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The concept of boranes as ligands

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Contents

Abstract

The idea that electron deficient boranes can act as novel electron-donor ligands has proved to be remarkably productive in developing new and unusual aspects of the chemistry of the boron hydrides. Polyhedral boranes and their anions have fewer valence electrons than orbitals available for bonding and are, therefore, normally classified as electron deficient species. However, many can act as excellent polyhapto ligands to form a variety of coordination complexes that are often more stable than the parent boranes themselves. Indeed, many of the binary boranes and their anions can themselves usefully be regarded as coordination complexes of a borane donor and a borane acceptor, i.e. a borane–borane adduct. Even BH_4^- (isoelectronic with methane and the ammonium ion) can act as an effective monohapto, dihapto or trihapto ligand to appropriate acceptor moieties. Furthermore, direct boron–metal bonds can also be formed, and examples are now known in which borane clusters can exhibit the full range of hapticities from η^1 to η^6. The exciting synthetic and structural implications of these ideas will be indicated.

Keywords: Boron hydrides; Electron deficient ligands; Polyhapto B_nM bonding; Metalloboranes

1. Introduction

Boron is the element immediately preceding carbon in the periodic table and so it has one less electron than it has orbitals available for bonding. As a consequence, many of its molecular compounds, such as the boron hydrides, are ‘electron deficient’ in the sense that there are insufficient electrons to form two-centre, two-electron bonds between each contiguous pair of atoms. One way of relieving this electron deficiency is for the borane species to act as an electron-pair acceptor by interaction with a Lewis base, L, i.e. $L\cdot BH_3$ where $L = CO$, Me_2O, Me_2S, Me_3N, H^- etc. Another way of relieving their so-called electron deficiency is by forming polyhedral cluster molecules in which pairs of electrons simultaneously bond more than two atoms by means of three-centre or polycentre bonds. In diagrams showing the structure of these compounds it is important to realise that straight lines between the atoms do not necessarily indicate pairs of electrons: they merely indicate the geometrical shape of the cluster.

About 35 years ago, in the mid 1960s, we began to realise that, far from being deficient in electrons, many boranes and their anions could act as very effective polyhapto ligands. That is, they could form donor–acceptor complexes or coordination compounds in which the borane cluster was itself acting as the electron

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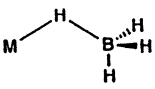
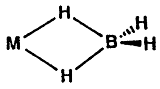
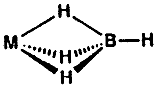
donor or ligand. This lecture explores the startling implications of this astonishing concept and illustrates how it has extended enormously the range of stable boron hydride cluster compounds that can be made. I will not follow a chronological or historical sequence [1–3] but will present a more systematic overview that has now become possible [4]. Mention should, however, be made to the parallel development of carbaborane species as ligands following M.F. Hawthorne's seminal recognition in 1965 that the *nido*-dicarbaborane anion, $C_2B_9H_{11}^{2-}$, could act as a pentahapto analogue of the cyclopentadienide ligand, $C_5H_5^-$ [5]. It will become clear from the following sections that binary borane species, even in the absence of carbon atoms in the cluster skeleton, can likewise act as excellent ligands either by the donation of the electron pair in a B–H bond itself to form a bent B–H–M three-centre bond, or by forming direct B_nM multicentre bonds in which all hapticities from η^1 to η^6 are known. The metalloborane complexes so formed are often far more stable than the parent borane ligands themselves.

2. Interactions involving B–H–M bonds

The simplest binary borane species is the tetrahydroborate anion, BH_4^-, which is isoelectronic with CH_4 and NH_4^+. Many salts of this anion, such as $LiBH_4$ and $NaBH_4$, are essentially ionic and have been used for nearly 60 years as versatile reducing agents [4,6]. However, BH_4^- can also react by ligand displacement to form covalently bonded complexes via three-centre B–H→M bonds to somewhat less electropositive metals in which it acts as a monohapto, dihapto or trihapto ligand [7–9]:

