12})]_2$ *showing positions of boron, cadmium, and oxygen atoms. The shortest* Cd—B *distances are in the range* 237—246 pm *and the* Cd—O *distances are* 224—238 pm. *The non-bonding* Cd—Cd *distance is* 486 pm *and the angle* OCdO *is* 87°

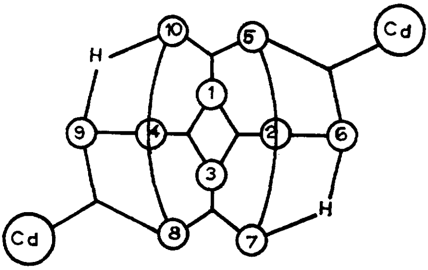

Figure 3 *Topology of the* $B_{10}H_{12}$ *unit showing the three-centre bonding to the two bridging cadmium atoms*

In solvents such as water, ethanol, and methyl cyanide the compound (and the bis-tetrahydrofuranate) dissolved to give a 2:2 electrolyte as shown in equation (11). This proved to be a general route to the novel series of metalloborane

$$[(Et_2O)_2CdB_{10}H_{12}]_2 \longrightarrow Cd^{2+} + [Cd(B_{10}H_{12})_2]^{2-} + 4Et_2O \qquad (11)$$

complexes $[M(B_{10}H_{12})_2]^{2-}$ (M = Mg, Zn, or Cd), which could be obtained as yellow or orange crystalline solids when precipitated from solution by large cations such as Me_4N^+ and Ph_3MeP^+.[18,20,22] The isostructural mercury complexes were obtained by the alternative routes discussed in Section 6.

The structure of $[Ph_3MeP]^+_2[Zn(B_{10}H_{12})_2]^{2-}$ was determined by single-crystal *X*-ray diffraction analysis, and the positions of all 121 atoms in the compound were located.[23] The anionic complex, shown in Figure 4, can be considered to comprise two bidentate $B_{10}H_{12}^{2-}$ ligands co-ordinated tetrahedrally to zinc, as indicated in Figure 5. The distances between zinc and B(5), B(10), B(5′), and B(10′) fall in the range 220—221 pm, and the distances between zinc and B(6), B(9), B(6′), and B(9′) fall in the range 243—247 pm. The average B—H (terminal) distance is 105 pm and the average B—H (bridge) is 131 pm, which are within the normal range. Most of the boron–boron distances within

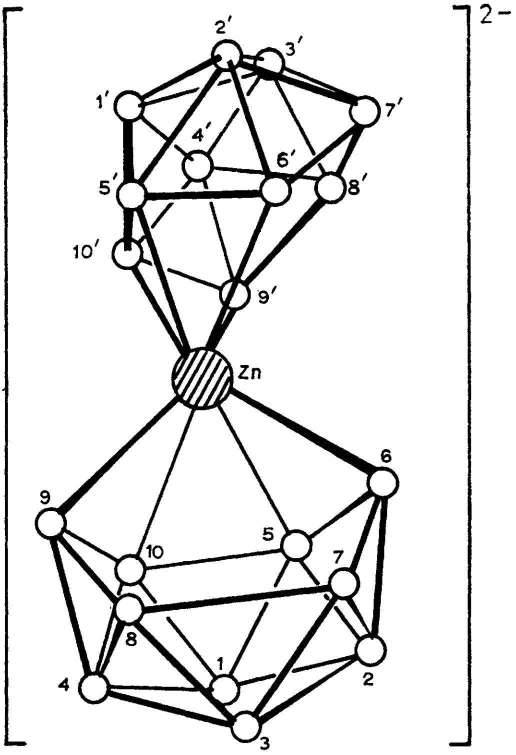

Figure 4 *Structure of the anion* $[Zn(B_{10}H_{12})_2]^{2-}$ *showing the positions of the zinc and boron atoms only; each boron has one hydrogen atom attached and each cluster has two hydrogen atoms bridging the* 6,7 *and* 8,9 *positions*

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[22] N. N. Greenwood and N. F. Travers, *J. Chem. Soc.* (*A*), 1971, 3257.
[23] N. N. Greenwood, J. A. McGinnety, and J. D. Owen, *J. Chem. Soc.* (*A*), 1971, 809.

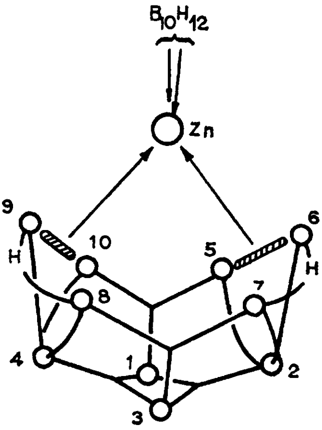

Figure 5 *A three-dimensional representation of the* 2640 *topology suggested for the bidentate ligand* $B_{10}H_{12}{}^{2-}$

the clusters are similar to those in decaborane, the greatest deviations (5—13 pm) occurring, as expected, for those boron atoms closest to the zinc atom. The angles subtended at zinc by the mid points of B(5)B(6) and B(9)B(10) are 77.4° and 77.2° for the two cages, implying substantial deviation from the ideal tetrahedral angle of 109°.

The i.r., u.v., and n.m.r. spectra of these compounds, including the high-resolution ^{11}B n.m.r. spectra at 80.53 MHz, have been reported.[18,20,22]

The reaction of other boranes with Group II metal alkyls has been much less extensively studied but it is known that hexaborane(10) reacts with the dimethyls of magnesium, zinc, and cadmium (but not mercury) to form somewhat unstable compounds of formula $MeMB_6H_9,n$THF:[24]

$$B_6H_{10} + Me_2M \xrightarrow{THF} MeMB_6H_9,n\text{THF} + Me$$

In the case of the magnesium compound the product is still sufficiently reactive to form a bishexaboranyl derivative [reaction (13)], which is stable for weeks at room temperature.

$$B_6H_{10} + MeMgB_6H_9,n\text{THF} \xrightarrow{THF} Mg(B_6H_9)_2,x\text{THF} + MeH \qquad (13)$$

No structural data were published but the ^{11}B n.m.r. spectra indicated that the B_6 cluster remained intact and that there was an equivalent interaction (at least on the n.m.r. time-scale) between all the basal boron atoms and the metal atom. B_6H_{10} was also shown to react with MeMgBr to give B_6H_9MgBr and methane.[24]

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[24] D. L. Denton and S. G. Shore, Abstracts of 162nd meeting of A.C.S., Washington D.C., 1971, INORG, 4.

B. Group III Metals.—Trimethylthallium reacts with decaborane in diethyl ether to give two dimethylthallium derivatives by competing reactions:[25]

$$B_{10}H_{14} + Me_3Tl \xrightarrow{Et_2O} [Me_2Tl]^+[B_{10}H_{13}]^- + MeH \qquad (14)$$

$$B_{10}H_{14} + 2Me_3Tl \xrightarrow{Et_2O} [Me_2Tl]^+[B_{10}H_{12}TlMe_2]^- \qquad (15)$$

The yellow crystalline product of reaction (14) is simply the dimethylthallium salt of the tridecahydrodecaborate(1 –) anion but the product of reaction (15) is a true metalloborane complex. Thus the ^1H n.m.r. spectrum of the compound in hexadeuterioacetone showed three distinct sets of methyl protons in the ratio 2:1:1, the more intense of which corresponded in chemical shift and Tl–(C)–H coupling constant to the known Me_2Tl^+ cation. The other two non-equivalent sets of methyl protons were assigned to the 9,10,5,6-*tetrahapto*-complex shown in Figure 6. This would be analogous to the known chelating tendency of $B_{10}H_{12}^{2-}$ in $[M(B_{10}H_{12})_2^{2-}]$ (see Figure 4). However, it would imply a high-resolution ^{11}B n.m.r. spectrum in which there were six doublets (in the absence of accidental overlap): four with relative intensity 2 and two with intensity 1. Unpublished work at 80.53 MHz[21] suggests that there may be a resolved triplet of relative total intensity 1 (implying the presence of a BH_2 group) together with three partially resolved doublets of intensity 1 and three doublets of intensity 2. This could be explained if the Me_2Tl group were bonded to the decaborane cluster by a three-centre, two-electron bond involving B(5) and B(6), whilst the

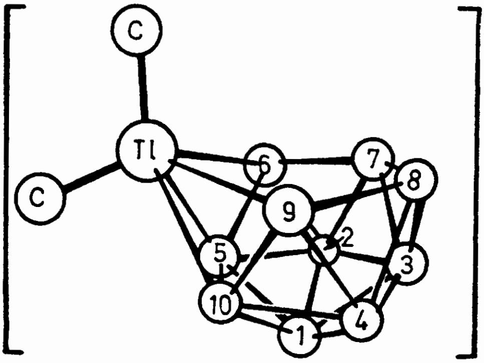

Figure 6 *Proposed heavy-atom structure of the anion* $[B_{10}H_{12}TlMe_2]^-$; *numbering as in decaborane*(14). *Each boron atom carries one terminal hydrogen atom and there are bridging hydrogen atoms between* B(6)—B(7) *and* B(8)—B(9)

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[25] N. N. Greenwood, N. F. Travers, and D. W. Waite, *Chem. Comm.*, 1971, 1027.

B(9) atom carried two terminal hydrogen atoms – this would destroy the C_{2v} symmetry of the borane cluster and render each boron atom structurally distinct, though it would be expected that several pairs of boron atoms would be sufficiently similar to give apparently coincident doublets of relative intensity 2, as observed. It is also possible that the structure in solution differs from that in the solid.

The reaction of trimethylindium with decaborane in benzene solution[26] is analogous to that of the corresponding thallium compound. Methane is evolved and, depending on the stoicheiometry of the reagents, two products are produced, $[Me_2In]^+[Me_2InB_{10}H_{12}]^-$, which crystallizes from solution during the course of the reaction, and $Me_2InB_{10}H_{13}$, which remains in solution. $[Me_2In]^+[Me_2InB_{10}H_{12}]^-$ is a pale yellow crystalline solid, the formulation of which is confirmed by analytical, i.r., n.m.r., and conductivity data. The proposed structure of the $[Me_2InB_{10}H_{12}]^-$ anion is analogous to that of the thallium derivative (see Figure 6). $Me_2InB_{10}H_{13}$ is a yellow solid which is formulated as a simple derivative of $B_{10}H_{14}$.

3 Borane plus Transition-metal Complex

The first report of the preparation of a metalloborane by this route involved the direct reaction of (cleaved) diborane in ethereal solution with carbonyl derivatives of manganese and rhenium:[27]

$$\mathrm{THF,BH_3 + NaMn(CO)_5 \rightarrow Na^+[(CO)_5Mn(BH_3)]^- + THF} \qquad (16)$$

$$\mathrm{THF,BH_3 + Na^+[(Ph_3P)Mn(CO)_4]^- \rightarrow Na^+[(Ph_3P)Mn(CO)_4(BH_3)]^- + THF} \qquad (17)$$

In a reaction analogous to (16) the rhenium complex $NaRe(CO)_5$ absorbed either one or two moles of borane from solution in bis-(2-methoxyethyl) ether:

$$\tfrac{1}{2}\mathrm{B_2H_6 + NaRe(CO)_5 \xrightarrow{\text{diglyme}} Na^+[(CO)_5Re(BH_3)]^-} \qquad (18)$$

$$\tfrac{1}{2}\mathrm{B_2H_6 + Na^+[(CO)_5Re(BH_3)]^- \xrightarrow{\text{diglyme}} Na^+[(CO)_5Re(BH_3)_2]^-} \qquad (19)$$

These sodium salts of pentacarbonyl metal boranes crystallize as ethereal solvates but the non-solvated Et_4N^+ and Bu_4P^+ salts were isolated by metathesis in THF. The manganese analogue was less stable and lost diborane on standing for several days at −25 °C:

$$\mathrm{[(CO)_5Mn(BH_3)]^- \underset{-78\,^\circ C}{\overset{>-25\,^\circ C}{\rightleftharpoons}} [Mn(CO)_5]^- + THF,BH_3} \qquad (20)$$

However, the phosphine derivative [reaction (17)] was stable at room temperature. The i.r., electronic, and n.m.r. spectra led to the conclusion that the metal was acting as an electron-pair donor to the borane, *i.e.* $[L_5M{\rightarrow}BH_3]^-$ where

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[26] N. N. Greenwood and B. S. Thomas, unpublished observations.

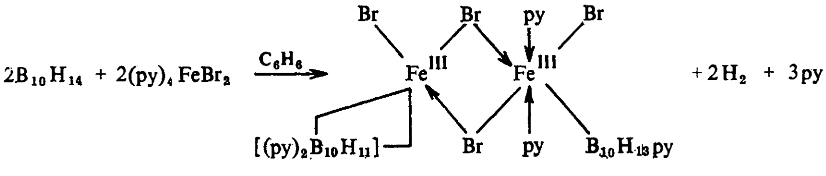
[27] G. W Parshall, *J. Amer. Chem. Soc.*, 1964, **86**, 361.

L = Ph_3P and M = Mn or Re. The reaction of decaborane with a hydridoplatinum chloride complex affords another example of this class of reaction:[28]

$$B_{10}H_{14} + 2(Et_3P)_2Pt(H)Cl \longrightarrow [Pt(B_{10}H_{12})(Et_3P)_2] + (Et_3P)_2PtCl_2 + 2H_2 \qquad (21)$$

This is a variant of a more general reaction to be considered in the next section.

