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Analogies between the chemical bonding topologies in metal–olefin complexes and in metallaboranes: the role of three-center two-electron bonding

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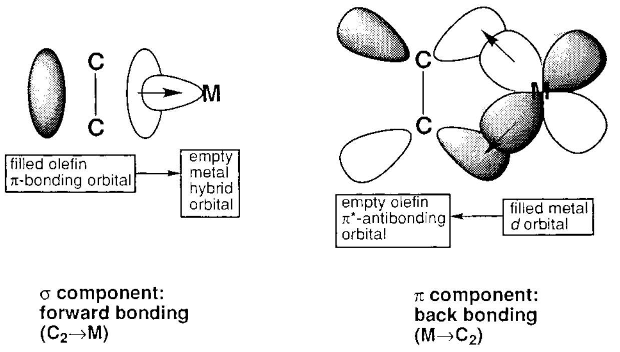
Abstract

Three-center two-electron (3c-2e) interactions are found both in the C_2M σ-bonding in the Dewar–Chatt model of the olefin–metal bond and in the B_2H and B_3 bonding in borane structures based on deltahedra or deltahedral fragments. Incorporation of metals as vertices of boron deltahedra frequently changes their shapes to provide degree 6 and even degree 7 vertices for the metal atoms. In addition, metal incorporation frequently modifies the core + surface skeletal bonding of the original $B_nH_n^{2-}$ to pure surface bonding consisting mainly or entirely of 3c-2e bonds. In such structures the resulting 3c-2e B_2M bonds are related to the C_2M σ-bonding in the Dewar–Chatt model. The skeletal bonding of deltahedral metallaboranes containing two or more metal vertices can also include 2c-2e metal–metal bonding through the center of the deltahedron. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Chemical bonding topology; Three-center bonds; Boranes; Metallaboranes

1. Introduction

The first organometallic complex to be prepared was the platinum–ethylene complex $K[PtCl_3(C_2H_4)]$, discovered by Zeise in 1827. However, the nature of the olefin–metal bond in this and related complexes remained a mystery for more than a century. This enigma was resolved by Dewar, who published a seminal review of 'π-complex theory' in 1951 [1]. At about the same time Chatt and coworkers reported experimental studies on olefin and acetylene complexes of the platinum metals which provided experimental support for Dewar's bonding model [2].



σ component: forward bonding ($C_2 \rightarrow M$)

π component: back bonding ($M \rightarrow C_2$)

Fig. 1. The Dewar–Chatt model for olefin–metal bonding.

Another seminal development in transition metal organometallic chemistry contemporaneous with this work by Dewar and Chatt was the serendipitous discovery of ferrocene [3,4]. The original discoverers of ferrocene did not recognize its famous pentagonal antiprismatic 'sandwich' structure, which was postulated by Wilkinson et al. [5] shortly after its discovery and subsequently confirmed by X-ray crystallography [6]. The discovery of ferrocene showed that cyclic hydrocarbons as well as olefins could form stable transition metal complexes.

The Dewar–Chatt model for olefin–metal bonding (Fig. 1) was originally interpreted to consist of the following two components: (1) a σ-type bond involving donation of the electron pair in the carbon–carbon π-bond of the olefin to an empty metal hybrid orbital;

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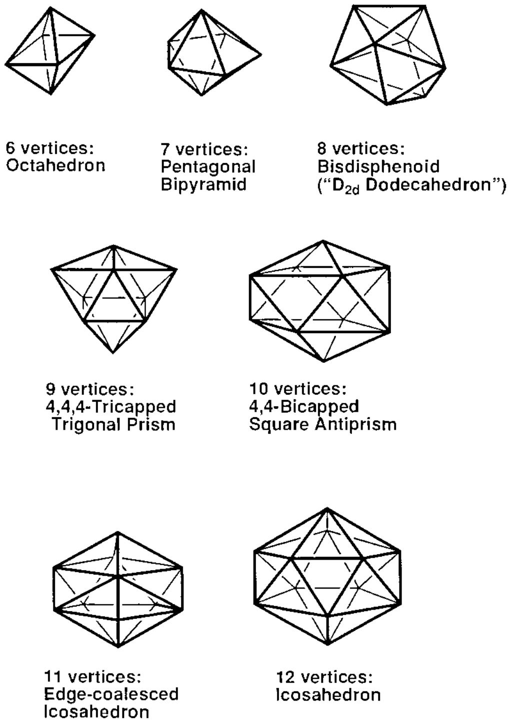