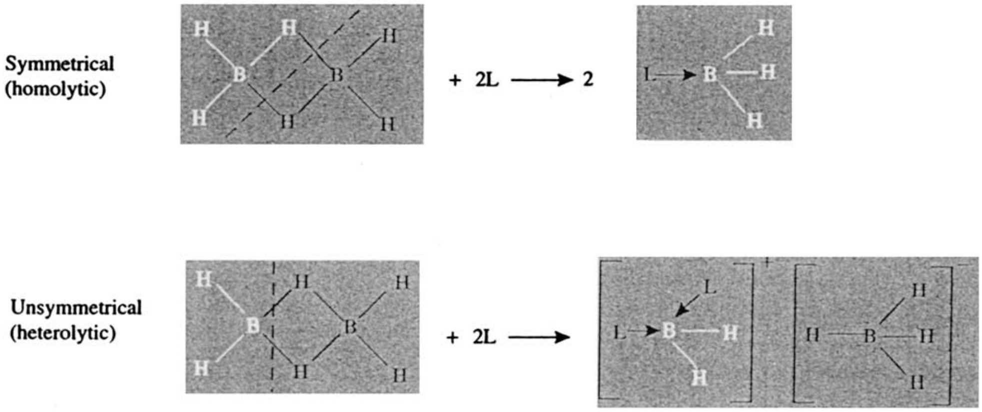






Examples are $[Cu(\eta^1\text{-}BH_4)(PMePh_2)_3]$ [10], $[Cu(\eta^2\text{-}BH_4)(PPh_3)_2]$ [11] and $[Zr(\eta^3\text{-}BH_4)_4]$ [12]. Indeed, BH_4^- affords a rare example of a ligand that can act in at least six coordination modes because, in addition to the η^1, η^2 and η^3 modes mentioned above, examples of bridging modes are also known in which it is $\mu(\eta^2,\eta^2)$, $\mu(\eta^3)$ and $\mu(\eta^4)$ [4]. The hapticity is influenced both by the steric requirements of the coligands (e.g. $PMePh_2$ is less demanding than PPh_3) and by the size of the central metal atom (e.g. Zr, which can accommodate simultaneous ligation by 12 H atoms). With the very large actinide elements, Th, Pa and U, the coordination number of the central metal rises to 14 in the polymeric complexes $[M(BH_4)_4]$, i.e. $[M(\eta^3\text{-}BH_4)_2(\mu\text{-}\eta^2,\eta^2\text{-}BH_4)_2]$. A particularly important example of the dihapto mode is the octahedral Al complex $[Al(\eta^2\text{-}BH_4)_3]$, which was not only the first covalent borohydride to be characterised (1940) but also the first compound of any element in which the now widespread phenomenon of fluxionality was observed, all 12 H atoms being equivalent on the NMR timescale [13].

So far we have been considering complexes in which the BH_4^- ligand coordinates to a metal acceptor centre. But, suppose the acceptor moiety is itself a binary borane species—then we could create borane–borane adducts. For example, diborane (B_2H_6) could formally be regarded either as a coordination complex of η^2-BH_4^- with the notional cation $\{BH_2^+\}$, or as a dimer formed by the mutual coordination of two monodentate $\{BH_3\}$ units. Replacement of the η^2-BH_4^- or η^1-BH_3 ligands by suitable (stronger) Lewis bases would then result in the well-known diborane reactions of unsymmetrical (heterolytic) and symmetrical (homolytic) cleavage, respectively [14,15]:



The factors that determine which course the reaction will take have recently been re-examined and it appears that, in most cases, steric effects do not play a dominant role: rather it is the dielectric constant of the reaction medium that is the deciding factor [16].

These ideas can readily be extended to the higher boranes. The 'butterfly' structure of B_4H_{10} can be considered as a coordination complex formed either by the

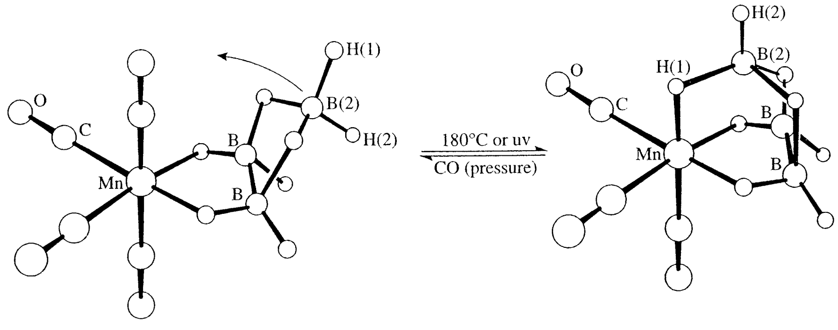


Fig. 1. Ligand replacement reaction of $[Mn(\eta^2\text{-}B_3H_8)(CO)_4]$ (see text).

mutual monodentate donor–acceptor interaction of the fugitive ligand/acceptor moieties $\{BH_3\}$ and $\{B_3H_7\}$ or as the chelation of $\{BH_2^+\}$ by the known anion $B_3H_8^-$ acting as a dihapto ligand. Accordingly, B_4H_{10} can be cleaved either homolytically (e.g. with $L = NMe_3$) to give $L{\cdot}BH_3$ plus $L{\cdot}B_3H_7$ or heterolytically (e.g. with $L = NH_3$) to give $[L_2BH_2]^+[B_3H_8]^-$ [15]. Likewise, ligand replacement reactions in which, for example, the halide ions of classical coordination complexes are displaced by the $B_3H_8^-$ anion can lead to a variety of metallated derivatives of tetraborane such as the tetrahedrally coordinated copper complex, $[Cu(\eta^2\text{-}B_3H_8)(PPh_3)_2]$, in which the wing-tip $\{BH_2^+\}$ group has been replaced by the isolobal $\{Cu(PPh_3)_2^+\}$ group [17]. The octahedrally coordinated manganese complex, $[Mn(\eta^2\text{-}B_3H_8)(CO)_4]$, is an even more instructive example of this structure-type, since, when it is heated to 180 °C or irradiated with ultraviolet light, it loses one of the four CO ligands, and a further B–H group then coordinates to give the trihapto complex *fac*-$[Mn(\eta^3\text{-}B_3H_8)(CO)_3]$ [18]. Treatment of this product with an excess of CO under moderate pressure results in the reformation of the original dihapto species. These reactions are now best represented as straightforward ligand replacement reactions (see Fig. 1). A more complex example of trihapto coordination of a borane to a metal centre via B–H–M bonds is *fac*-$[Mn(\eta^3\text{-}B_8H_{13})(CO)_3]$ (Fig. 2), in which a triangular face of three B–H groups coordinates to the manganese atom [19]. Chelation and bridging via pairs of edge-related B–H groups are also known, for example, in the binuclear Cu(I) complex, $[Cu(PPh_3)_2(\mu\text{-}\eta^2,\eta^2\text{-}closo\text{-}B_{10}H_{10})]$ [20], and in the closely related polymeric structure of $[Cu_2B_{10}H_{10}]$ which features octahapto tetra-bridging coordination of *closo*-$B_{10}H_{10}^{2-}$ [21].