Another synthesis of a metalloborane by the reaction of a borane with a transition-metal complex involved the novel use of decaborane as an oxidizing agent.[29] Thus decaborane reacts with $(py)_4Fe^{II}Br_2$ in benzene according to equation (22) to give the Fe^{III} compound (A) in 94% yield and this, on treatment with THF, was cleaved to give an insoluble complex $(py)FeBr_2B_{10}H_{11}(py)_2$ and a compound that was soluble in THF and which, on recrystallization, gave an almost quantitative yield of the brown, tetrahedral, high-spin iron(III) complex $(py)FeBr_2B_{10}H_{13}(py)$ (B). Complex (B) was monomeric and non-conducting in methyl cyanide and had a magnetic moment $\mu_{eff} = 5.60$ BM. Infrared spectroscopy confirmed the presence of pyridine co-ordinated both to iron and to the boron cluster respectively, thus leading to the formulation of the complex as a *monohapto*-metalloborane (Figure 7). This structure can be thought of as being derived from $B_{10}H_{15}^-$ in which the H^- ligand has been replaced by py and one hydrogen atom substituted by the iron complex. Analogous but more complicated oxidative reactions occurred between decaborane and complexes of cobalt(II) and tin(II).



(A)

More recently,[30] hexaborane(10) has been shown to react with $K[(\eta\text{-}C_2H_4)PtCl_3]$ at low temperatures to give the compound $(B_6H_{10})_2PtCl_2$, which is unstable at room temperature but forms yellow crystals below −20 °C:

$$2B_6H_{10} + [(\eta\text{-}C_2H_4)PtCl_3]^- \rightarrow (B_6H_{10})_2PtCl_2 + C_2H_4 + Cl^- \qquad (23)$$

The complex has been shown by single-crystal *X*-ray diffraction analysis to have the *trans*-square-planar configuration about the platinum atom, each B_6 unit being bridge-bonded *via* the unique B(4)B(5) basal boron atoms (see Figure 8). The most noteworthy feature of the icosahedral B_6 fragments is the lengthening of the unusually short B(4)—B(5) distance (160 pm) found in uncomplexed

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[28] F. Klanberg, P. A. Wegner, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, 1968, **7**, 2072.

[29] N. N. Greenwood and H. Schick, *Chem. Comm.*, 1969, 935.

[30] J. P. Brennan, R. Schaeffer, A. Davison, and S. S. Wreford, *J.C.S. Chem. Comm.*, 1973, 354.

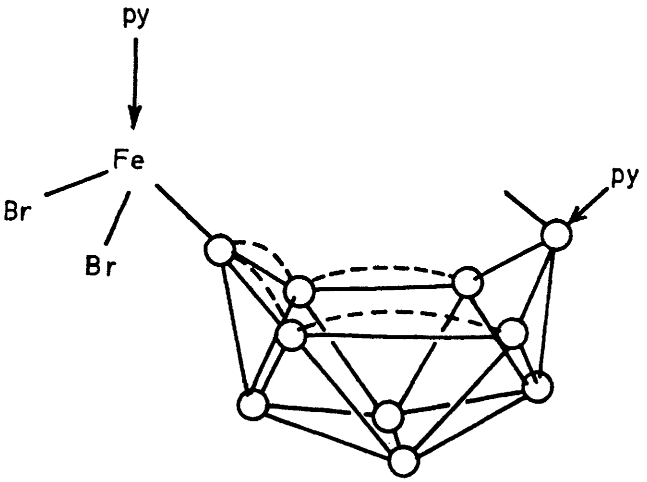

Figure 7 *Proposed structure of the iron*(III) *complex* (py)FeBr$_2$(B$_{10}$H$_{13}$py); *each of the nine boron atoms* B(1)—B(5) *and* B(7)—(10) *carries a terminal hydrogen atom, shown only for* B(9), *in addition to the four bridge hydrogens indicated*

B$_6$H$_{10}$ to a value typical of B—B distances in triangulated boranes (~ 182 pm). Each borane cluster is thus acting as a neutral *dihapto*-ligand and the three-centre two-electron B(4)B(5)Pt bonds are nearly perpendicular to the Cl—Pt—Cl axis.

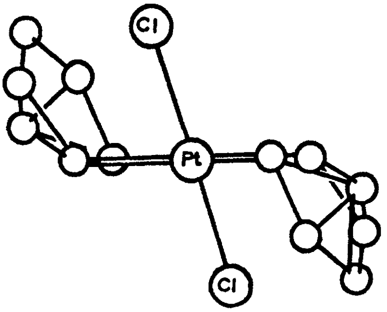

Figure 8 *Molecular structure of* (B$_6$H$_{10}$)$_2$PtCl$_2$; *typical interatomic distances are* Pt—Cl 231.3 pm, Pt—B 227 pm, *all* B—B 182 ± 5 pm; *angles about boron* 60 ± 2°, *internal angles of basal boron atoms* 108 ± 2°

4. Borane Anion plus Transition-Metal Complex

This route to metalloboranes was first exploited in an extensive series of reactions by the du Pont group[28] and has since been employed to obtain a wide variety of metalloboranes. The results will be reviewed in order of decreasing size of the co-ordinating borane moiety.

A. Higher Borane Anions.—A series of transition-metal complexes of n-$B_{18}H_{20}^{2-}$ and i-$B_{18}H_{20}^{2-}$ have been prepared by direct reaction with phosphine- and carbonyl-substituted complexes of Co, Rh, Ni, Pd, and Pt.[31] The compounds have the general formula $(B_{18}H_{20})M(\text{ligand})_n$ and typical reactions are shown in equations (24)—(28).

$$Na^+{}_2[\text{n-}B_{18}H_{20}]^{2-} + (Ph_3P)_2NiCl_2 \xrightarrow{\text{THF}} (\text{n-}B_{18}H_{20})Ni(Ph_3P)_2 \text{ (red)} \quad (24)$$

$$Na^+{}_2[\text{n-}B_{18}H_{20}]^{2-} + (\text{diphos})MCl_2 \xrightarrow{\text{THF}} (\text{n-}B_{18}H_{20})M(\text{diphos}) \text{ (purple, Ni; yellow, Pd)} \quad (25)$$
$$\{\text{diphos} = Ph_2PCH_2CH_2PPh_2;\ M = \text{Ni or Pd}\}$$

$$Na^+{}_2[\text{i-}B_{18}H_{20}]^{2-} + (\text{diphos})MCl_2 \xrightarrow[(C_6H_6)]{\text{THF}} (\text{i-}B_{18}H_{20})M(\text{diphos}) \text{ (red, Ni; yellow, Pd and Pt)} \quad (26)$$
$$\{M = \text{Ni, Pd, or Pt}\}$$

$$Na^+{}_2[\text{n-}B_{18}H_{20}]^{2-} + \tfrac{1}{2}Co_2(CO)_8 \xrightarrow[\text{(ii) }Me_4NCl]{\text{(i) THF}} [Me_4N]^+[\text{n-}B_{18}H_{20})Co(CO)_3]^- \text{ (orange-red)} \quad (27)$$

$$[Me_4N]^+{}_2[\text{n-}B_{18}H_{20}]^{2-} + (Ph_3P)_2Rh(CO)Cl \xrightarrow{\text{MeCN}} [Me_4N]^+[(\text{n-}B_{18}H_{20})Rh(CO)Ph_3P] \text{ (red)} \quad (28)$$

The i.r., u.v.—visible, and ^{11}B n.m.r. spectra of several of these complexes were studied and it is suggested that the metal atom is bonded to one of the open faces of the $B_{18}H_{20}^{2-}$ ion as a *tetrahapto* bidentate chelating ligand, as illustrated in Figure 9.

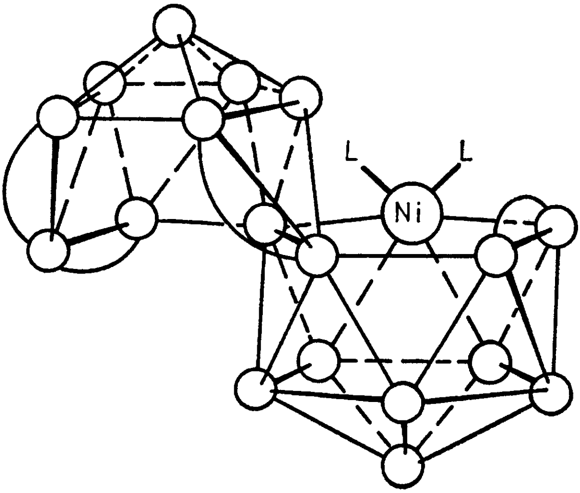

Figure 9 *Proposed structure of* $(\text{n-}B_{18}H_{20})Ni(Ph_3P)_2$

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[31] R. L. Sneath and L. J. Todd, *Inorg. Chem.*, 1973, **12**, 44.

It is convenient to consider at this point some sandwich compounds formed by the reaction of thiaundecaborate anions with transition metals. During an extensive study of thiaboranes and their derivatives Muetterties and his co-workers showed that the reaction of the $B_{10}H_{10}S^{2-}$ dianion with a variety of transition-metal halides gave a series of icosahedral metallothiaboranes such as $[(B_{10}H_{10}S)_2Co]^-$.[32] Thus decaborane was found to react quantitatively with aqueous ammonium polysulphide to give $B_9H_{12}S^-$, which could then be converted into $B_{10}H_{11}S^-$ by pyrolysis at 200 °C. Subsequent treatment with a strong base such as butyl-lithium gave the required intermediate $B_{10}H_{10}S^{2-}$. In THF solution anhydrous $FeCl_2$ gave the complex $[(B_{10}H_{10}S)_2Fe]^{2-}$, isolated as the pink bis(tetramethylammonium) salt or the maroon di-caesium monohydrate salt. These compounds could be polarographically oxidized to $[(B_{10}H_{10}S)_2Fe]^-$ and partially halogenated with chlorine or bromine. A similar sequence of reactions using anhydrous $CoCl_2$ gave the brown crystalline cobalt(III) salt $[Me_4N]^+[(B_{10}H_{10}S)_2CO]^-$; the yellow-orange complex $Cs^+[(B_{10}H_{10}S)_2Co]^-$ and the orange crystalline compound $[(C_5H_5)_2Co]^+[(B_{10}H_{10}S)_2Co]^-$ were also characterized. The spectroscopic properties of these metallothiaborane anions encourage their formulation as sandwich compounds structurally similar to the carbollyl complexes of $B_9C_2H_{11}^{2-}$ (see Figure 10). Other sandwich compounds were prepared by ligand-replacement reactions, *e.g.* the yellow complex $[(B_{10}H_{10}S)Pt(Et_3P)_2]$ and the colourless anion $[(B_{10}H_{10}S)Re(CO)_3]^-$.[32]

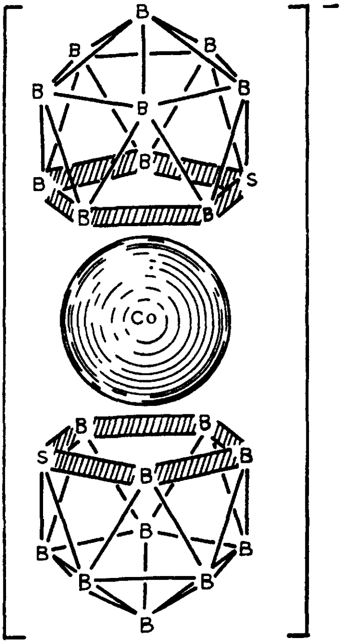

Figure 10 *Proposed structure of the anion* $[(B_{10}H_{10}S)_2Co]^-$

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[32] W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, 1967, 6, 1696.

B. Decaborate Anions.—The $B_{10}H_{13}^-$ anion reacts with a wide variety of transition-metal halide complexes to give three types of metal–decaborane complexes, $[M(B_{10}H_{12})_2]^{2-}$, $[M(B_{10}H_{12})L_3]^-$, and $[M(B_{10}H_{12})L_2]$, in which the $B_{10}H_{12}^{2-}$ dianion can be considered to be acting as a *tetrahapto* bidentate chelating ligand.[28] Typical reactions are as follows:

$$4B_{10}H_{13}^- + (Ph_3P)_2MCl_2 \rightarrow [M(B_{10}H_{12})_2]^{2-} + 2B_{10}H_{14} + 2Ph_3P + 2Cl^- \quad (29)$$

$$M = \text{Co, Ni, Pd, or Pt}$$

$$2B_{10}H_{13}^- + (Ph_3P)_2M(CO)Cl \longrightarrow [M(B_{10}H_{12})(CO)(Ph_3P)_2]^- + B_{10}H_{14} + Cl^- \quad (30)$$

$$M = \text{Co, Rh, or Ir}$$

$$2B_{10}H_{13}^- + (Et_3P)_2PtCl_2 \rightarrow [Pt(B_{10}H_{12})(Et_3P)_2] + B_{10}H_{14} + 2Cl^- \quad (31)$$

This last reaction type also occurs with bis(triarylphosphine)dichloropalladium, but not when the bis(trialkylphosphine)dichloropalladium analogues are used. In general, good yields were obtained from reactions (29)—(31) by using $NaB_{10}H_{13}$ in diethyl ether or THF and then precipitating the anionic complexes with large cations such as Me_4N^+ or Bu_3PH^+.

