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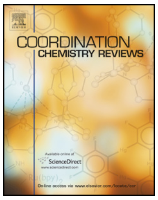

Review

Macropolyhedral metallaboranes – Aspects of preparation, constitution and structure

John D. Kennedy

School of Chemistry, University of Leeds, Leeds, Yorkshire LS2 9JT, UK

Contents

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ABSTRACT

Macropolyhedral boron-containing cluster compounds are those in which single clusters are intimately fused such that the covalent multicentre bonding characteristics typical of the boranes extend through and are part of the intercluster conjunction. Many of the most significant developments in macropolyhedral boron-containing cluster chemistry have occurred since the mid-to-late 1990s. Of these, metal-containing macropolyhedral species are reviewed here, with particular emphasis on syntheses and the novel skeletal structures that result.

1. Introduction

Boron can form extensive series of stable hydrides – the boranes. Other main-group non-metallic elements can be involved, to yield heteroboranes, for example $SB_{11}H_{11}$ and the very stable and very well-known trio of $C_2B_{10}H_{12}$ isomers. Transition-element and main-group metallic centres can also be incorporated to generate metallaboranes and metallaheteroboranes. The basic structural units that characterise the resulting boron-containing cluster compounds are typically based on closed or open triangulated deltahedral single clusters and cages, generally containing three or more boron atoms. The cage vertices are defined by the positions of the boron and the hetero atoms, with the hydrogen atoms generally bound around the cluster periphery, in *exo*-terminal positions held radial to the cluster, and in open-face *endo*-terminal or bridging positions held tangential to the cluster. In contrast to the two-electron two-centre *sigma*-bonding networks that, for example, characterise much of carbon hydride chemistry, the electronic constitution of the cluster compounds of the boron hydrides is governed and characterised by multicentre bonding.

There is a tremendous variety of boranes, heteroboranes, and metallaboranes known that have cluster sizes of between two and thirteen vertices. There are increasingly severe difficulties in preparing boron-containing single cages with increasingly more than twelve vertices. Beyond fifteen vertices or so, syntheses become very difficult. A large volume of additional Chemical Space is revealed by the perception that a big borane chemistry needs to be developed by seeking means to link single boron-containing cluster units together. This can be accomplished by simply linking individual cluster units together using simple two-centre *sigma*-bonds, as in isomers of $(B_{10}H_{13})_2$ (schematic skeletal structure **1**) [1] or more elaborate *sigma*-bonded linkages of types familiar from carbon-based chemistry, *e.g.*, at its simplest, $(B_{10}H_{13})_2O$ (schematic skeletal structure **2**, where X is an oxygen atom) [2]. However, such simple connections often cannot significantly change the known chemistry of the individual single clusters. One caveat here,

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E-mail address: j.d.kennedy@leeds.ac.uk

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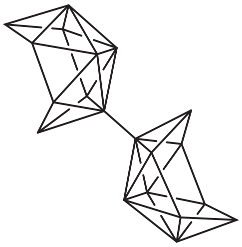
however, is that ostensibly simple *sigma* linkage may not always be completely innocent, and may provide a support for intercluster *pi–pi* interactions that could introduce more significant cluster perturbations. Further, the overall nature of a *sigma*-linked ensemble, particularly if it were to contain many individual single clusters, may engender properties to add to those of the individual units (see, for example, near schematics **75** and **76** below).



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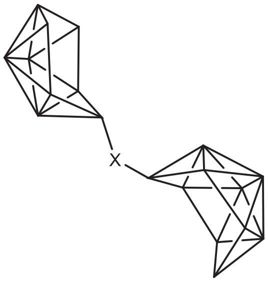

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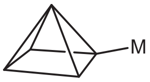
More progressive is to consider molecular assemblies in which two or more individual single clusters may be regarded as being more intimately joined together, *i.e.* fused such that the covalent multicentre bonding characteristics typical of the boranes extend through and are part of the intercluster conjunction. Such fused cluster species have become known as 'macropolyhedral' species, a term first coined in the early 1980s [3,4]. The individual clusters are thence no longer separate entities; rather, they can be regarded as 'fused' with one, two, three, or more atoms held in common at the point of fusion. This review is concerned with metallaboranes that fall within the macropolyhedral category. Metallaboranes themselves have been well reviewed over the years [5–9], although the most recent comprehensive dedicated surveys only cover the literature up to about 2003 [9]. However, many ongoing developments are summarised in the *Annual Reports* of the Royal Society of Chemistry [10].