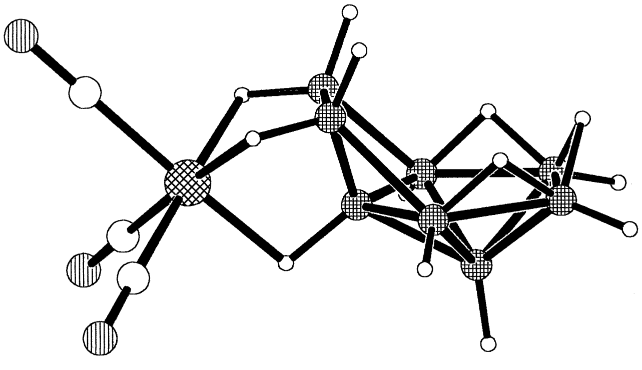


Fig. 2. Molecular structure of *fac*-$[Mn(\eta^3\text{-}B_8H_{13})(CO)_3]$.

So far, all the examples discussed of boranes or borane anions acting as ligands have involved B–H–B or B–H–M bonding. In the next section, the discussion is broadened to consider compounds in which there is direct bonding between the boron and metal, leading to a variety of coordination compounds in which the borane moiety displays hapticities from η^1 upwards.

3. Direct η^n-B_nM bonding from borane ligands to metals

Replacement of a terminal H atom in borane by a metal centre results in the formation of an η^1-bonded metalloborane, as exemplified by compounds in which Ir^{III}, Mn, Re or Fe^{II} is bonded to a basal boron atom in $-B_5H_8$ via a direct B–M bond [22–24]. Examples of η^1-B–M bonding are now also known for several other boranes [25]. In fact, the $B_5H_8^-$ anion gives η^2 complexes more frequently when used in ligand replacement reactions. Thus, deprotonation of B_5H_9 (by means of KH, for example) leads to $B_5H_8^-$, in which two basal boron atoms are joined by a direct two-centre two-electron B–B bond. This bond can donate its electron density to a (bridging) proton, thereby regenerating B_5H_9, or it can donate to an isolobal metal centre via a ligand displacement reaction involving, typically, a metal–halogen bond. One of the first examples of this bonding mode was $[Cu(\eta^2\text{-}B_5H_8)(PPh_3)_2]$ [26], and the structure of the complex as determined by X-ray diffraction analysis [27] is shown in Fig. 3. Similar complexes are now also known for Ni, Pd, Pt; Ag, Au; Cd, Hg; Si, Ge, Sn, Pb; and even B itself [28].

Neutral borane molecules can act similarly as η^2 ligands. A particularly important example is the reaction of *nido*-B_6H_{10} with Zeise's salt [29]:

$$\mathrm{K[Pt(\eta^2\text{-}C_2H_4)Cl_3] + 2B_6H_{10}}$$
$$\rightarrow \textit{trans}\text{-}\mathrm{[Pt(\eta^2\text{-}B_6H_{10})_2Cl_2] + C_2H_4 + KCl}$$

The molecular structure of the yellow crystalline product is shown in Fig. 4 [30]. There are now many such related complexes, for example, with Fe, Rh and Ir as the metal centre. An ingenious application of this propensity of B_6H_{10} to act as a powerful η^2 ligand was devised by Riley Schaeffer to prepare previously unknown boranes. Thus, the nonaborane *nido*-B_9H_{13} has only a transient existence unless it is stabilised by a ligand such as Me_2S. Using B_6H_{10} as the ligand afforded the new crystalline *conjuncto*-borane $B_{15}H_{23}$, i.e. $[(\eta^2\text{-}B_6H_{10})B_9H_{13}]$ as illustrated in Fig. 5 [31]. This shows that the B_6H_{10} subcluster (on the left) is η^2-bonded to a single B atom of the B_9H_{13} subcluster (on the right) via a three-centre BBB bond. Similarly, the novel *conjuncto*-borane $B_{14}H_{22}$ was made by the addition of B_6H_{10} to the unstable B_8H_{12} [31].

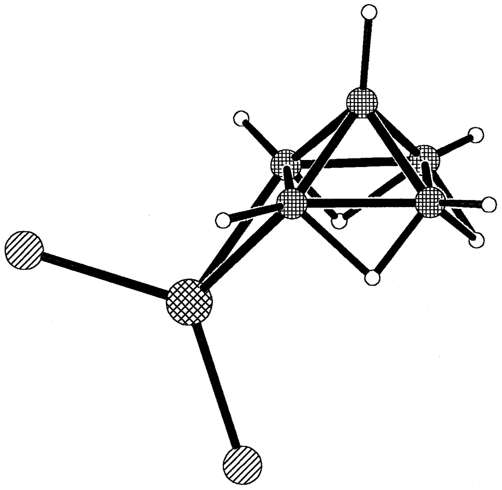


Fig. 3. Molecular structure of $[Cu(\eta^2\text{-}B_5H_8)(PPh_3)_2]$, omitting the six phenyl groups for clarity.

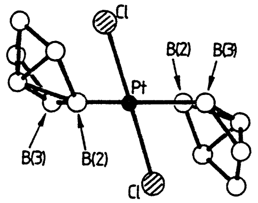


Fig. 4. Molecular structure of *trans*-$[Pt(\eta^2\text{-}B_6H_{10})_2Cl_2]$.

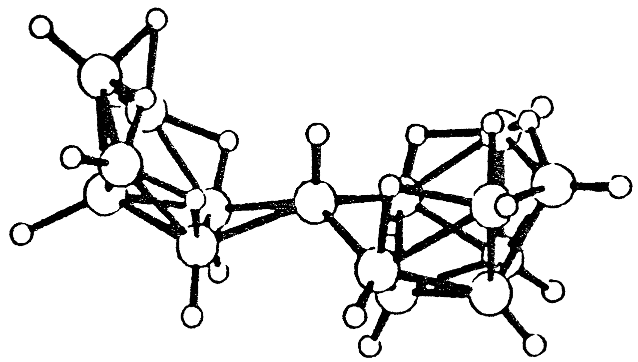


Fig. 5. Molecular structure of *conjuncto*-$B_{15}H_{23}$, i.e. $[(\eta^2\text{-}B_6H_{10})B_9H_{13}]$.