Extensive i.r. and n.m.r. data were reported on these compounds but the structure-motif was established by the single-crystal *X*-ray analysis of $[Me_4N]^+_2[Ni(B_{10}H_{12})_2]^{2-}$.[33] The structure of the anion is shown in Figure 11;

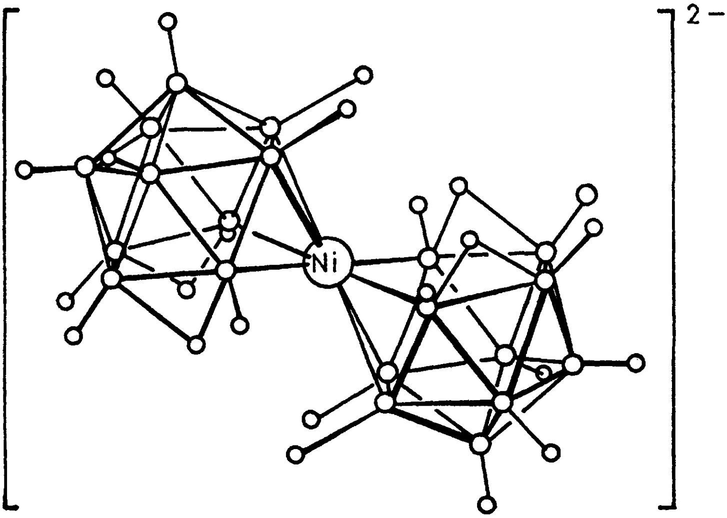

Figure 11 *The structure of the anion* $[Ni(B_{10}H_{12})_2]^{2-}$

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[33] L. J. Guggenberger, *J. Amer. Chem. Soc.*, 1972, **94**, 114.

it comprises two bidentate $B_{10}H_{12}^{2-}$ units chelating on to the central nickel ion in such a way as to preserve planar bonding geometry. The relation to the structure of the $[Zn(B_{10}H_{12})_2]^{2-}$ ion in Figure 4 is obvious, the only difference being the relative orientation of the chelating borane clusters; thus, rotation of one of the borane clusters through 90° about the z-axis transforms one structure into the other. The shortest nickel–boron distances involved positions 5, 6, 9, and 10, with the Ni—B(5) and Ni—B(10) distances (211 and 218 pm) being significantly shorter than those of Ni—B(6) and Ni—B(9) (224 and 222 pm). Boron–boron distances were similar to those in decaborane, as expected, with an average B—B distance of 179 pm. The average B—H terminal distance of 122 pm and B—H bridge distance of 134 pm are also within the expected range. The angle subtended at the nickel atom from the midpoints of the B(5)—B(6) and B(9)—B(10) bonds is 80.8°.

The caesium salts of $[M(B_{10}H_{12})_2]^{2-}$ (M = Co, Ni, Pd, or Pt) were soluble in water and could be purified by crystallization as the tetramethylammonium salt from this solvent. The Me_4N^+ salts were moderately soluble in ethanol and very soluble in methyl cyanide, acetone, and DMF. They behave as normal 2:1 electrolytes in methyl cyanide. Salts of the cobalt complex are burgundy red, the nickel complex is orange, and the palladium and platinum are yellow. There is also a significant difference in thermal stability, the cobalt and nickel complexes decomposing below 180 °C in nitrogen, the palladium complex at about 240 °C, and the platinum complex above 300 °C. A qualitative ordering of the hydrolytic stability of the dianion series is $Pt > Pd > Ni \gg Co$, the complexes being moderately stable at $pH < 7$ but rapidly degrading to $B_9H_{14}^-$ and metal hydroxides in basic solutions. The neutral complexes $M(B_{10}H_{12})(R_3P)_2$ behave similarly.

The dianion $B_{10}H_{14}^{2-}$ can also be used to prepare complexes of $B_{10}H_{12}^{2-}$, the overall reaction being:[34]

$$2B_{10}H_{14}^{2-} + M^{2+} \rightarrow [M(B_{10}H_{12})_2]^{2-} + 2H_2 \qquad (32)$$

Thus $Cs_2B_{10}H_{14}$ reacted with $NiCl_2$ and $CoCl_2$ in aqueous acetone to give the complex anions in 55% yield, the products being isolated as the insoluble tetramethylammonium salts. Likewise, (cyclo-octa-1,5-diene)di-iodoplatinum reacted to give $[Me_4N]^+{}_2[Pt(B_{10}H_{12})_2]^{2-}$ in 30% yield, and the analogous palladium complex was obtained in 25% yield by a similar route. Despite these reactions, $PtCl_2$ itself gave only a 7% yield of $[Pt(B_{10}H_{12})_2]^{2-}$ with $B_{10}H_{14}^{2-}$ and $PdCl_2$ was completely reduced; zinc chloride was unreactive, as were $(Ph_3P)_2Ir(CO)Cl$ and $(Ph_3P)_2PdCl_2$.

In a parallel study it was shown that the progress of reactions involving the $B_{10}H_{13}^-$ anion is critically dependent on the counter-cation used. Thus, although reactions (29)—(31) proceed smoothly with $NaB_{10}H_{13}$ in ethereal solution, the reaction of this salt with mercury(II) halides yields unstable products; however, $Me_4NB_{10}H_{13}$ reacts smoothly with $HgCl_2$ in THF to give the desired product

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[34] A. R. Siedle and T. A. Hill, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3874.

$[Me_4N]^+_2[Hg(B_{10}H_{12})_2]^{2-}$.[35] Likewise $NaB_{10}H_{13}$ could not be made to react with $(py)_2CoCl_2$ or $(py)_2CoBr_2$, but when either $Me_4NB_{10}H_{13}$ or $Et_3NHB_{10}H_{13}$ was used, reaction (33) proceeded to give an 80% yield of the complex anions $[(py)CoX_2(B_{10}H_{11}py)]^-$:[35]

$$Me_4NB_{10}H_{13} + (py)_2CoX_2 \xrightarrow{THF} [Me_4N]^+[(py)CoX_2(B_{10}H_{11}py)]^- + H_2 \quad (33)$$

The brown crystalline products were insoluble in ethers, slightly soluble in methyl cyanide, and more soluble in nitromethane, in which they were shown to be 1:1 electrolytes. The effective magnetic moments at room temperature fell within the range 3.3—4.0 BM, consistent with the presence of Co^{II}, d^7 with 3 unpaired electrons. The i.r. spectra show the presence of two types of pyridine, bound to the metal and to the borane cluster, respectively. These various properties, in conjunction with the structures determined by *X*-ray diffraction already shown in Figures 4 and 11, strongly suggest that the structure of the anionic complex is as shown in Figure 12. In this structure the $(B_{10}H_{11}py^-)$ moiety can be considered as a bidentate chelating ligand that is isoelectronic with $B_{10}H_{12}^{2-}$ in which one H^- has been replaced by py as a ligand.

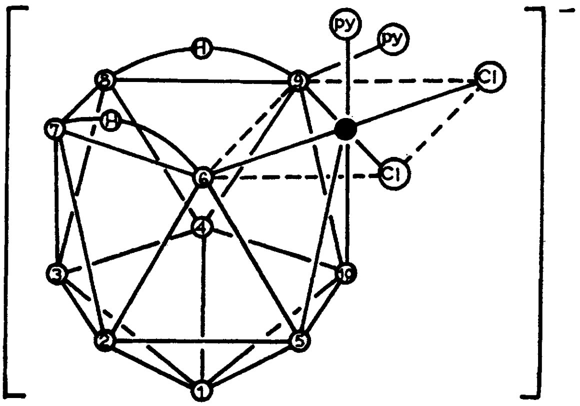

Figure 12 *Proposed structure of the anion* $[(py)CoCl_2(B_{10}H_{11}py)]^-$; *the* B(9) *atom carries a pendent pyridine ligand and each of the other nine boron atoms is covalently bonded to a terminal hydrogen atom* (*not shown*)

C. Smaller Borane Anions.—Three new classes of *nido*-metalloboranes were reported by the du Pont group in 1970.[36] The thiaborane anion $B_9H_{12}S^-$ reacted with *trans*-$[(Et_3P)_2Pt(H)Cl]$ with evolution of hydrogen as indicated in equation (34):

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[35] N. N. Greenwood and D. N. Sharrocks, *J. Chem. Soc.* (*A*), 1969, 2334.

[36] A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1970, **92**, 2571.

$$CsB_9H_{12}S + \mathit{trans}\text{-}[(Et_3P)_2Pt(H)Cl] \rightarrow \mathit{cis}\text{-}[(Et_3P)_2Pt(H)B_9H_{10}S] + H_2 \quad (34)$$

The neutral platinum–thiaborane complex was monomolecular in solution and has a Pt—H stretching vibration at 2214 cm^{-1}. ^1H and ^{31}P n.m.r. spectra indicate non-equivalent phosphine ligands, and the definitive structure of the complex was established by single-crystal *X*-ray analysis (see Figure 13). It can be seen that both platinum and sulphur are incorporated within the 11-atom icosahedral fragment. The Pt—S distance is 243 pm and the three close Pt—B contacts are in the range 220—225 pm. The $B_9H_{10}S^-$ ligand is isoelectronic with $B_{10}H_{12}^{2-}$ considered in the preceding subsection, thereby implying that the platinum co-ordination polyhedron is a quasi-five-co-ordinate distorted square pyramid.

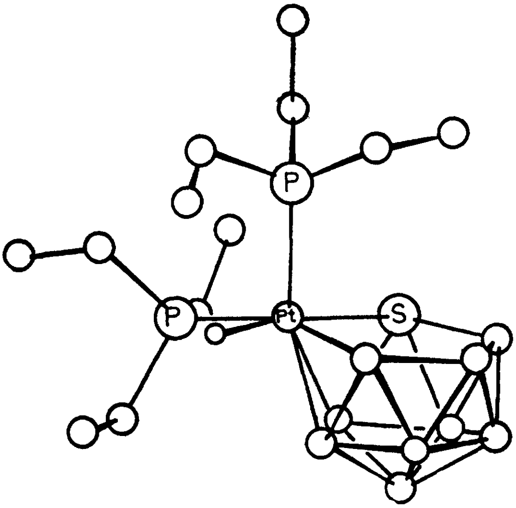


Figure 13 *Structure of* $(Et_3P)_2Pt(H)B_9H_{10}S$; *each of the nine boron atoms is bonded to a terminal hydrogen atom (not shown) and a further borane hydrogen atom (also not depicted) is probably associated with one or more of the atoms in the open face of the icosahedral fragment*

The other new types of metalloborane were $(Et_3P)_2PtB_9H_{11}L$ and $(Et_3P)_2PtB_8H_{12}$. Thus the $B_9H_{12}^-$ anion reacts with *trans*-$[(Et_3P)_2Pt(H)Cl]$ in the presence of donor molecules, liberating one mole of hydrogen to give the PtB_9 complexes, and these can be degraded in alcohol to the PtB_8 species:[36]

$$CsB_9H_{12} + \mathit{trans}\text{-}[(Et_3P)_2Pt(H)Cl] + L \longrightarrow (Et_3P)_2PtB_9H_{11}L + CsCl + H_2 \quad (35)$$

$$(Et_3P)_2PtB_9H_{11}L + 3EtOH \rightarrow (Et_3P)_2PtB_8H_{12} + B(OEt)_3 + L + H_2 \quad (36)$$

Organic ligands based on amines, nitriles, phosphines, and sulphides function effectively as L in reaction (35). ^1H and ^{31}P n.m.r. spectra do not distinguish between the two Et_3P ligands bonded to platinum, and the most reasonable structure is that shown in Figure 14, in which the $B_9H_{11}L^{2-}$ ligand is effectively *trihapto*-bidentate, with the square-planar platinum orbitals bisecting the B(2)—B(5) and B(2)—B(7) edges. The PtB_8 species could then plausibly be derived from this by elision of $BH(L)^{2+}$ and the addition of two bridge protons to give the structure shown in Figure 15.