An initial perception by Williams [11] recognised that the structures of polyhedral boron-containing species could be largely interpreted in terms of patterns set by (a) a set of *closo* compounds $[B_nH_n]^{2-}$ that had skeletons that are closed deltahedral polyhedra of highest symmetry, (b) a set of *nido* compounds B_nH_{n+4} with skeletons derived from the *closo* polyhedra by the removal of one vertex of highest connectivity, and (c) a set of *arachno* compounds B_nH_{n+6} with skeletons derived by the removal of a further vertex from a *nido* skeleton. Wade [12] thence perceived that the number of particularly counted skeletal electrons in these sets can be correlated with the structures as follows: the *n*-vertex *closo* deltahedral boranes are particularly stable if they contain $2n+2$ skeletal electrons, the *n*-vertex *nido* boranes B_nH_{n+4} retain the $2(n+1)+2$ skeletal electrons of the $(n+1)$-vertex deltahedra from which they are derived and thus are $2n+4$ skeletal-electron systems, and the *n*-vertex *arachno* boranes B_nH_{n+6} are correspondingly $2n+6$ skeletal-electron systems. These considerations, together with considerations involving the incorporation of non-boron atoms within the clusters [12–14], are often called 'Wade's Rules', and are well-recognised and well-rehearsed in contemporary general Inorganic Chemistry textbooks.

In the categorisation of the interaction of metal centres with boron-containing cages and clusters, one simplistic but useful approach is to consider the formal orbital availability of the metal centres. A one-orbital availability, for example in a five-ligand d^2sp^3 classical octahedral configuration, means that the metal centre can formally replace a cluster-bound *exo*-terminal hydrogen atom, and so a simple two-electron two-centre *sigma* binding of the metal centre can result, as with the $\{IrBr_2(CO)(PR_3)_2\}$ unit in $[Ir(B_5H_8)Br_2(CO)(PR_3)_2]$ (schematic skeletal structure **3**) [15]. Throughout, in diagrams such as this, **M** generally represents the metal centre together with its sphere of *exo*-cluster ligands. Alternatively a bridging hydrogen atom can be replaced (schematic skeletal structure **4**), which can occur with less sterically demanding metal centres such as three-ligand sp^3 classical tetrahedral or dsp^2 classical square-planar units, as with the $\{SiMe_3\}$ unit in $[Me_3SiB_5H_7Br]$ [16] and as with the $\{PtCl(PMe_2Ph)_2\}$ unit in $[Cl(PMe_2Ph)_2PtB_5H_8]$ [17], which bind to the borane units with simple two-electron three-centre M-BB *sigma* linkages.



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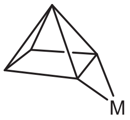

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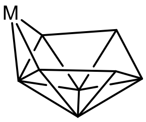
With a two-orbital availability, as in a four-ligand d^2sp^3 octahedral unit, or in a two-ligand sp^3 or dsp^2 unit, then a cluster $\{BH_2\}$ unit can formally be replaced, as with the $\{IrCl(CO)PR_3)_2\}$ moiety in $[(PMe_3)_2(CO)ClIrB_8H_{12}]$ (schematic skeletal structure **5**) [18], formally an analogue of the $[$*arachno*-$B_9H_{14}]^-$ anion (schematic skeletal structure **6**), and as with the $\{Pt(PMe_2Ph)_2\}$ moiety in $[(PMe_2Ph)_2PtB_{10}H_{12}]$ (schematic skeletal structure **7**) [19], formally an analogue [20] of the $[$*nido*-$B_{11}H_{14}]^-$ anion (schematic skeletal structure **8**) [20].



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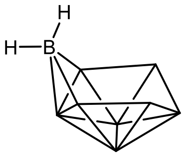

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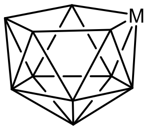

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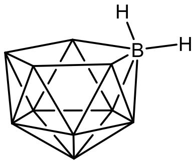

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In the latter case, the $\{Pt(PMe_2Ph)_2\}$ unit can alternatively be visualised as replacing two bridging hydrogen atoms of *nido*-decaborane, $B_{10}H_{14}$ (schematic skeletal structures **9A** and **9B**) [21]: the two three-centre bonds to the bridging hydrogen atoms are replaced by two three-centre bonds to the metal centre. A three-orbital availability, as in a three-ligand d^2sp^3 octahedral unit, or in a one-ligand sp^3 or dsp^2 unit, can engender the notional replacement of a cluster $\{BH\}$ unit, as with the iridium(III) $\{Ir(CO)PPh_3)_2\}$ entity in $[(PPh_3)_2(CO)IrB_5H_8]$ (schematic skeletal structure **10**) [22], formally an analogue of the $[$*nido*-$B_6H_9]^-$ anion. The one-orbital → two-orbital → three-orbital progression is associated with an increasing assimilation of the metal centre into the cluster. A further increase in intimacy of assimilation is seen in a series of so-called '*isocloso*' compounds [23], such as for the $\{IrH(PMe_3)_2\}$ unit in $[(PMe_3)_2HIrB_9H_9]$ (schematic skeletal structure **11**) [24]. It has been proposed that such increased intimacies may be the result of a four-orbital involvement of the metal centre with the cluster, which would then, in this example [25,26], imply a high formal oxidation state of iridium (V); however other interpretations have also long been proposed, [27] and this interesting

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