The ability of B_6H_{10} to coordinate to polyborane fragments is also a crucial factor in the complex gas-phase thermolysis reactions by which diborane can be converted to higher boranes, notably decaborane, $B_{10}H_{14}$. The early steps in this process lead to B_4H_{10} and B_5H_9 but the absence of isolable amounts of B_6H_{10} and other intermediate-sized clusters remained a puzzle. Recent detailed kinetic studies of the cothermolysis reactions of B_6H_{10} with other small boranes such as B_2H_6 and B_4H_{10} have given results that are entirely consistent with the suggestion that the known reactive intermediates $\{B_3H_7\}$ and $\{B_4H_8\}$, acting as Lewis acids, are rapidly scavenged by the reaction with the ligand B_6H_{10} to form B_9H_{15} plus either H_2 or $\{BH_3\}$, respectively [32].

Turning next to η^3-B_3M bonding, the best characterised trihapto-bonded metalloborane is the white, air-stable Ir complex $[Ir(\eta^3\text{-}B_3H_7)(CO)H(PPh_3)_2]$, which was made by the stoichiometric reaction of TlB_3H_8 with *trans*-$[Ir(CO)Cl(PPh_3)_2]$ [33]. TlCl is eliminated and a H atom is transferred from the borane to the iridium as shown in Fig. 6: the structure is best visualised as that of B_4H_{10} with one of its two hinge {BH} groups replaced by the $\{Ir(CO)H(PPh_3)\}$ moiety. Further examples can be found in Ref. [25]. An alternative route to η^3-borane complexes unexpectedly emerged during the reaction of $B_5H_8^-$ with *trans*-$[Ir(CO)Cl(PPh_3)_2]$: in-

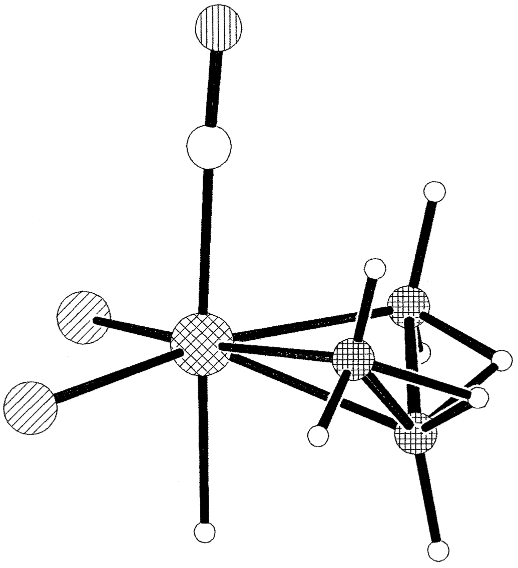


Fig. 6. Molecular structure of $[Ir(\eta^3\text{-}B_3H_7)(CO)H(PPh_3)_2]$ with the six phenyl groups omitted for clarity.

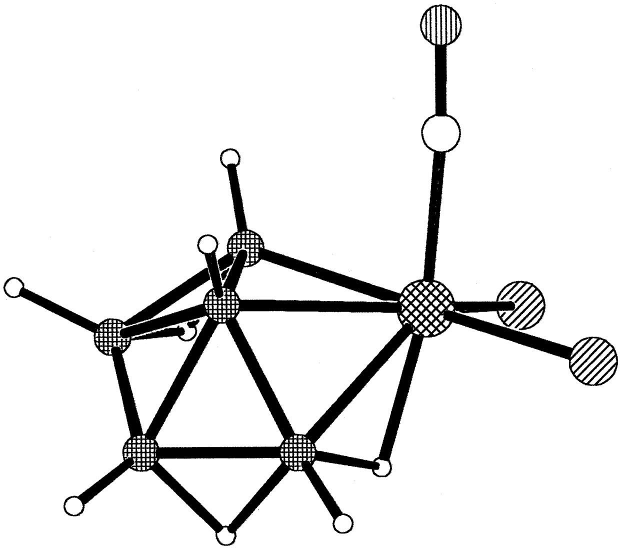


Fig. 7. Molecular structure of $[Ir(\eta^3\text{-}B_5H_8)(CO)(PPh_3)_2]$ with the six phenyl groups omitted for clarity.

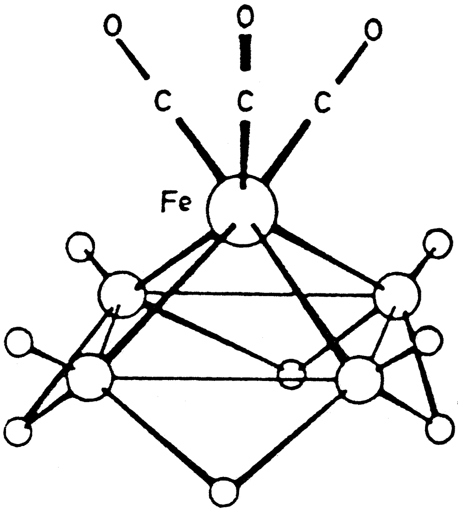


Fig. 8. Structure of $[Fe(\eta^4\text{-}B_4H_8)(CO)_3]$ showing similarity to *nido*-B_5H_9.

stead of simple displacement of Cl by $\eta^2\text{-}B_5H_8^-$, as in Fig. 3, further reaction ensued via oxidative insertion to give $[Ir(\eta^3\text{-}B_5H_8)(CO)(PPh_3)_2]$. As seen in Fig. 7, the result is a structural analogue of *nido*-B_6H_{10} with one basal $\{BH_tH_\mu\}$ group replaced by the Ir^{III} centre [34].