Fig. 2. The 'most-spherical' deltahedra found in deltahedral boranes $B_nH_n^{2-}$ $(6 \leq n \leq 12)$.

and (2) a π-type bond involving back donation of electron density from filled metal d orbitals into empty π* antibonding orbitals. Note that the σ-type bond in this model arises from overlap of orbitals from both carbon atoms of the double bond with a metal orbital so that it can alternatively be considered as a three-center two-electron (3c-2e) C_2M bond.

At about the time that Dewar and Chatt elucidated the chemical bonding in metal–olefin complexes, Lipscomb and coworkers [7] were studying the chemical bonding in another series of the then puzzling compounds, namely the boron hydrides (boranes). In this case the difficulty was the presence of too few bonding electrons for bonding models involving exclusively two-center two-electron (2c-2e) bonds, such as those characteristic of hydrocarbon chemistry. For example, diborane, B_2H_6, has the same apparent chemical formula as ethane, C_2H_6, but two fewer bonding electrons so that boron hydrides were then considered to be 'electron deficient' molecules in contrast to the 'electron-precise' hydrocarbons. Again the key to the dilemma of the chemical bonding in boron hydrides was the recognition of 3c-2e bonds in B_2H_6 and higher boron hydrides [7]. There is thus an analogy between the chemical bonding in boron hydrides and transition metal olefin complexes, both of which involve 3c-2e bonding.

A subsequent major development in boron hydride chemistry was the recognition of the special stability of polyhedral boranes based on the 'most spherical' deltahedra [8], often called *closo* deltahedra by boron chemists. Such *closo* deltahedral boranes (Fig. 2) were recognized as examples of three-dimensional (3D) aromatic systems [9–11] exhibiting special chemical stability as compared with boranes having more open structures. Thus some deltahedral boranes and isoelectronic carboranes, notably the icosahedral species $B_{12}H_{12}^{2-}$ and the three isoelectronic carborane isomers $C_2B_{10}H_{12}$, were completely air stable and thermally stable to temperatures as high as ~ 500°C, whereas the previously discovered neutral boron hydrides such as B_2H_6, B_4H_{10}, B_5H_9, and $B_{10}H_{14}$, were highly flammable, sometimes spontaneously in air, and of much more limited thermal stability.

Further development of transition metal organometallic chemistry and boron hydride chemistry eventually led to their merger in the chemistry of metallaboranes [12]. The first metallaboranes were species such as $C_5H_5CoC_2B_9H_{11}$ which are derived from the very stable icosahedral carborane 1,2-$C_2B_{10}H_{12}$ by replacement of one BH vertex with an isoelectronic and isolobal C_5H_5Co vertex (Fig. 3). In such metallaboranes the bonding of the transition metal unit to the boron cage could be viewed as closely related to the metal-ring bonding in ferrocene and related metal complexes of cyclic hydrocarbons. However, as metallaborane chem-