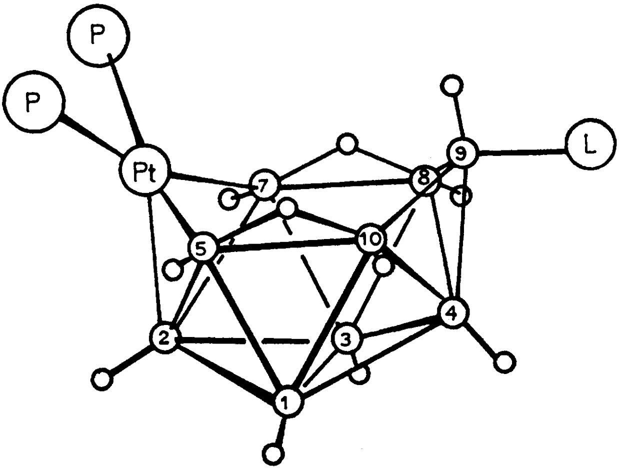


Figure 14 *Proposed structure of* $(Et_3P)_2Pt(B_9H_{11}L)$

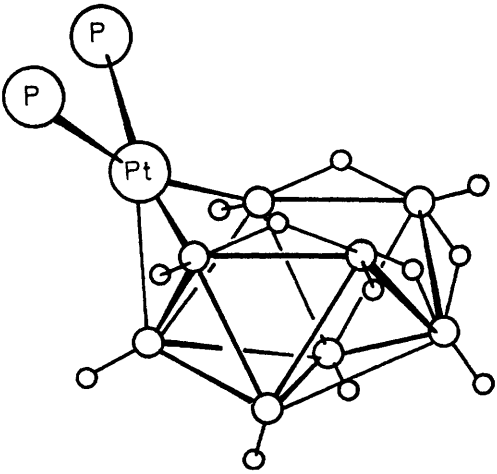


Figure 15 *Proposed structure of* $(Et_3P)_2Pt(B_8H_{12})$

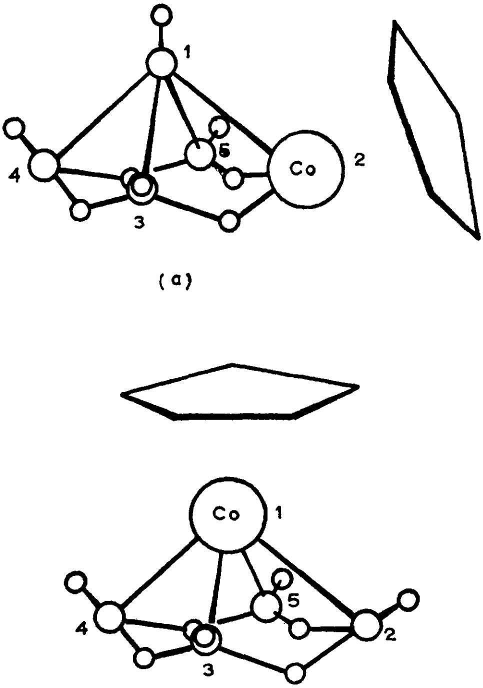
The metalloboranes $(Ph_3P)_2CuB_5H_8$ and $(Ph_3P)_2CuB_6H_9$ have been synthesized by reaction of the corresponding potassium boranates with tris(triphenylphosphine)copper(I) chloride in the mixed solvent methylene chloride–THF at −78 °C:[37]

$$KB_5H_8 + (Ph_3P)_3CuCl \rightarrow (Ph_3P)_2CuB_5H_8 + KCl + Ph_3P \qquad (37)$$

$$KB_6H_9 + (Ph_3P)_3CuCl \rightarrow (Ph_3P)_2CuB_6H_9 + KCl + Ph_3P \qquad (38)$$

Both complexes are white crystalline solids and are the first air-stable derivatives of B_5H_9 and B_6H_{10}, respectively. The parent boranes can be regenerated in 75% yield by treating the complexes with ethereal hydrogen chloride. The structure of the complexes has not been elucidated but may consist of a bridging $(Ph_3P)_2Cu$ group spanning two of the basal boron atoms in each case.

In a short communication it has been reported that NaB_5H_8 reacts with an excess of $CoCl_2$ and NaC_5H_5 in THF to give a wide range of products.[38] The new compounds isolated so far are shown in Figure 16, and include dark-red needles



(a)

(b)

Fig 16 (a *and* b)

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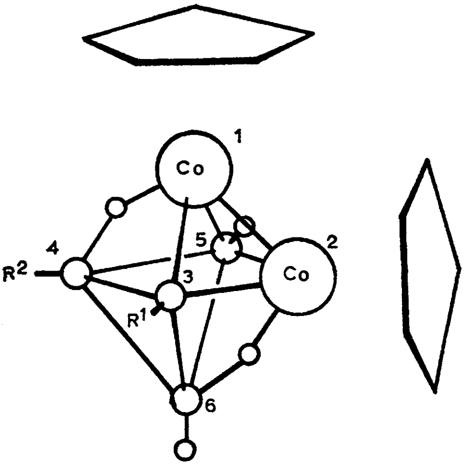
[37] V. T. Brice and S. G. Shore, *Chem. Comm.*, 1970, 1312.

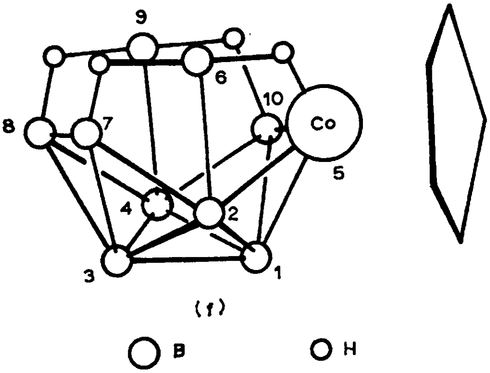
[38] V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, 1973, **95**, 5078.



(c) $R^1 = R^2 = H$

(d) $R^1 = \text{cyclo-}C_5H_9, R^2 = H$

(e) $R^1 = H, R^2 = \text{cyclo-}C_5H_9$



(f)

Figure 16 *Proposed structures for cobalt–borane complexes (see text); the terminal hydrogen atoms in (f) have been omitted for clarity* of (π-C_5H_5)Co(B_4H_8) (a), which are converted into the pale-yellow crystalline isomer (b) by gas-phase pyrolysis at 200 °C for thirty minutes; (π-C_5H_5)$_2$-Co_2(1,2-B_4H_6) (c), which is a violet, crystalline solid isoelectronic with $C_2B_4H_6$ and $B_6H_6^{2-}$; (π-C_5H_5)$_2$$Co_2$(3-cyclo-$C_5H_9$-1,2-$B_4H_5$) (d), which contains equivalent (π-C_5H_5) groups; (π-C_5H_5)$_2$$Co_2$(4-*cyclo*-$C_5H_9$-1,2-$B_4H_5$) (e), which contains non-equivalent (π-C_5H_5) groups; and (π-C_5H_5)Co(5-B_9H_{13}) (f), which is a red solid, isoelectronic with decaborane(14). The proposed structures in Figure 16(a)—(f) have been formulated on the basis of ^1H and ^{11}B n.m.r. spectra and mass spectrometric evidence.

An intriguing series of π-borallyl (π-$B_3H_7^{2-}$) complexes with nickel, palladium, and platinum have recently been synthesized and the stabilities have been found to increase in the order Ni < Pd < Pt.[39,40] The π-$B_3H_7^{2-}$ dianion is isoelectronic with the π-allyl ion π-$C_3H_5^-$. The platinum complexes were synthesized by allowing caesium octahydrotriborate(1−) to react with *cis*-[(R_3P)$_2$PtCl_2] in the mixed solvent methyl cyanide–triethylamine:

$$CsB_3H_8 + cis\text{-}[(R_3P)_2PtCl_2] + Et_3N \rightarrow (R_3P)_2PtB_3H_7 + CsCl + Et_3NHCl \qquad (39)$$

The complexes were white, or off-white, and typical phosphine ligands were Et_3P, Et_2PhP, Ph_3P, Me_2PhP, (p-tol)$_3$P, and $Ph_2PCH_2CH_2PPh_2$. The structure determined by *X*-ray diffraction of the bis(dimethylphenylphosphine) complex is shown in two projections in Figure 17. The two phosphine ligands and the

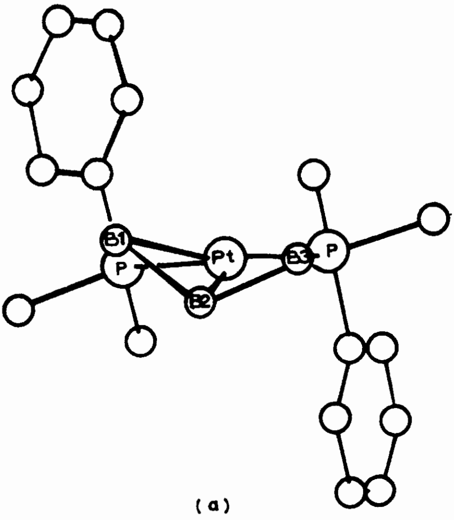


Figure 17 (a)

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[39] L. J. Guggenberger, A. R. Kane, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 5665.

[40] E. L. Muetterties, *Pure Appl. Chem.*, 1972, **29**, 585.

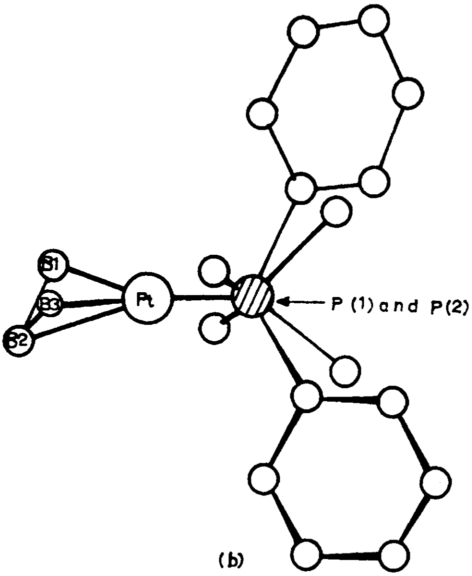

Figure 17 (a) *The molecular configuration of* $(Me_2PhP)_2Pt(\pi\text{-}B_3H_7)$, *all hydrogen atoms being omitted for clarity*; (b) *a side view of the molecule, illustrating the angle between the* π*-borallyl plane and the* P(1)PtP(2) *plane.* (*The two phosphorus atoms overlap in this view*)

asymmetrically bonded $\pi\text{-}B_3H_7{}^{2-}$ ligand complete an essentially square-planar co-ordination environment around the platinum. The PPtP bond angle is 96° and the Pt—P distances are 230.1 and 231.1 pm. The Pt—B distances are 238 pm to B(1) in the PPtP plane and 218, 213 pm to B(2) and B(3), whose mid point lies in this plane. The interboron distances are 186 ± 5 pm for B(1)—B(2) and 192 ± 4 pm for B(2)—B(3), and the dihedral angle between the B_3 plane and the PtP_2 plane is 117°. The B(1)—B(3) distance is 315 pm, *i.e.* non-bonding. Although the hydrogen atoms in the $\pi\text{-}B_3H_7{}^{2-}$ ligand were not specifically located because of disorder, they are considered to be similar to those in $B_3H_8{}^-$ [in which B(1) and B(3) are directly bonded]. The bonding is perhaps best considered in molecular orbital terms as an essentially π-bonded $B_3H_7{}^{2-}$ group but in the valence-bond σ–π formalism the dsp^2 hybrid orbitals on the platinum would be directed to B(3) and to the mid-point of B(1)—B(2), as indicated by the resonance form in Figure 18.

The i.r., *X*-ray, photoelectron, and n.m.r. spectra of the complexes were also studied, and the ^1H n.m.r. spectra in particular showed that the π-borallyl complexes were stereochemically more rigid than the (hydrogen-bridged) $\sigma\text{-}B_3H_8{}^-$ metalloborane complexes. An interesting additional reaction of the π-borallylplatinum complex was the facile replacement of the $\pi\text{-}B_3H_7{}^{2-}$ ion by

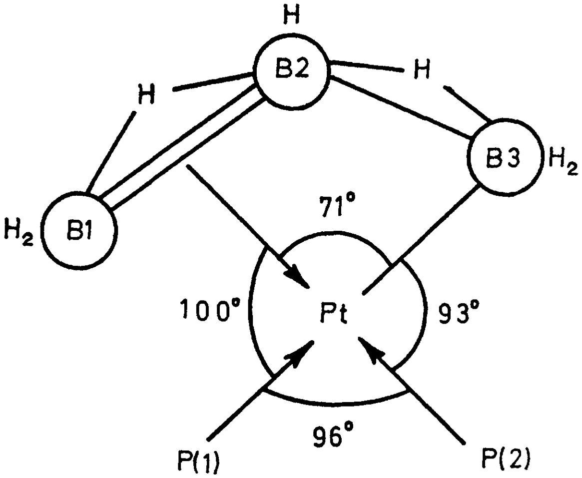

Figure 18 *A valence-bond description of the bonding in the π-borallyl complex shown in Figure* 17

trialkylphosphines to produce the first examples of tetrakis(trialkylphosphine)platinum(0). For example, a solution of $(Et_3P)_2PtB_3H_7$ when heated at 125 °C for 10 min in Et_3P gave a dark orange-red solution from which off-white crystals of $(Et_3P)_4Pt$ were obtained on cooling to −40 °C.

5 Metathesis (Interchange of Metal Atoms)

Several metalloboranes of types similar to those discussed in preceding sections can be prepared by metathetical reactions. Thus, the red complex $[Me_4N]^+{}_2[Co(B_{10}H_{12})_2]^{2-}$ can readily be prepared by treating a solution of $[(THF)_2Zn(B_{10}H_{12})]_2$ in acetone with a solution of anhydrous $CoCl_2$ in the same solvent followed by precipitation with aqueous Me_4NCl. In view of the known behaviour of the dimer in solution [see equation (11)] it seems likely that the reaction proceeds as follows:

$$[(THF)_2Zn(B_{10}H_{12})]_2 \xrightarrow{Me_2CO} Zn^{2+}[Zn(B_{10}H_{12})_2]^{2-} + 4THF$$
$$[Zn(B_{10}H_{12})_2]^{2-} + CoCl_2 \xrightarrow{Me_2CO} [Co(B_{10}H_{12})_2]^{2-} + ZnCl_2 \qquad (40)$$

Another typical metathesis occurs when $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ reacts with MeHgCl in THF; an orange crystalline product was obtained as shown in equation (41).[21]

$$MeHgCl + [Me_2Tl]^+[B_{10}H_{12}TlMe_2]^- \xrightarrow{THF} [Me_2Tl]^+[B_{10}H_{12}HgMe,THF]^- + Me_2TlCl \qquad (41)$$

The product was then allowed to react with [Ph_3MeP]Br in dichloromethane to give crystals of unsolvated [$Ph_3MeP]^+[B_{10}H_{12}HgMe]^-$. Spectroscopic properties suggest that the anion has the chelated structure shown in Figure 19, though a bridging μ-HgMe structure is not ruled out.