The classic examples of tetrahapto B_4M bonding are the *nido*-metallapentaboranes $[Fe(\eta^4\text{-}B_4H_8)(CO)_3]$ (Fig. 8) [35] and its isoelectronic cyclopentadienide analogue $[Co(\eta^4\text{-}B_4H_8)(\eta^5\text{-}C_5H_5)]$ [36]. The former can best be prepared as an orange-coloured liquid by cothermolysis of B_5H_9 with $Fe(CO)_5$ in a hot/cold reactor at 220/20 °C. It will be noted that $[Fe(\eta^4\text{-}B_4H_8)(CO)_3]$ is also precisely isoelectronic with the well-known cyclobutadiene complex $[Fe(\eta^4\text{-}C_4H_4)(CO)_3]$, both compounds exemplifying the stabilisation of the otherwise fugitive ligands by coordination. Likewise, progressive notional replacement of further $\{BH_t\}$ groups of B_5H_9 by the isolobal $\{Fe(CO)_3\}$ group leads to the isostructural series $[\{Fe(CO)_3\}_n\{BH_t\}_{5-n}(H_\mu)_4]$ and ultimately to the carbido metal–metal cluster $[\{Fe(CO)_3\}_5C]$, the unique five-coordinate C atom being isoelectronic with $4H_\mu$ [4].

In all the compounds mentioned in this section the metal acceptor has been isolobal with either $\{H\}$, $\{BH_t\}$ or $\{BH_tH_\mu\}$. However, it is possible to envisage other cluster vertex bonding stereochemistries, such as, for example, square-planar Pt^{II}, and this should permit the construction of previously unknown cluster geometries. This possibility is explored in the following section.

4. Clusters of clusters

A useful introductory example is the binuclear complex $[Pt_2(\mu\text{-}\eta^3\text{-}B_6H_9)_2(PMe_2Ph)_2]$, in which each of the two pentagonal pyramidal *nido*-$B_6H_9^-$ units is attached in a trihapto bridging mode to the linear L–Pt–Pt–L core [37]. The centrosymmetric skeletal structure, as elucidated by X-ray analysis, and the proposed bonding scheme are shown in Fig. 9. Notional replacement of the two $\{Pt(PMe_2Ph)\}$ groups by isolobal $\{BH\}$ groups would lead to the hypothetical binary borane $B_{14}H_{20}$, i.e. $[(BH)_2(\mu\text{-}\eta^3\text{-}B_6H_9)_2]$, in which the two B_6 units are in the *anti* configuration, as shown in Fig. 10a; this contrasts with the *syn* disposition of the two B_6 subclusters observed in the known *conjuncto*-borane, $B_{14}H_{20}$ (Fig. 10b).

More complex macropolyhedral platinaborane clusters can be prepared by appropriate thermolysis of the *arachno* nine-vertex platinaborane $[Pt(\eta^3\text{-}B_8H_{12})(PMe_2Ph)_2]$ in refluxing toluene solution. For example, the stable, red 17-vertex species $[(PMe_2Ph)Pt(\eta^6\text{-}B_{16}H_{18})(PMe_2Ph)]$ shown in Fig. 11 features hexahapto ligation of the *conjuncto*-borane moiety to platinum with all six B–Pt distances falling in the range 223–229 pm [38,39]. A coproduct was the green triplatina 17-vertex cluster $[(PMe_2Ph)_4Pt_3B_{14}H_{16}]$ shown in Fig. 12a [39,40]. Fig. 12b shows the same structure in a slightly different orientation with the phosphine ligands removed for clarity and Fig. 12c removes the three Pt atoms to reveal the boron skeleton of the B_{14} ligand. It will be seen that this comprises two B_6 subclusters joined by a B_2 group in the ‘end-on’ configuration rather than the ‘side-on’ configuration of the known binary borane $B_{14}H_{20}$ (see discussion of Figs. 9 and 10). It is clear that the compound can be viewed either as a 17-vertex macropolyhedral triplatinaborane or as an example of the stabilisation of an unusual 14-vertex *conjuncto*-borane stabilised by coordination to a central belt of three Pt atoms. Other macropolyhedral coproducts of the thermolysis reaction have also been isolated

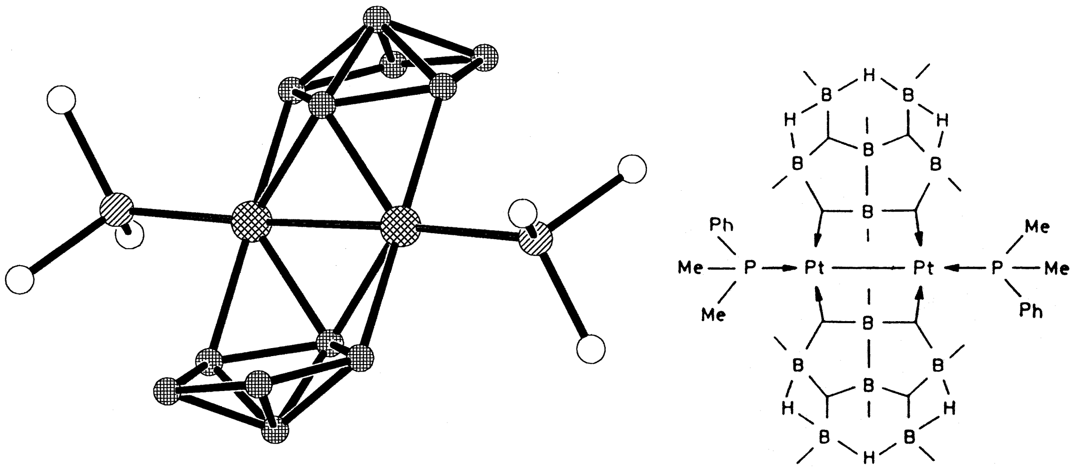


Fig. 9. The skeletal cluster structure and localised bonding scheme for $[Pt_2(\mu\text{-}\eta^3\text{-}B_5H_9)_2(PMe_2Ph)]$ showing the approximately square-planar distribution of bonding orbitals around the Pt vertices.