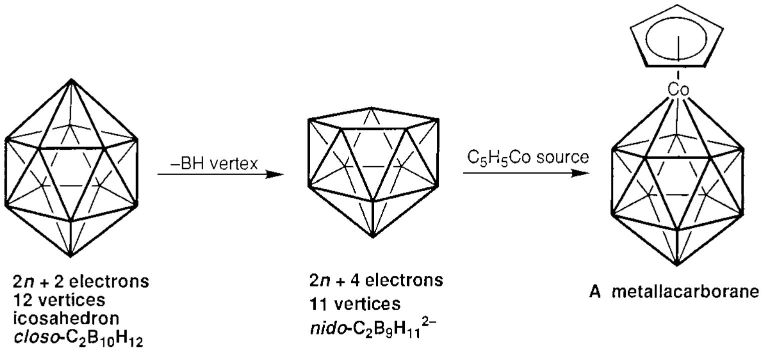
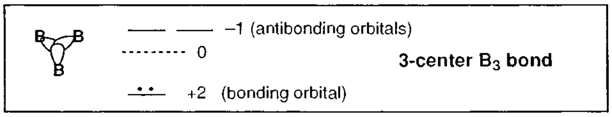
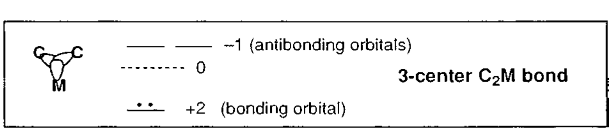


Fig. 3. Conversion of an icosahedral carborane into an icosahedral metallacarborane by removal of a BH vertex followed by introduction of a transition metal (C_5H_5Co) vertex.



Boron framework bonding in polyhedral boranes



The σ forward olefin-metal bonding in metal-olefin complexes

Fig. 4. Comparison of 3c-2e B_3 bonds in polyhedral boranes and 3c-2e C_2M bonds in metal–olefin complexes.

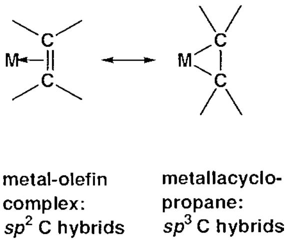


Fig. 5. Resonance hybridization between an olefin–metal complex and a metallacyclopropane.

istry developed through the synthesis of a greater variety of structures, compounds were eventually discovered based on deltahedra different from those found in metal-free boranes. In general transition metals were often found to prefer vertices of higher degree, where the degree of a vertex is the number of edges meeting at the vertex in question. Thus whereas the deltahedra in the stable metal-free boranes and carboranes (with at least six vertices) were found to have exclusively degree 4 and 5 vertices except for the 11-vertex carboranes, some metallaborane deltahedra were found to have one or more degree 6 or even occasionally degree 7 vertices.

This paper surveys some aspects of the chemical bonding in metallaboranes with particular emphasis on the analogies in the chemical bonding between metal–olefin complexes and metallaboranes of certain types.

2. Three-center bonding in boranes and metal–olefin complexes

2.1. Comparison of three-center two-electron B_3 and C_2M bonds

The concept of three-center bonding was first developed to account for the apparent electron-deficiency of the boron hydrides (boranes). In the usual 2c-2e covalent bond, such as the C–C and C–H σ-bonds typically found in hydrocarbons, two atoms supply two orbitals, one centered on each atom. These atomic orbitals interact to form one bonding orbital and one antibonding orbital so that if two electrons are available, they will just fill the bonding orbitals and constitute the standard covalent bond. In the 3c-2e covalent bonding found in boranes, three atoms supply three orbitals, one on each atom. These atomic orbitals interact to form one bonding and two antibonding orbitals so that two electrons may thus fill the bonding orbital to form a 3c-2e bond (Fig. 4). In the case of borane derivatives such 3c-2e bonding can involve either orbitals from three boron atoms overlapping in a (triangular) face of a borane deltahedron or deltahedral fragment (i.e. a 3c-2e B–B–B or B_3 bond) or orbitals from two boron atoms and one hydrogen atom forming a bridging hydrogen atom such as the two bridging hydrogen atoms in diborane (B_2H_6).