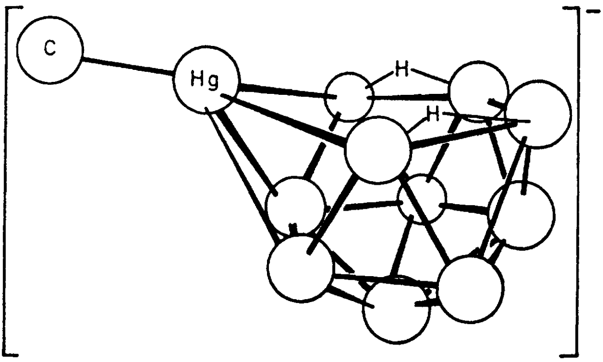

Figure 19 *Proposed structure of* $[B_{10}H_{12}HgMe]^-$; *the terminal hydrogen atoms attached to the boron atoms and the methyl carbon atom are not shown*

The related reaction type of reductive metathesis was used in a very early study to prepare the copper(I) metalloborane $Cu_2B_{10}H_{10}$ from an aqueous solution of the ionic *closo*-borane $Na_2B_{10}H_{10}$ and an excess of the copper(II) salt $Cu(ClO_4)_2$.[41] The detailed course of the reaction was not investigated but the colourless crystalline product was subjected to a detailed *X*-ray structural analysis. This established that the $B_{10}H_{10}{}^{2-}$ unit was indeed a bicapped square Archimedian antiprism, as had been postulated on the basis of n.m.r. data, but the most interesting structural feature was the close approach of the copper atoms to the centre of diagonally opposite edges of the borane cage as indicated in Figure 20(a). The actual Cu—B distances were in the range 214—233 pm, with a mean value of 220 pm, close to the estimated Cu—B distance of 213 pm for a covalent two-electron three-centre BCuB bond. Each copper(I) atom can be considered to be *sp*-hybridized and is equidistant from two such edges, so that the bonding environment of copper is as shown in Figure 20(b). The angle subtended by the two edge-boron atoms at the copper atom is only 46°, thus making a four-co-ordinate bonding model for copper less attractive. In the extreme view therefore the *closo*-$B_{10}H_{10}{}^{2-}$ anion can be considered as a tetrakis(*dihapto*) ligand donating one pair of electrons to each of four Cu^+ cations; at the opposite extreme the structure can be considered as a cross-linked covalent polymer $[Cu_2B_{10}H_{10}]_n$.

[41] R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **1962, 37, 1779.**

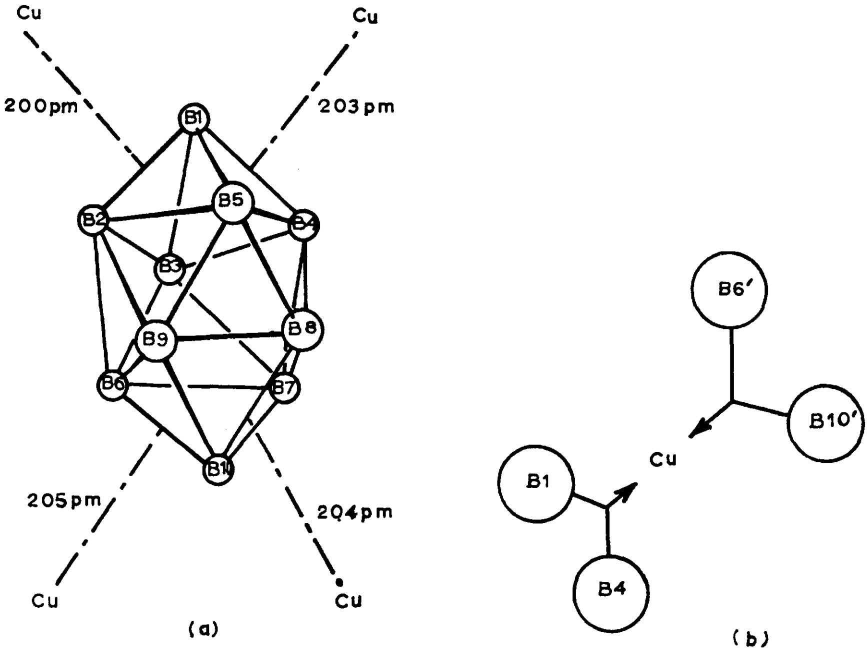

Figure 20 (a) *The structure of the ten-atom boron cluster in* $Cu_2B_{10}H_{10}$ *showing the close approaches of four copper*(I) *ions to opposite edges of the polyhedron*; (b) *the digonal dative-bonding environment of the copper*

6 Borane Anion plus Metal Halide (or Alkylmetal Halide)

It was mentioned in Section 2 that, unlike the dialkyls and diaryls of zinc and cadmium, organomercury compounds did not react with decaborane to give $(R_2O)_2Hg(B_{10}H_{12})$, and that alternative routes to the derived bischelated anion $[Hg(B_{10}H_{12})_2]^{2-}$ had to be devised.[22] It was also found that $NaB_{10}H_{13}$ did not give a satisfactory reaction with methylmercury(II) halides.[42] However, decaboranylmagnesium iodide reacted with methylmercury(II) halides in ethereal solution to give air-sensitive, orange crystalline solids of general formula $Mg_6[Hg(B_{10}H_{12})_2]X_{10},n Et_2O$. The rates of reaction were in the order Cl > Br $\gg$ I, as expected from the polarities of the respective Hg—X bonds, and indicate that the borane is acting as a pseudoanion $B_{10}H_{13}{}^{\delta-}MgI^{\delta+}$. The compounds dissolved in water or ethanol, from which the orange tetramethylammonium salt $[Me_4N]^+{}_2[Hg(B_{10}H_{12})_2]^{2-}$ could be precipitated. The original products should thus be formulated as the mixed salts $Mg[Hg(B_{10}H_{12})_2],5MgX_2,n Et_2O$. The $[Hg(B_{10}H_{12})_2]^{2-}$ anion was found to be isostructural with the zinc and cadmium analogues (see Figure 4) and the high-resolution ^{11}B n.m.r. spectra of all three species have been studied in detail.[22] The i.r. spectra of the three tetramethyl-

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[42] N. N. Greenwood and N. F. Travers, *Chem. Comm.*, 1967, 216.

ammonium salts were identical except for a single band, which can therefore be assigned to the asymmetrical metal–boron stretching vibration of the tetrahedral MB_4 unit (see Figure 5). This occurs at 278, 235, and 225 cm^{-1} for the zinc, cadmium, and mercury complexes, respectively.

An alternative route to $[Hg(B_{10}H_{12})_2]^{2-}$ is by allowing two moles of $Me_4NB_{10}H_{13}$ to react with mercury(II) chloride in THF:[35]

$$2Me_4NB_{10}H_{13} + HgCl_2 \rightarrow [Me_4N]^+{}_2[Hg(B_{10}H_{12})_2]^{2-} + 2HCl \qquad (42)$$

An unidentified green powder was also formed in addition to the orange crystalline mercury complex. The reaction is particularly sensitive to conditions and could not be run successfully with other salts of $B_{10}H_{13}^-$, other mercury halides, or other solvents.

The decaborane dianion $B_{10}H_{12}^{2-}$ has also been used successfully to synthesize metalloborane complexes from metal halides and alkylmetal halides. Thus, $(Ph_4As)_2B_{10}H_{12}$ reacted with anhydrous $SnCl_2$ in two ways in a mixed THF–methylene chloride solvent as indicated in equations (43) and (44).[43]

$$(Ph_4As)_2B_{10}H_{12} + SnCl_2 \rightarrow [Ph_4As]^+{}_2[B_{10}H_{10}]^{2-} + Sn + 2HCl \qquad (43)$$

$$(Ph_4As)_2B_{10}H_{12} + SnCl_2 \rightarrow [Ph_4As]^+{}_2[(B_{10}H_{12})SnCl_2]^{2-} \qquad (44)$$

In reaction (43) the chlorine is acting as a proton abstractor which transforms the *nido*-$B_{10}H_{12}^{2-}$ anion into the *closo*-$B_{10}H_{10}^{2-}$ anion with precipitation of elemental tin. In reaction (44) the $B_{10}H_{12}^{2-}$ anion acts as a bidentate chelating ligand to give the desired stannaborane complex. The ^{119}Sn Mössbauer spectrum of $[(B_{10}H_{12})SnCl_2]^{2-}$ at liquid-nitrogen temperature established the continuing presence of Sn^{II} rather than Sn^{IV}, the chemical isomer shift with respect to $BaSnO_3$ being $\delta = 3.17$ mm s^{-1} and the quadrupole splitting $\Delta = 1.26$ mm s^{-1} The basis for this conclusion rests on the observation that the chemical isomer shift for tin(II) compounds is always greater than 2.9 mm s^{-1} and that for tin(IV) compounds is always less than 2.0 mm s^{-1} with respect to $BaSnO_3$.[44] The structure of the complex anion is considered to involve a *tetrahapto*-borane group as shown in Figure 21.

A related series of reactions of $(Ph_4As)_2B_{10}H_{12}$ with dimethyltin(IV) chloride also involved both disproportionation and co-ordination, as set out in equations (45) and (46).[43]

$$(Ph_4As)_2B_{10}H_{12} + Me_2SnCl_2 \rightarrow [Ph_4As]^+{}_2[B_{10}H_{10}]^{2-} + 2H^+ + Me_2SnCl_2{}^{2-} \qquad (45)$$

$$(Ph_4As)_2B_{10}H_{12} + Me_2SnCl_2 \rightarrow [Ph_4As]^+{}_2[(B_{10}H_{12})Sn(Me_2)Cl_2]^{2-} \qquad (46)$$

The structure of the metalloborane anion is considered to involve a *tetrahapto*-bidentate chelating $B_{10}H_{12}^{2-}$ unit as in Figure 17 but with the bonding environ-

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[43] N. N. Greenwood and B. Youll, to be published; B. Youll, Ph.D. thesis, 1970, Univ. Newcastle upon Tyne, England.

[44] N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy', Chapman and Hall, London, 1971, p. 375.

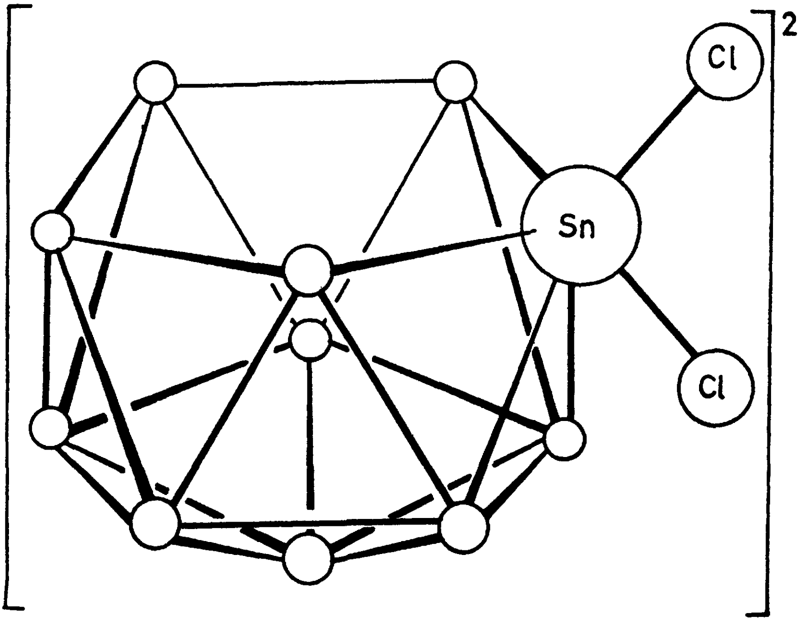

Figure 21 *Proposed structure of the anion* $[(B_{10}H_{12})SnCl_2]^{2-}$

ment about the tin atom expanded from four-co-ordinate to six-co-ordinate. The presence of Sn^{IV} was confirmed by the Mössbauer parameters: chemical isomer shift $\delta = 1.75$ mm s^{-1} with respect to $BaSnO_3$, quadrupole splitting $\Delta = 3.13$ mm s^{-1}. The corresponding diethyl derivative was also prepared but the diphenyl analogue was less stable.