(in smaller yield) and fully characterised, notably the dark orange, air-stable 18-vertex diplatinaborane $[(PMe_2Ph)_2Pt_2B_{16}H_{15}(C_6H_4Me)(PMe_2Ph)]$ [41].

The earliest examples of binary borane species acting as polyhapto ligands actually emerged from work on main group metals [42]. The original motivation was to see whether the well-known cluster-expansion reactions of decaborane with borane adducts such as $L\cdot BH_3$ could be paralleled with adducts of Al and Ga. $B_{10}H_{14}$ was found to react readily with $[AlH_3(NMe_3)]$ in ether solution to give the novel, highly reactive anion $[AlB_{10}H_{14}]^-$ which is now probably best regarded as an analogue of *nido*-$B_{11}H_{14}^-$, i.e. $[H_2Al(\eta^4\text{-}B_{10}H_{12}]^-$. The reaction was subsequently extended to give a variety of stable crystalline complexes of Mg; Zn, Cd, Hg; Al, Ga, In, Tl; Si, Ge Sn^{II} and Sn^{IV} [43]. For example, deprotonation of $B_{10}H_{14}$ with $TlMe_3$ in ether solution gave the anion $[Me_2Tl(\eta^4\text{-}B_{10}H_{12}]^-$ whose structure, as shown in Fig. 13, was confirmed by X-ray analysis [44]. With zinc dialkyls the reaction proceeds further to give the *commo* dianion $[Zn(\eta^4\text{-}B_{10}H_{12})_2]^{2-}$ in which the two $B_{10}H_{12}^{2-}$ clusters are each acting as bis(dihapto) chelating ligands $(\eta^2,\eta^2\text{-}B_{10}H_{12})^{2-}$ (see Fig. 14) [45]. By contrast, the corresponding reaction with cadmium dialkyls in diethyl ether [46] leads to the neutral bridged dimeric complex $[\{Cd(\mu\text{-}\eta^2,\eta^2\text{-}B_{10}H_{12})(OEt_2)_2\}_2]$. As shown in Fig. 15, the decaborane ligands still act in an η^2,η^2 mode but ligation is from a *transoid* pair of B–B bonds in each case rather than a contiguous pair as in the preceding Zn and Tl examples. Other structure types have also emerged and large numbers of related metal–decaborane complexes have subsequently been prepared, including those of transition metals such as Cr, Mo, W; Re; Fe, Ru, Os; Co, Rh, Ir; Ni, Pd, Pt; and Cu [25]. Recent examples include the *syn* and *anti* isomers of the dianion $[Pt(B_{18}H_{20})_2]^{2-}$ [47], the 21-vertex molecular cluster $[(PMe_2Ph)_3HReB_{20}H_{15}Ph(PHMe_2)]$ [48], and the remarkable orange 27-vertex *conjuncto*-dimetallaborane $[(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2]$ which, as shown in Fig. 16, comprises conjoined IrB_{18} and IrB_8 subclusters, the former of which features octahapto ligation of the borane to the $\{Ir(PMe_3)_2\}$ centre [49].

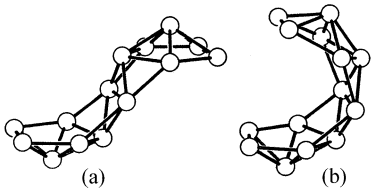


Fig. 10. The skeletal structures of: (a) the hypothetical *anti*-$B_{14}H_{20}$ having the same disposition of the two B_6 subclusters as in Fig. 8; and (b) the known *conjuncto*-$B_{14}H_{20}$ showing the *syn* configuration.

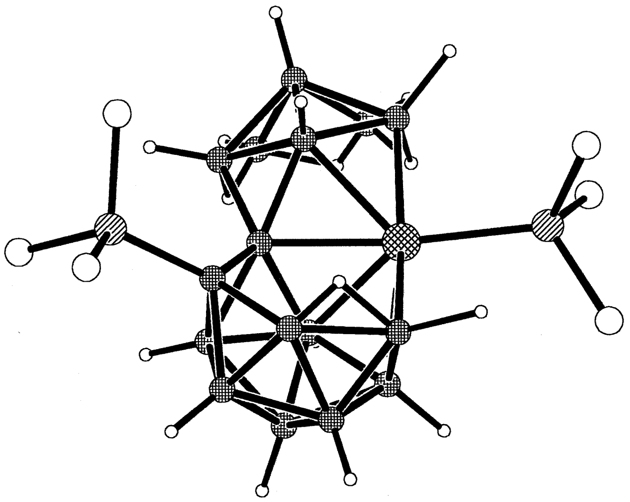


Fig. 11. Molecular structure of $[(PMe_2Ph)Pt(\eta^6\text{-}B_{16}H_{18})(PMe_2Ph)]$, including only the *ipso* carbon atoms on the phosphine ligands.