A related 3c-2e model can be used for a description of the σ-type component in the Dewar–Chatt model of an olefin–metal bond (Fig. 4). In this case the three atoms furnishing the orbitals are the two carbon atoms of the complexed olefin and the metal atom so that the σ-component of the olefin–metal bond can be described as a 3c-2e C_2M bond. A type of 3c-2e bond intermediate between the σ-component of the olefin–metal bond and the 3c-2e B_3 bond found in localized structures of deltahedral boranes is a B_2M 3c-2e bond found in certain faces of polyhedral metallaboranes [13,14]. These will be discussed later in this paper.

There is an important difference between the 3c-2e bonding in boron networks and that in olefin–metal complexes. In boron networks the 3c-2e B_3 bond is the major interaction between B_3 units in the underlying localized bonding topology. However, in olefin–metal complexes the 3c-2e C_2M forward σ-bond is supplemented by the π-type back bonding involving the empty π* antibonding orbital of the olefin C=C bond and a filled metal d orbital of the required π-type symmetry (Fig. 1). By making an extra pair of electrons from the filled metal d orbital available for bonding, a three-atom C_2M four-electron system is converted into a three-atom six-electron system with enough electrons for three 2c-2e bonds along the edges of the C_2M triangle similar to the bonding in cyclopropane. Indeed metal complexes of electronegative olefins such as tetrafluoroethylene and tetracyanoethylene may be regarded as metallacyclopropanes through the resonance hybridization depicted in Fig. 5.

2.2. Construction of borane structures from 2c-2e and 3c-2e bonds: Lipscomb's topological rules

Lipscomb [15–17] has studied the topology of the distribution of 2c-2e B_2 and 3c-2e B_3 bonds in networks of boron atoms using the following assumptions:

1. Only the 1s orbital of hydrogen and the four sp^3 orbitals of boron are used.
2. Each terminal B–H bond is regarded as a typical 2c-2e single bond requiring the hydrogen 1s orbital, one hybridized boron orbital, and one electron each from the hydrogen and boron atoms. Because of the very small electronegativity difference between hydrogen and boron, these bonds are assumed to be non-polar.
3. Each B_2H 3c-2e 'bridge bond' corresponds to a filled three-center localized bonding orbital requiring the hydrogen orbital and one hybrid orbital from each boron atom.
4. The orbitals and electrons of any particular boron atom are allocated to satisfy first the requirement of the external B–H single bonds and the bridge B–H–B bonds. The remaining orbitals and electrons are allocated to the skeletal molecular orbitals of the boron framework.

The relative numbers of orbitals, electrons, hydrogen, and boron atoms as well as bonds of various types can be expressed in a systematic way [15–17]. Consider a neutral boron hydride B_pH_{p+q} containing s *bridging* hydrogen atoms, x *extra* 2c-2e B–H bonds in terminal BH_2 groups rather than BH groups, t 3c-2e B_3 bonds, y 2c-2e B_2 bonds, and at least one hydrogen atom bonded to each boron atom. Balancing the hydrogen atoms in such a boron hydride leads to $s+x=q$. Since each boron atom supplies four orbitals but only three electrons, the total number of 3c-2e bonds in a binary boron hydride is the same as the number of boron atoms, namely $s+t=p$. This leads to the following equations of balance:

$$2s+3t+2y+x=3p$$

(orbital balance with three orbitals/BH vertex) (1a)

$$s+2t+2y+x=2p$$

(electron balance with two skeletal electrons/ BH vertex) (1b)

3. The normal borane and metallaborane deltahedra

3.1. The metal-free borane deltahedra as three dimensional (3D) aromatic systems

Structural information on the metal-free boranes $B_nH_n^{2-}$ and the isoelectronic carboranes $C_2B_{n-2}H_n$ ($6 \leq n \leq 12$) [18–23] show all of these species to have the deltahedral structures (Fig. 2) as originally suggested by Williams in 1971 [8]. This group of deltahedra has been described by Williams [24] as the 'most spherical' deltahedra since they are those with the most uniformly or most homogeneously connected vertices. This corresponds to deltahedra having exclusively degree 4 and 5 vertices for $B_nH_n^{2-}$ and $C_2B_{n-2}H_n$ ($n = 6$, 7, 8, 9, 10, and 12) and having all degree 4 and 5 vertices except for a single degree 6 vertex in $B_{11}H_{11}^{2-}$ and $C_2B_9H_{11}$.