An alternative route to stannaboranes utilized the reaction of $NaB_{10}H_{13}$ with Me_3SnCl in ether at 75 °C; Me_3GeBr reacted similarly.[45]

$$NaB_{10}H_{13} + Me_3SnCl \rightarrow Me_2SnB_{10}H_{12} + NaCl + MeH \quad (47)$$

$$NaB_{10}H_{13} + Me_3GeBr \rightarrow Me_2GeB_{10}H_{12} + NaBr + MeH \quad (48)$$

The air-stable products melted at 123 and 82 °C, respectively, and their structure is considered to be as in Figure 21 but with Me_2Sn^{2+} or Me_2Ge^{2+} groups replacing the $SnCl_2$. The +4 oxidation state in the neutral complex was confirmed by reaction with HCl to yield Me_2SnCl_2 and regenerate $B_{10}H_{14}$ in >95% yield. The analogous reaction with DCl gave the bis bridge-deuteriated borane μ-$B_{10}H_{12}D_2$.

The reaction of $B_{10}H_{13}^-$ with the corresponding silane Me_3SiCl is strongly dependent on the alkali-metal cation used, the ethereal solvent chosen, and the

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[45] R. E. Loffredo and A. D. Norman, *J. Amer. Chem. Soc.*, 1971, **93**, 5587.

temperature of reaction [see comments above on reaction (42)]. Thus, solvated $LiB_{10}H_{13}$ prepared in diethyl ether at 35 °C or in THF at 100 °C gave no reaction but $LiB_{10}H_{13}$,THF prepared at 50 °C reacted smoothly with an excess of Me_3SiCl over a period of 1 day at 120—140 °C:[46]

$$LiB_{10}H_{13}{,}THF + Me_3SiCl \rightarrow Me_3SiB_{10}H_{13}{,}THF + LiCl \qquad (49)$$

The structure of the red, hygroscopic oily product was not determined. Likewise, various solvates of $NaB_{10}H_{13}$ and $KB_{10}H_{13}$ were either unreactive or reacted in only small yields whereas unsolvated $KB_{10}H_{13}$, formed by the reaction of $B_{10}H_{14}$ and an excess of KOH in THF at −30 °C, reacted well. The product presumably comprises a decaborane skeleton in which either a bridge or a terminal proton has been replaced by the SiH_3 group, as established in the analogous derivatives of pentaborane(9) to be discussed in the next paragraph.

Lithium octahydropentaborate(1−) reacts with a variety of trialkyl Group IV metal halides in diethyl ether at −30 °C to give base-bridged products of general formula μ-R_3M-B_5H_8:[47,48]

$$LiB_5H_8 + R_3MX \rightarrow \mu\text{-}R_3M\text{-}B_5H_8 + LiX \qquad (50)$$
$$M = \text{Si or Ge}; \quad X = \text{Cl, Br, or I}; \quad R = \text{H, Me, or Et};$$
$$M = \text{Sn or Pb}; \quad X = \text{Cl, Br, or I}; \quad R = \text{Me};$$

The structure of these *dihapto*-metalloboranes was first deduced from their ^{11}B and ^{1}H n.m.r. spectra and later confirmed by an *X*-ray single-crystal structure determination on 1-Br-μ-Me_3Si-B_5H_7 (see Figure 22).[49] This compound was chosen because μ-H_3Si-B_5H_8 is a liquid at room temperature and μ-Me_3Si-B_5H_8 melts at 17 °C; the bromo-derivative was prepared by direct bromination of μ-Me_3Si-B_5H_8 using bromine at room temperature. The structure is closely related to that of pentaborane(9), the μ-Me_3Si-group replacing one of the bridging protons, and the bonding is best considered as involving a two-electron, three-centre bond between B(2)SiB(3). The distance of the Si atom from the mid-point of B(2)B(3) is 216 pm.

The compound μ-Me_3Si-B_5H_8 was shown to be monomeric by mass spectrometry. It was hydrolysed quantitatively by aqueous hydrochloric acid according to equation (51):

$$2Me_3SiB_5H_8 + 31H_2O \rightarrow 10B(OH)_3 + (Me_3Si)_2O + 24H_2 \qquad (51)$$

The bridged Me_3Si- and Me_3Ge-derivatives of pentaborane isomerize quantitatively at room temperature to the corresponding 2-substituted derivatives when in the presence of weak Lewis bases such as Me_2O or Et_2O, and the progress of this isomerization could be followed readily by n.m.r. spectroscopy.[47] The corresponding compounds μ-Me_3Sn-B_5H_8 and μ-Me_3Pb-B_5H_8 were too unstable to allow the isomerization to be studied in this way.

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[46] E. Amberger and P. Leidl, *J. Organometallic Chem.*, 1969, **18**, 345.
[47] D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, 1968, **90**, 6617.
[48] D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, 1967, **89**, 4249.
[49] J. C. Calabrese and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 6042.

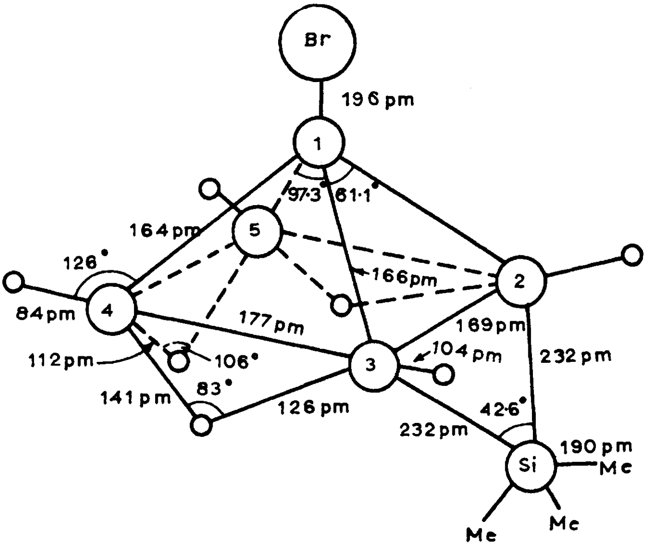

Figure 22 *Structure of* 1-Br-μ-Me_3Si-B_5H_7 *and main interatomic distances. The dihedral angle between* B(1)B(2)B(3) *and* B(3)B(2)Si *is* 182°, *between* B(1)B(3)B(4) *and* B(4)B(3)H(3,4) *is* 194°, *and between* B(1)B(4)B(5) *and* B(5)B(4)H(4,5) *is* 204°

Although metallocarbaborane complexes are not being considered specifically in this review, a number of R_3M derivatives of the *nido*-carbaboranes $C_2B_4H_8$ and $(MeC)_2B_4H_6$ in which the metal atom replaces a bridging hydrogen atom between two basal boron atoms will be discussed since their structures are very similar to those of the μ-R_3M-B_5H_8 species just considered, both sets of compound involving a three-centre two-electron BMB bond. Thus $NaC_2B_4H_7$ reacted with R_3MCl (R = H or Me; M = Si or Ge) in THF at 0 °C to give good yields of μ-H_3M-$C_2B_4H_7$:[50]

$$NaC_2B_4H_7 + R_3MCl \rightarrow \mu\text{-}R_3M\text{-}C_2B_4H_7 + NaCl \qquad (52)$$

An alternative route using the lithium salts gave good yields only in the case of μ-H_3Si-$C_2B_4H_7$. The compounds were structurally characterized by their ^1H and ^{11}B n.m.r. spectra and their mass spectra, and in each case were shown to have the $\mu_{4,5}$-bridged-2,3-dicarba-*nido*-hexaborane(8) structure illustrated in Figure 23. The compounds were colourless liquids with low vapour pressures in the range ~ 1—0.1 mmHg at room temperature. When heated to temperatures in the range 80—200 °C (depending on the compound) they readily isomerized quantitatively to the terminal 4-R_3M-derivatives. Heating 4-$Me_3SiC_2B_4H_7$ at 220—400 °C yields the carbon-substituted derivative 2-$Me_3SiC_2B_4H_7$, and

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[50] M. L. Thompson and R. N. Grimes, *Inorg. Chem.*, 1972, 11, 1925.

further heating converts the product into derivatives of the *closo*-carbaboranes $C_2B_3H_5$ and $C_2B_5H_7$, presumably by disproportionation of the *closo*-C_2B_4 cage.

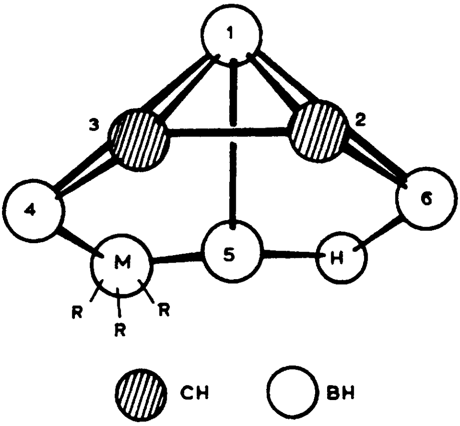
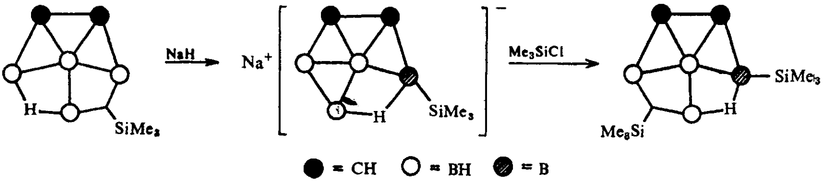


Figure 23 *Proposed structure of* μ-R_3M-$C_2B_4H_7$ (M = Si *or* Ge; R = H *or* Me)

Subsequent work showed that $NaC_2B_4H_7$ reacted smoothly with Me_3SnBr and Me_3PbCl in THF at room temperature to yield the corresponding μ-tin and -lead derivatives as involatile, colourless liquids ($p < 0.1$ mmHg at 25 °C).[51] The structures were again established by n.m.r. techniques. By contrast to the silicon and germanium compounds, however, the tin and lead derivatives showed no tendency to isomerize from bridge- to terminal-substitution: the tin compound was stable indefinitely at 120 °C but decomposed rapidly at 220 °C to give Me_3SnH and the parent carbaborane $C_2B_4H_8$; the lead derivative was less stable and decomposed to the corresponding products in 2 days at room temperature and more rapidly at 120 °C. Both compounds reacted quantitatively with HCl and DCl to give the parent $C_2B_4H_8$ and μ-$DC_2B_4H_7$ respectively.

In an extension of these studies a bis(trimethylsilyl) derivative was obtained as indicated in the Scheme.[51] The product contained both a bridging B(4)B(5)-and



Scheme

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[51] A. Tabereaux and R. N. Grimes, *Inorg. Chem.*, 1973, **12**, 792.

a terminal B(6)-trimethylsilyl group. The related μ,μ'-bis(carbaboranyl)silane was obtained as a white solid by reaction (53), and two possible structural isomers are illustrated in Figure 24.

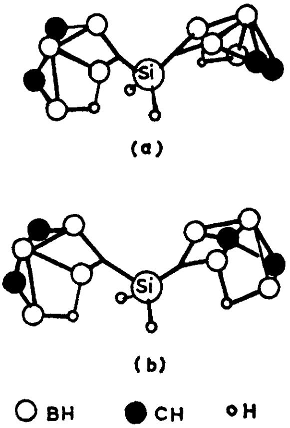

Figure 24 *Proposed structures of the two possible geometrical isomers of* μ,μ'-$(C_2B_4H_7)_2SiH_2$

$$2NaC_2B_4H_7 + SiH_2Cl_2 \xrightarrow{\text{THF}} \mu,\mu'\text{-}(C_2B_4H_7)_2SiH_2 + 2NaCl \tag{53}$$

A further variation was obtained by allowing the *nido*-carbaborane anion $(MeC)_2B_4H_5^-$ to react with methylhalogeno-silanes and -germanes in ether, and an unstable product containing an added bridging boron atom was likewise synthesized using Me_2BCl:[52]

$$Na(MeC)_2B_4H_5 + Me_3SiCl \rightarrow 2,3,\mu\text{-}Me_3Si(MeC)_2B_4H_5 + NaCl \tag{54}$$

$$Na(MeC)_2B_4H_5 + Me_2SiCl_2 \rightarrow 2,3,\mu\text{-}Me_2Si(Cl)(MeC)_2B_4H_5 + NaCl \tag{55}$$

$$Na(MeC)_2B_4H_5 + Me_3GeBr \rightarrow 2,3,\mu\text{-}Me_3Ge(MeC)_2B_4H_5 + NaBr \tag{56}$$

$$Na(MeC)_2B_4H_5 + Me_2BCl \rightarrow 2,3,\mu\text{-}Me_2B(MeC)_2B_4H_5 + NaCl \tag{57}$$

Sodium can be replaced by lithium in these reactions. Of the four compounds so prepared, only the Me_3Ge derivative isomerized to the terminal isomer.

7 Borane (or Borane Anion) plus Transition-metal Carbonyl Complex

The reaction of cleaved diborane in THF solution with the carbonyl anions of manganese and rhenium has already been mentioned in Section 3. A variety of other reaction types have also been reported.

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[52] C. G. Savory and M. G. H. Wallbridge, *J.C.S. Dalton*, 1972, 918.