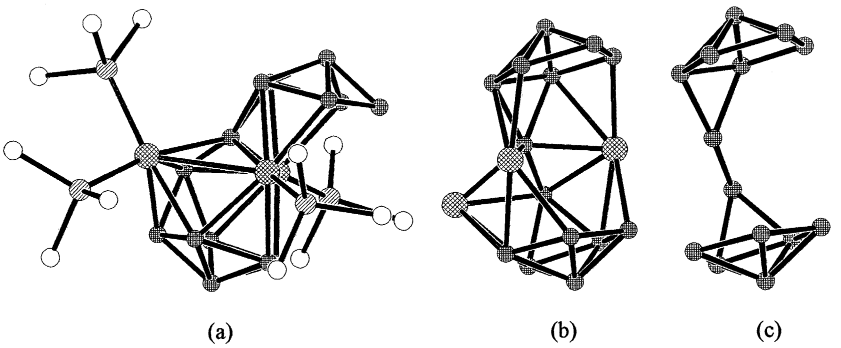


Fig. 12. (a) Molecular structure of $[(PMe_2Ph)_4Pt_3B_{14}H_{16}]$; (b) a slightly different orientation of the same structure with the four phosphine ligands removed for clarity; (c) the B_{14} skeleton remaining after removal of the three Pt atoms (cf. Fig. 9).

5. Conclusions

This brief account has presented a systematic overview of a new general approach to the development of novel aspects of boron hydride chemistry. By applying the principles of coordination chemistry, dozens of new structural types have been synthesised in which boron hydrides or their anions can be considered to act as polyhapto ligands to a large variety of metal centres thereby forming unusual and often completely unprecedented polyhedral metalloborane clusters. Over 40 metals have so far been found to act in this way. Even new binary boranes themselves can be synthesised by combining notional borane ligands and borane acceptors to give borane–borane complexes. The didactic and educational value of these new ideas has also been indicated. For example, the approach has proved to be particularly helpful in emphasising the close interconnections between several previously separated branches of chemistry, notably between boron hydride cluster chemistry, metalloborane and carbaborane chemistry on the one hand and the vast domains of organometallic chemistry and metal–metal cluster chemistry on the other. All are now seen to be parts of a coherent whole, superficially separated only by the differing pictorial conventions used to represent the structures of organometallic clusters involving, for example, η^5-C_5H_5 and η^6-C_6H_6 ligands.

As a final example, which incorporates all these aspects within a single molecule we can consider the bright red, air-stable compound $[Ru_3\{\eta^6\text{-}B_{10}H_8(OEt)_2\}(\eta^6\text{-}C_6Me_6)_2(\mu_2\text{-}H)_3(\mu_3\text{-}H)]$ shown in Fig. 17. This was formed in 32% yield by heating under reflux an ethanolic solution of the four-vertex metalla-

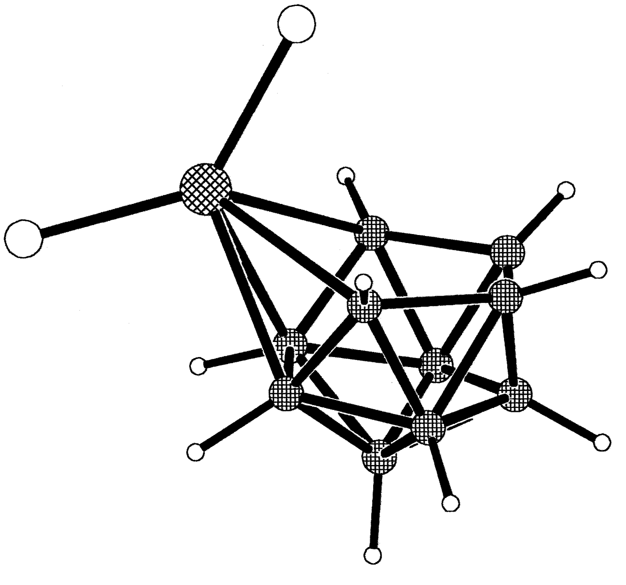


Fig. 13. Structure of the anion $[Me_2Tl(\eta^4\text{-}B_{10}H_{12})]^-$ (the two bridging H atoms are not shown).

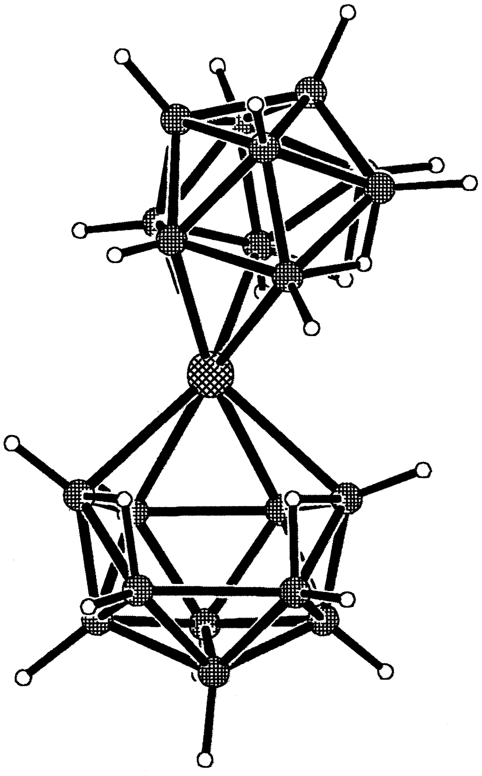


Fig. 14. Structure of the dianion $[Zn(\eta^4\text{-}B_{10}H_{12})_2]^{2-}$.