These deltahedral boranes and carboranes are characterized by unusual stability compared with the reactive and frequently unstable neutral binary boron hydrides B_pH_q ($q=p+4$ or $p+6$). This suggests that the concept of aromaticity, originally developed for two-dimensional (2D) polygonal molecules and ions to account, for example, for the unusual stability of benzene relative to polyolefins, might be extended to 3D polyhedral molecules and ions to account for the unusual stability of deltahedral boranes and carboranes. An explicit suggestion of 3D aromaticity in deltahedral boranes was made by Aihara [25] in 1978, who used a graph-theoretical method to find significant positive resonance energies for deltahedral boranes with the experimentally very stable $B_{12}H_{12}^{2-}$ having the highest resonance energy. Meanwhile King and Rouvray [10] used methods derived from graph theory to demonstrate the analogy between the delocalization in 2D planar polygonal aromatic hydrocarbons such as benzene and that in 3D deltahedral boranes. Their topological analysis suggested a skeletal bonding model for $B_nH_n^{2-}$ ($6 \leq n \leq 12$) consisting of a single n-center two-electron core bond in the center of the deltahedron and n 2c-2e bonds in the surface of the deltahedron. Shortly thereafter Stone and Alderton [26] approximated borane deltahedra by spheres so that tensor surface harmonic theory mathematically similar to that used to generate atomic orbitals for (spherical) atoms could be used to generate the skeletal molecular orbitals for borane deltahedra.

The stable deltahedral boranes are all dianions $B_nH_n^{2-}$ rather than neutral molecules B_nH_n in accord with the stability of such structures having $2n+2$ rather than $2n$ skeletal electrons. In counting such skeletal electrons, the BH vertices are donors of two skeletal electrons since one of the three boron valence electrons is required for the 2c-2e bond to its external hydrogen atom. This $2n+2$ skeletal electron rule was first noted by Wade [27]. Rudolph and Pretzer [28,29] subsequently provided the first attempt to account for this rule using semi-empirical molecular orbital calculations. Mingos [30,31] incorporated these ideas into his 'polyhedral skeletal electron pair approach,' which provides a simple way to understand the structural diversity shown by polyhedral molecules. Because of the seminal work of Wade and Mingos in understanding electron counting in polyhedral molecules, the rules assigning $2n+2$ skeletal electrons to stable deltahedral boranes and related polyhedral species are frequently called the 'Wade–Mingos Rules.' The graph-theoretical [10] and tensor surface harmonic [26] models for 3D aromaticity in borane deltahedra account for the observed $2n+2$ skeletal electrons in such compounds exhibiting unusual stability.

3.2. Localized bonding models for deltahedral boranes: Kekulé-type structures

A central idea in the aromaticity of planar benzenoid hydrocarbons is the contribution of two or more different so-called Kekulé structures of equivalent energy consisting of alternating C–C single and C=C double bonds to a lower energy averaged so-called resonance hybrid structure. In benzene itself the two equivalent Kekulé structures contain three double and three single bonds alternating along the six edges of the C_6 hexagon.

The 2c-2e B_2 bonds and 3c-2e B_3 bonds in polyhedral boranes can be components of localized Kekulé-type structures similar to the C–C single and C=C double bonds in planar hydrocarbons [32]. Thus consider the deltahedral boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$). Such deltahedral boranes do not have any terminal BH_2 groups or 3c-2e B_2H bonds. However, they have two 'extra' electrons for the -2 charge on the ion so that $s = x = 0$ in the equations of balance (Eqs. (1a) and (1b)). These equations then reduce to the following equations in which n is the number of boron atoms in the deltahedron corresponding to p in Eqs. (1a) and (1b):