A unique carbonyl insertion into the $B_{10}H_{13}^-$ anion has been effected by irradiating a THF solution of $NaB_{10}H_{13}$ and Group VI metal hexacarbonyls at 350 nm in the absence of air:[53]

$$B_{10}H_{13}^- + M(CO)_6 \xrightarrow{h\nu,\text{THF}} [(B_{10}H_{10}COH)M(CO)_4]^- + H_2 + CO \qquad (58)$$

In reaction (58) M = Cr, Mo, or W, and the metallocarbonylborane was isolated in 50% yield as the tetramethylammonium salt. Treatment of these products with sodium hydride in THF gave quantitative yields of the yellow tetrabutylammonium salts of the dianion $[B_{10}H_{10}C\underbrace{OMC}O(CO)_3]^{2-}$:

$$[(B_{10}H_{10}COH)M(CO)_4]^- + H^- \xrightarrow{\text{THF}} [B_{10}H_{10}C\underbrace{OMC}O(CO)_3]^{2-} + H_2 \qquad (59)$$

The structure of the molybdenum compound was established by single-crystal *X*-ray analysis and found to contain a novel ester link between the oxygen atom of the carbonyl group inserted into the B_{10} cluster and a carbon atom of an adjacent metal-bonded carbonyl group, as shown in Figure 25. It is also clear from the Figure that the dianion comprises a *closo*-icosahedral $B_{10}CMo$ cluster in which the metal and carbon atoms are linked *via* a cyclic MC(O)OC grouping.

The monoanion [equation (59)] can be regenerated from the dianion (Figure 25) by direct protonation with aqueous acid under anaerobic conditions; this

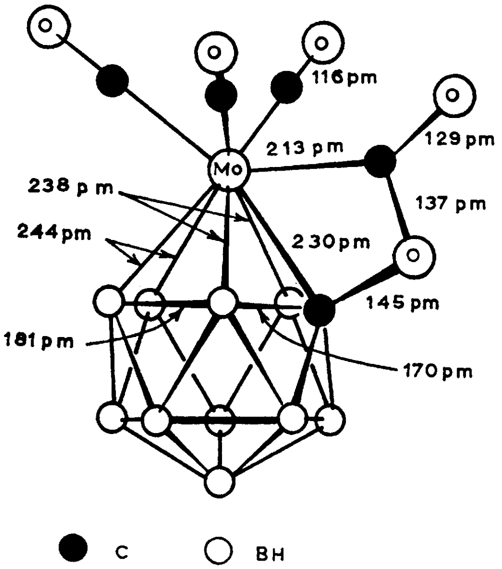

Figure 25 *Structure of the dianion* $[B_{10}H_{10}C\underbrace{OMoC}O(CO)_3]^{2-}$ *with terminal hydrogen atoms omitted for clarity; typical interatomic distances/*nm *are shown*

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[53] P. A. Wegner, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1970, **92**, 3473.

cleaves the ether linkage to give a simple tetracarbonyl of the $B_{10}CM$ icosahedron in which there is no bonding between the carbonyl groups and the cage. All spectral data are consistent with this formulation.[53] The mono- and di-anions of these metalloboranes of chromium, molybdenum, and tungsten undergo a further unusual reaction with base; this partially degrades the icosahedral cage with removal of the carbon atom, not a boron atom as normally occurs with carbaboranes. The resulting dianions $[B_{10}H_{12}M(CO)_4]^{2-}$ are very air-sensitive, especially in acid solutions, but there is no hydrolysis in the absence of oxygen; their structures are presumably analogous to those of the $B_{10}H_{12}{}^{2-}$ chelating complexes considered in Section 4(b).

A phosphaundecaborane–metal carbonyl complex has been made by first deprotonating decaborane with sodium hydride in ethereal solution and then adding an ethereal solution of $PhPCl_2$ to yield the *nido*-phosphaundecaborane $PhPB_{10}H_{12}$ in moderate yields; this was then allowed to react with two equivalents of sodium hydride and one equivalent of $(CO)_5MnBr$ in THF to give the yellow 'metallocene'-type ion $[(PhPB_{10}H_{10})Mn(CO)_3]^-$, which was isolated as the tetramethylammonium salt:[54]

$$NaB_{10}H_{13} + PhPCl_2 + NaH \xrightarrow{Et_2O} PhPB_{10}H_{12} + 2NaCl + H_2 \qquad (60)$$

$$PhPB_{10}H_{12} + 2NaH + (CO)_5MnBr \xrightarrow[Me_4NCl]{THF}$$

$$[Me_4N]^+[(PhPB_{10}H_{10})Mn(CO)_3]^- + NaCl + NaBr + 2H_2 + 2CO \qquad (61)$$

U.v., i.r., and n.m.r. data were reported, and the presumed 12-atom *closo*-structure is shown in Figure 26.

Very recently it has been shown that the $B_9H_{14}{}^-$ anion reacts with $(CO)_5MnBr$ in THF to produce several metalloboranes, from which the anion $[(B_9H_{13})Mn(CO)_3]^-$ and the solvate $[(B_9H_{12})Mn(CO)_3,THF]$ have been isolated.[55] The air-stable reddish-orange crystalline salt $[Me_4N]^+[B_9H_{13}Mn(CO)_3]^-$, m.p. 200 °C (decomp.), was obtained in 40% yield and shown to be a 1:1 electrolyte in methyl cyanide. The neutral solvate is also an air-stable reddish-orange crystalline material, m.p. 189 °C (decomp.), that can be sublimed in high vacuum at 50—70 °C. Both compounds have unusually high thermal, hydrolytic, and oxidative stability compared to that of other metalloboranes. The single-crystal *X*-ray structure of the neutral solvate is illustrated in Figure 27 and shows several unique features. The $Mn(CO)_3$ moiety can be considered to be substituting the B(6) position in the decaborane cluster, being bound to the B_9 ligand by two three-centre two-electron hydrogen-bridge bonds, BHMn, and a single boron–metal bond, B(2)→Mn, that contributes two electrons to the metal. The B_9 ligand is thus formally a terdentate five-electron donor, replacing two CO and one Br to preserve the 18-electron environment about manganese. The other unusual feature of the structure is the directly bonded THF donor which is

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[54] J. L. Little and A. C. Wong, *J. Amer. Chem. Soc.*, 1971, **93**, 522.

[55] J. W. Lott, and D. F. Gaines, H. Shenhav, and R. Schaeffer, *J. Amer. Chem. Soc.*, 1973, **95**, 3042.

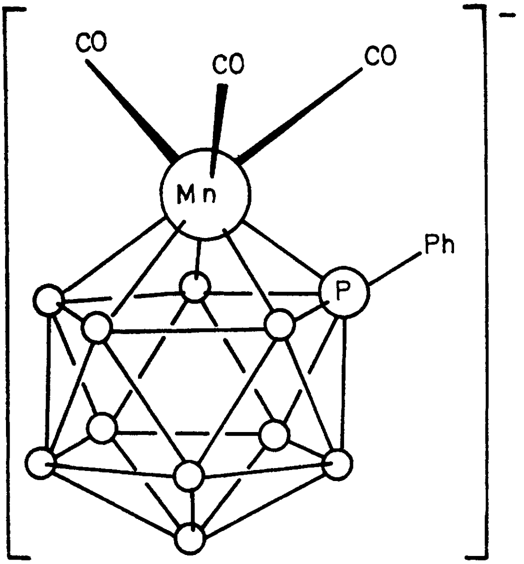

Figure 26 *Proposed structure of the anion* $[(PhPB_{10}H_{10})Mn(CO)_3]^-$

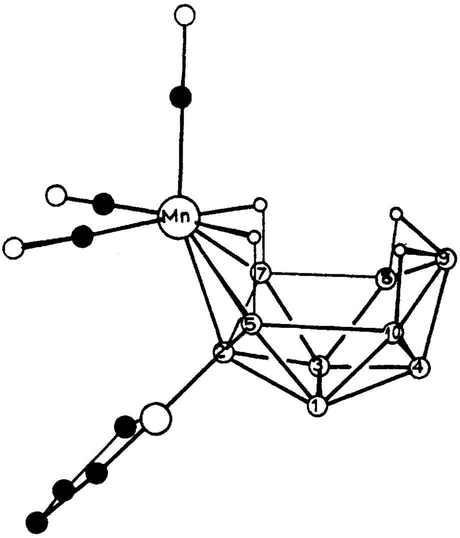

Figure 27 *The structure of* $[(B_9H_{12}THF)Mn(CO)_3]$ *omitting terminal hydrogen atoms on tetrahydrofuran and the eight boron atoms* 1, 3—5, *and* 7—10 *for clarity*

attached instead of a hydrogen atom to B(2). Typical bond distances are Mn—CO 179.3 pm, Mn—H 175 pm, Mn—B(2) 219.6 pm, Mn—B(5) 223.7 pm, and O—B(2) 152.6 pm. The bond angles subtended mutually by the three carbonyl groups and the two bridging hydrogen atoms at the manganese atom are all close to 90° but the angle B(2)MnH(bridge) is only 77.5°, and the angle B(2)MnCO(*trans*) is 161.4°. The carbonyl ligands in both the anion and the neutral complex can be replaced successively by triphenylphosphine ligands under selected photolytic conditions, and even the complexed THF in Figure 27 can be replaced.

Hexaborane(10) can act as a *dihapto*-two-electron donor in the volatile, yellow, crystalline complex μ-(B_6H_{10})Fe(CO)$_4$, m.p. 38 °C (decomp.). This is prepared by direct reaction of hexaborane(10) with $Fe_2(CO)_9$, as shown in reaction (62).[56] On the basis of i.r., n.m.r., and mass spectrometric data the

$$2B_6H_{10} + Fe_2(CO)_9 \rightarrow 2[\mu\text{-}(B_6H_{10})Fe(CO)_4] + CO \qquad (62)$$

complex is formulated as a derivative of $Fe(CO)_5$ in which one of the equatorial carbonyl ligands has been replaced by the unique B(4)—B(5) bond in the basal plane of B_6H_{10}, thereby forming a three-centre two-electron BFeB bond as indicated schematically in Figure 28. The complex can be handled for brief periods in air but is thermally and photolytically unstable. (See also footnote on p. 232).

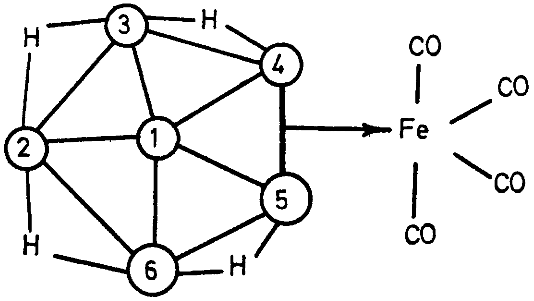

Figure 28 *Schematic representation of the structure of* [μ-(B_6H_{10})Fe(CO)$_4$]

Direct (*monohapto*-) σ-bonds between a borane and a metal carbonyl can be synthesized by the reaction of chloro- and bromo-derivatives of B_5H_9 with NaMn(CO)$_5$ and NaRe(CO)$_5$ [reaction (63)]. Only basal-halogenated pentaboranes 2-XB_5H_8 would react, and in no case were apex-halogenated pentaboranes 1-XB_5H_8 successfully used.[57]

$$2\text{-}XB_5H_8 + NaM(CO)_5 \xrightarrow{Et_2O} 2\text{-}[M(CO)_5]B_5H_8 \qquad (63)$$
$$X = Cl \text{ or } Br, \quad M = Mn \text{ or } Re$$

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[56] A. Davison, D. D. Traficante, and S. S. Wreford, *J.C.S. Chem. Comm.*, 1972, 1155.
[57] D. F. Gaines and T. V. Iorns, *Inorg. Chem.*, 1968, 7, 1041.

The rhenium compound melts at 11 °C and is stable at room temperature for several hours but the manganese derivative, upon melting at -10 °C, develops a yellow colour which becomes more pronounced as the sample is warmed to room temperature for several days. Spectroscopic properties indicate the structure shown in Figure 29.

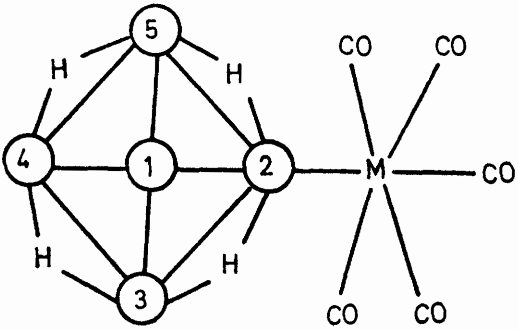

Figure 29 *Schematic representation of the structure of* 2-$[M(CO)_5]B_5H_8$ (M = Mn *or* Re)

The reaction takes a dramatically different course when lithium octahydropentaborate(1−) is treated with pentacarbonylmanganese hydride:[40]

$$LiB_5H_8 + HMn(CO)_5 \rightarrow Li^+[(B_5H_5)Mn(CO)_3]^- + 2H_2 + 2CO \qquad (64)$$

Little information on the compound has yet been published but it is considered to comprise a $B_5H_5^{2-}$ *tetrahapto*-ligand, electronically analogous to cyclobutadiene, in which the square open face of the B_5 moiety is π-bonded to the metal atom as indicated in Figure 30.