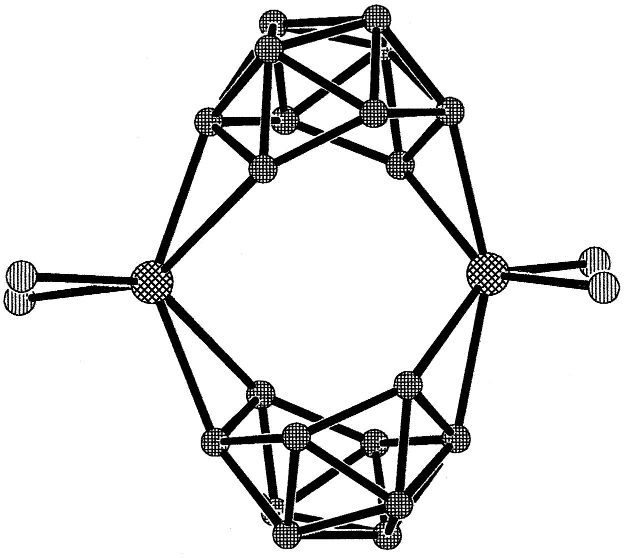


Fig. 15. Structure of the bridged dimeric complex [{Cd(μ-η^2,η^2-$B_{10}H_{12}$)(OEt_2)$_2$}$_2$].

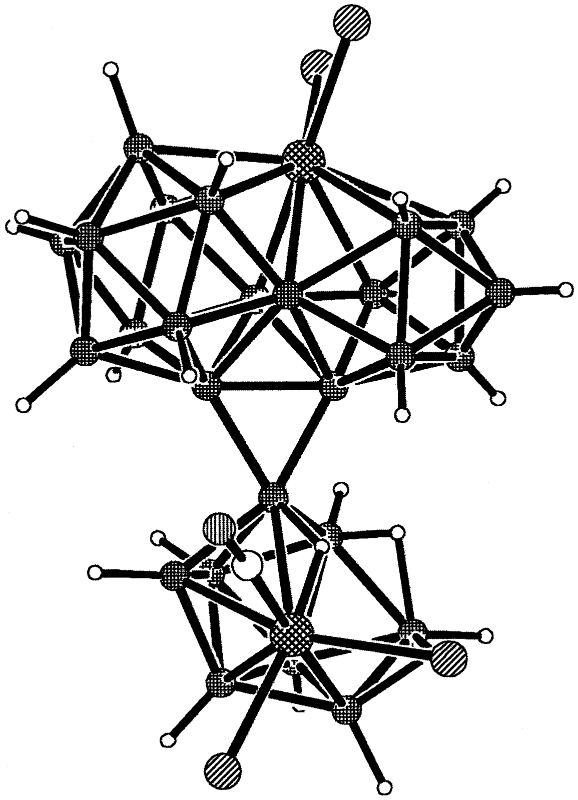


Fig. 16. Molecular structure of [$(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2$] showing octahapto coordination of the B_{18} subcluster to the upper Ir centre and tetrahapto coordination of the B_8 subcluster to the lower Ir.

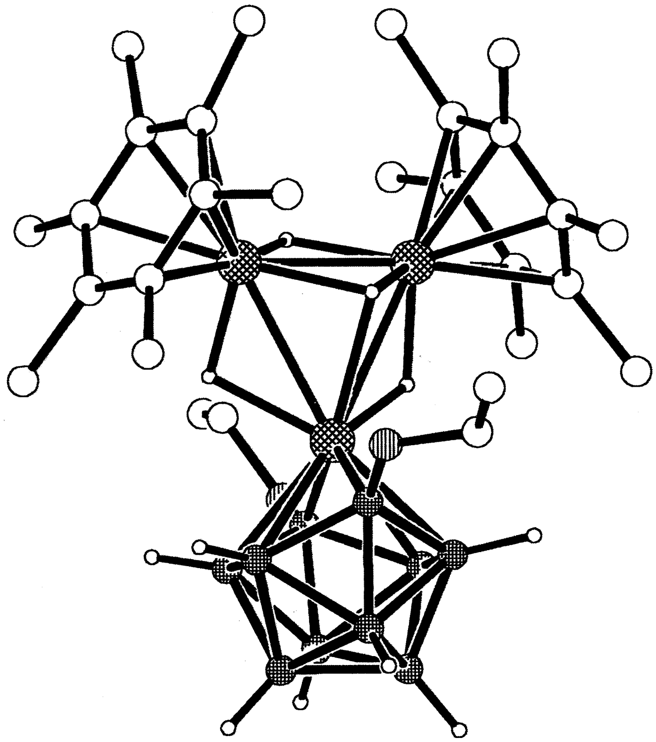


Fig. 17. Molecular structure of the compound [Ru_3{η^6-$B_{10}H_8(OEt)_2$}(η^6-C_6Me_6)(μ$_2$-H)$_3$(μ$_3$-H)].

borane cluster [$Ru(B_3H_8)(C_6Me_6)Cl$] and the *closo* dianion $B_{10}H_{10}^{2-}$ [50]. The Ru_3 triangle is unique in being the first and only such metal–metal cluster to have no attached CO ligands, the pendant groups being a hexahapto B_{10} ligand and two hexahapto hexamethylbenzene ligands together with three edge-bridging H atoms and one semi-capping, triply bridging H atom. It is, therefore, a *commo* metallaborane, which incorporates within a single compound, a metal–metal cluster, a polyhaptoborane ligand, and two organometallic moieties. The field continues to expand, with many innovative applications of these concepts, and their impact on synthetic and structural cluster chemistry continues to provide a plethora of polyhedral stereochemistries to perplex even the most imaginative theoretician.

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