$$3t + 2y = 3n \quad (2a)$$

$$2t + 2y = 2n + 2 \quad (2b)$$

Solving simultaneously Eqs. (2a) and (2b) leads to $y = 3$ and $t = n - 2$ implying the presence of exactly three 2c-2e B_2 bonds and $n - 2$ 3c-2e B_3 bonds. Since a deltahedron with n vertices has $2n - 4$ faces, the $n - 2$ 3c-2e B_3 bonds cover exactly half of the faces. In that sense a Kekulé-type structure for the deltahedral boranes $B_nH_n^{2-}$ has exactly half of its faces covered by 3c-2e B_3 bonds just like a Kekulé structure for a benzenoid hydrocarbon has half of its edges covered by C=C double bonds.

3.3. Introduction of metal vertices into deltahedral boranes

The boron vertices in borane deltahedra can be replaced with isolobal transition metal vertices bearing sufficient external ligands, e.g. carbonyl groups or perhapto planar cyclic hydrocarbons, to give the transition metal a suitable electronic configuration, most frequently the 18-electron configuration of the next noble gas. Examples of transition metal vertices isoelectronic and isolobal with a BH vertex and thus donors of two skeletal electrons include $Fe(CO)_3$, $(\eta^6\text{-}C_6H_6)Fe$, $(\eta^5\text{-}C_5H_5)Co$ as well as corresponding derivatives of their heavier congeners. Similarly $Co(CO)_3$, $(\eta^6\text{-}C_6H_6)Co$, $(\eta^5\text{-}C_5H_5)Ni$, and corresponding derivatives of their heavier congeners are donors of three skeletal electrons similar to a CH vertex in polyhedral carboranes. The hydrogen atoms in BH and CH vertices, as well as in the $\eta^5\text{-}C_5H_5$ and $\eta^6\text{-}C_6H_6$ rings bonded to transition metal vertices in metallaboranes, can be replaced by other monovalent groups, such as halogen, alkyl, aryl, etc., and the carbonyl groups in $M(CO)_3$ can be replaced by other two-electron donor ligands such as tertiary phosphines or isocyanides.

Deltahedral metallaboranes having n vertices, besides being derived from the corresponding deltahedral boranes by suitable isolobal/isoelectronic substitution of transition metal vertices for boron vertices as noted above, can also be regarded as metal complexes of *nido* borane ligands with $n - 1$ vertices. In this connection an $n - 1$-vertex *nido* borane ligand is derived from an n-vertex deltahedron by removal of one vertex, typically a vertex of highest degree. For example removal of one BH vertex, formally as BH^{2+}, from the icosahedral carborane $C_2B_{10}H_{12}$ gives an 11-vertex *nido* species $C_2B_9H_{11}^{2-}$ having an open pentagonal face (Fig. 3). Complexing a transition metal (e.g. a CpCo unit where $Cp = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}Me_5C_5$, or other substituted cyclopentadienyl ligands) to the open pentagonal face of $C_2B_9H_{11}^{2-}$ reconstitutes the icosahedral structure in the form of a metallacarborane (i.e. $CpCoC_2B_9H_{11}$ in the case of a CpCo vertex). The bonding of the cobalt atom to the pentagonal face of $C_2B_9H_{11}^{2-}$ is analogous to the pentahapto bonding of a cobalt atom to pentagonal $C_5H_5^-$ (or the iron-ring bond in ferrocene).

4. Anomalous deltahedra in metallaboranes

4.1. The 'isocloso' polyhedra and their 'disobedient' electron counts

Initially it was assumed that the deltahedra in metallaboranes would be the same as the deltahedra in isoelectronic metal-free boranes (Fig. 2) after considering isolobal/isoelectronic relationships. However, as metallaborane chemistry was developed, particularly by Kennedy and co-workers [33–36], some nine- and ten-vertex deltahedral metallaborane structures were discovered based on deltahedra topologically distinct from the deltahedra found in simple metal-free boranes and carboranes. Such metallaborane structures have the transition metal located at a degree 6 vertex whereas the metal-free boron deltahedra with the same number of vertices have only degree 4 and 5 vertices (Fig. 2). Even more interesting was the observation that such 'anomalous' metallaborane deltahedra are also 'disobedient' in having electron counts corresponding to only $2n$ skeletal electrons rather than the $2n+2$ skeletal electrons for the metal-free borane deltahedra. Such metallaborane structures are called *isocloso* structures (Fig. 6) and can be derived from the *closo* deltahedra with the same number of vertices by so-called diamond–square–diamond rearrangements [37,38].