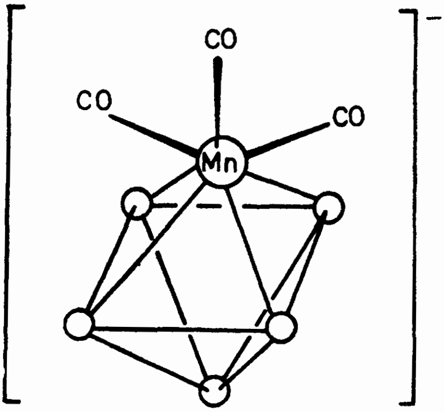

Figure 30 *Proposed structure of the anion* $[(B_5H_5)Mn(CO)_3]^-$

8 Concluding Summary of Structures and Bond-types

Despite the considerable diversity of structures and bond-types adopted by metalloboranes, a general pattern is now beginning to emerge which enables the borane ligands to be classified according to their connexity (*polyhapto*-nature)[58] and the number of electrons formally donated from the borane to the metal. It is a measure of the changed emphasis brought about by the synthesis of metalloboranes that it is the electron-*donor* capacity of the boranes rather than their electron-*acceptor* capacity which is being exploited. Indeed, of all the metalloboranes mentioned in this review, the only ones in which the borane unambiguously acts as an electron-acceptor are the *monohapto*-complexes of manganese and rhenium, $[(CO)_5M{\rightarrow}BH_3]^-$ and $[(Ph_3P)(CO)_4Mn{\rightarrow}BH_3]^-$. The germanylborane anion $[H_3GeBH_3]^-$ could likewise be regarded as an adduct of the hypothetical anion GeH_3^-, in which BH_3 is acting as an electron-pair acceptor $[H_3Ge{\rightarrow}BH_3]^-$, although it is also possible to formulate this adduct as a germyl-substituted BH_4^- anion in which both H_3Ge and BH_3^- contribute one electron to the covalent bond.[16]

The number of boron atoms involved in bonding to the metal, and the number of electrons formally donated from the borane ligand to the metal acceptor, are summarized in the Table. The classic two-electron σ-donor–acceptor bond is exemplified by the *monohapto*-ligand $pyB_{10}H_{13}^-$, which donates a pair of

Table *Classification of borane donors in metalloboranes* (*n = number of electrons donated by the borane moiety*)

Ligand	*n*	*Examples*		*Fig.*	*Ref.*
monohapto					
$\cdot BH_3^-$	1	$[H_3GeBH_3]^-$		—	16
$\cdot B_5H_8$	1	$2\text{-}Me_3M\text{-}B_5H_8$	M = Si or Ge	—	47
	1	$2\text{-}[M(CO)_5]B_5H_8$	M = Mn or Re	29	57
$pyB_{10}H_{13}^-$	2	$[(pyB_{10}H_{13})Fe(py)Br_2]$		7	29
dihapto					
$B_5H_8^-$	2	$\mu\text{-}R_3M\text{-}B_5H_8$	M = Si, Ge, Sn, or Pb	22	47, 48
$B_5H_7Br^-$	2	$\mu\text{-}Me_3Si\text{-}B_5H_7Br$		22	49
B_6H_{10}	2	$\mu\text{-}B_6H_{10}Fe(CO)_4$		28	56
	2	$(B_6H_{10})_2PtCl_2$		8	30
$C_2B_4H_7^-$	2	$\mu\text{-}R_3M\text{-}C_2B_4H_7$	M = Si or Ge	23	51
$\cdot B_{10}H_{12}\cdot$	2	$[(B_{10}H_{12})AlH_2]^-$ (chelate)		1	14
trihapto					
$\pi\text{-}B_3H_7^-$	3	$(R_3P)_2Pt(\pi\text{-}B_3H_7)$	(also Ni, Pd)	18	39, 40
(or $\pi\text{-}B_3H_7^{2-}$)	4	$(R_3P)_2Pt(\pi\text{-}B_3H_7)$	(also Ni, Pd)	17	39, 40
B_4H_8	2	$(\pi\text{-}C_5H_5)Co(B_4H_8)$	(donor atoms BH_2)	16a	38
$B_8H_{12}^{2-}$	4	$(Et_3P)_2PtB_8H_{12}$		15	36
$B_9H_{11}L^{2-}$	4	$(Et_3P)_2Pt(B_9H_{11}L)$		14	36
$C_2B_4H_6$	3	$6\text{-}Me_3Si\text{-}\mu\text{-}Me_3Si\text{-}C_2B_4H_6$ (*i.e. mono-* plus *di-hapto*)		—	51

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[58] F. A. Cotton, *J. Amer. Chem. Soc.*, 1968, **90**, 6230.

Ligand	*n*	*Examples*		*Fig.*	*Ref.*
tetrahapto					
B_4H_8	2	$(\pi\text{-}C_5H_5)Co(B_4H_8)$ (donor atoms B_4)		16b	38
$B_5H_5^{2-}$	4	$[(B_5H_5)Mn(CO)_3]^-$		30	40
$B_9H_{13}^-$	2	$(\pi\text{-}C_5H_5)Co(5\text{-}B_9H_{13})$ (donor atoms B_3H)		16f	38
$B_{10}H_{12}^{2-}$	4	$[M(B_{10}H_{12})_2]^{2-}$ M = Mg, Zn, Cd, or Hg		4	23
	4	$[M(B_{10}H_{12})_2]^{2-}$ M = Co, Ni, Pd, or Pt		11	33
	4	$[Pt(B_{10}H_{12})(Et_3P)_2]$		—	28
	4	$[M(B_{10}H_{12})(CO)(Ph_3P)_2]^-$ M = Co, Rh, Ir		—	28
	4	$[(B_{10}H_{12})HgMe]^-$		19	21
	4	$[(B_{10}H_{12})TlMe_2]^-$		6	25
	4	$[(B_{10}H_{12})SnCl_2]^{2-}$, $[(B_{10}H_{12})Sn(Me_2)Cl_2]^{2-}$		21	43
	4	$[(B_{10}H_{12})GeMe_2]$, $[(B_{10}H_{12})SnMe_2]$		21	45
	4	$[(B_{10}H_{12})M(CO)_4]^{2-}$ M = Cr, Mo, or W		—	53
$B_{10}H_{11}py^-$	4	$[(B_{10}H_{11}py)Co(py)X_2]^-$ X = Cl or Br		12	35
$B_9H_{10}S^-$	4	$[(Et_3P)_2Pt(H)B_9H_{10}S]$		13	36
$n\text{-}B_{18}H_{20}^{2-}$	4	$[(n\text{-}B_{18}H_{20})ML_2]$ M = Ni, Pd, or Rh		9	31
	4	$[(n\text{-}B_{18}H_{20})Co(CO)_3]^-$		—	31
$i\text{-}B_{18}H_{20}^{2-}$	4	$[(i\text{-}B_{18}H_{20})M(diphos)]$ M = Ni, Pd, or Pt		—	31
bis-dihapto					
$B_{10}H_{12}^{2-}$	4	$[(Et_2O)_2Cd(B_{10}H_{12})]_2$ (also Zn)		2	19
pentahapto			*Donor atoms*		
$B_{10}H_{10}COH^-$	4	$[(B_{10}H_{10}COH)M(CO)_4]$			
		M = Cr, Mo, or W	(B_4C)	—	53
$B_{10}H_{10}CO^{2-}$	4	$[(B_{10}H_{10}C\underline{O)MC}O(CO)_3]^{2-}$			
		M = Cr, Mo, or W	(B_4C)	25	53
$B_9H_{13}^-$	5	$[(B_9H_{13})Mn(CO)_3]^-$	(B_3H_2)	—	55
$B_9H_{12}THF$	5	$[(B_9H_{12}THF)Mn(CO)_3]$	(B_3H_2)	27	55
$B_{10}H_{10}PPh^-$	5	$[(B_{10}H_{10}PPh)Mn(CO)_3]^-$	(B_4P)	26	54
$B_{10}H_{10}S^{2-}$	6	$[(B_{10}H_{10}S)_2Co]^-$, $[(B_{10}H_{10}S)_2Fe]^{2-}$	(B_4S)	10	32
	6	$[(B_{10}H_{10}S)Pt(Et_3P)_2]$		—	32
	6	$[(B_{10}H_{10}S)Re(CO)_3]^-$	(B_4S)	—	32
hexahapto		no examples (yet!)			
heptahapto		no examples (yet!)			
octahapto		(*i.e.* tetrakis-*dihapto*)			
closo-$B_{10}H_{10}^{2-}$	8	$Cu_2B_{10}H_{10}$		20	41

electrons into the tetrahedral iron(III) atom as shown in Figure 7. By contrast the *monohapto*-ligand $\cdot B_5H_8$ donates only one electron to the B—M bond in $2\text{-}Me_3MB_5H_8$ and $2\text{-}[M(CO)_5]B_5H_8$, thereby implying that a normal σ-two-electron two-centre terminal B—H bond in B_5H_9 has been replaced by a B—MMe_3 or B—$M(CO)_5$ bond (see Figure 29). The $B_5H_8^-$ unit can act as a *dihapto*-('π-bonded') ligand in which the borane moiety donates both electrons to form a three-centre two-electron bond, as in μ-R_3M-B_5H_8 and μ-Me_3Si-B_5H_7Br (see Figure 22). Similar bonding is shown by the B_6H_{10} complexes illustrated in Figures 8 and 28. Dihapticity can also be generated by a bis-*monohapto* chelating ligand, and a possible example of this is the $[(B_{10}H_{12})AlH_2]^-$ ion shown in Figure 1.

trihapto-Borane ligands can donate 2, 3, or 4 electrons to a metal atom. An example of a two-electron *trihapto*-ligand is B_4H_8 in $(\pi$-$C_5H_5)Co(B_4H_8)$, the connecting atoms being the apex boron and two bridging hydrogen atoms [Figure 16(a)]. This complex can also exist as a structural isomer [Figure 16(b)] in which the B_4H_8 group acts as a two-electron *tetrahapto*-ligand, with the four basal boron atoms now being equally bonded to the cobalt atom. Three-electron *trihapto*-ligands are exemplified by the '*mono*-plus-*dihapto*'-carbaborane $C_2B_4H_6$ (connected to the metal atom by three boron atoms) and the π-borallyl complex $(R_3P)_2Pt(\pi$-$B_3H_7)$. If the bonding in this latter complex is considered to be σ-plus-π-bonding from $B_3H_7^-$, as illustrated in Figure 18, then it is a three-electron donor, involving Pt^I; alternatively, as suggested by Figure 17, it may be considered as a true π-borallyl four-electron donor involving $B_3H_7^{2-}$ and Pt^{II}. This is an ambiguity which finds many counterparts in organometallic chemistry. Figures 14 and 15 illustrate borane clusters acting as four-electron *trihapto*-ligands, the $B_9H_{11}L^{2-}$ and $B_8H_{12}^{2-}$ groups acting as bidentate chelates, with pairs of electrons from B(2)B(5) and B(2)B(7) completing the square-planar bonding environment about the platinum atom in each case.

tetrahapto-Borane ligands comprise the most numerous class to date. In many of the examples listed in the Table the borane acts as a bidentate chelate, donating four electrons to the metal. The bonding has already been fully discussed in connection with tetrahedral $[Zn(B_{10}H_{12})_2]^{2-}$ (Figures 4 and 5) and square-planar $[Ni(B_{10}H_{12})_2]^{2-}$ (Figure 11). Further examples are illustrated in Figures 6, 9, 12, 13, 19, and 21. In addition, $B_{10}H_{12}^{2-}$ can generate tetrahapticity by acting as a bis-*dihapto*-ligand in the dimeric complex $[(Et_2O)_2Cd(B_{10}H_{12})]_2$, as discussed in connection with Figure 2. Three other modes of *tetrahapto* interaction are also known. The two-electron donation in $(\pi$-$C_5H_5)Co(B_4H_8)$ has already been alluded to on p. 252. A similar geometrical arrangement occurs in the four-electron donor $B_5H_5^{2-}$, which is an analogue of cyclobutadiene (see Figure 30). Finally, $B_9H_{13}^-$ can act as *tetrahapto* two-electron ligand by bonding to cobalt *via* three boron atoms and one bridging hydrogen atom as illustrated in Figure 16(f) [though by analogy with the isostructural cluster in decaborane(14) itself the cobalt atom occupying the B(5) position could equally be thought of as being connected to B(1)B(2)B(6)B(10)H, thus making the ligand formally *pentahapto*].

pentahapto-Borane ligands are known which donate 4, 5, or 6 electrons. It is interesting to note, as indicated in the Table, that all such ligands that have so far been prepared have at least one heteroatom involved in the bonding to the metal acceptor, and that when this heteroatom is C, P, or S, the formal number of electrons donated by the ligand is 4, 5, and 6. Illustrations are in Figures 25, 26, and 10, respectively. Bridge-bonding *via* hydrogen also occurs, as exemplified by the B_9–manganese complex shown in Figure 27.

No examples of *hexahapto-* and *heptahapto*-borane ligands have yet been synthesized though, of course, in the carbaborane–metal complexes a connexity of higher than five occasionally occurs, particularly if the carbaborane skeleton is joined to more than one metal atom. One example of an *octahapto*-ligand is known, namely $Cu_2B_{10}H_{10}$; this high connexity is achieved by having four pairs of boron atoms bonding to four different copper atoms. The details of the bonding in this compound have not been fully elucidated, though it is certain that the picture given in Figure 20 of electron-pair donation into three-centre BCuB orbitals is an oversimplification, particularly in view of the known electron delocalization in the parent *closo*-borane anion $B_{10}H_{10}^{2-}$.

In conclusion, it can be stated that the new and rapidly expanding field of metalloboranes has now reached a stage where preliminary systematization is possible. A wide variety of structural and bonding types is apparent and these give promise of still further rapid advances in the near future.