The reason for the disobedient electron counts in the *isocloso* structures (i.e. two electrons less than the $2n+2$ skeletal electrons expected from the Wade–Mingos rules [27,30,31]) has been the cause for some speculation. Initially proposed ideas to rationalize this were based on orbital degeneracies in the HOMO/LUMO region [39–42] and the use of four internal orbitals rather than the usual three internal orbitals by the transition metal vertex to provide the 'extra' electron pair. Subsequently, Johnston et al. [43] used molecular orbital calculations on the *isocloso* structures to show that in most cases these anomalous electron counts are associated with the delocalized deltahedral bonding rather the transition metal vertices. Recently I showed that the anomalous electron counts in *isocloso* deltahedra are compatible with chemical bonding topologies consisting of exclusively 3c-2e B_3 and B_2M bonds in some of the deltahedral faces [13,14]. Thus consider the chemical bonding topology in an *isocloso* metallaborane deltahedron with n vertices, which can be shown by Euler's theorem [44] to have $2n-4$ faces and $3n-6$ edges like the corresponding *closo* deltahedron with the same number of vertices. If each vertex (e.g. a neutral BH vertex or isoelectronic/isolobal equivalent) contributes three skeletal (internal) orbitals and two skeletal electrons (i.e. a $2n$ skeletal electron system), then the numbers of skeletal orbitals and electrons are correct for 3c-2e bonds in n of the $2n-4$ faces leaving $n-4$ faces without 3c-2e bonds.

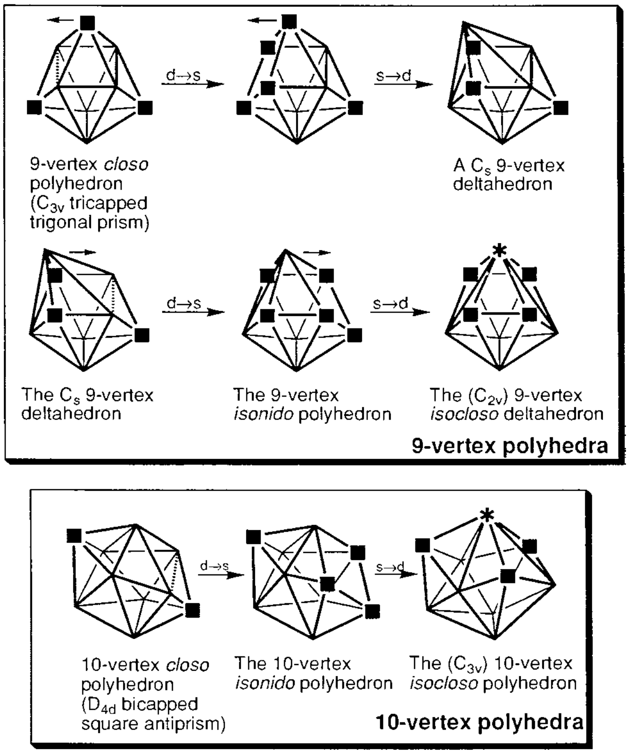


Fig. 6. Generation of the nine- and ten-vertex *isocloso* deltahedra from the corresponding *closo* deltahedra by diamond–square–diamond (dsd) rearrangements. For clarity in Figs. 5, 8 and 9, vertices of degrees 3, 4, 6, and 7 are marked with the symbols ▲, ■, *, and '7', respectively, and the vertices of degree 5 are unmarked.

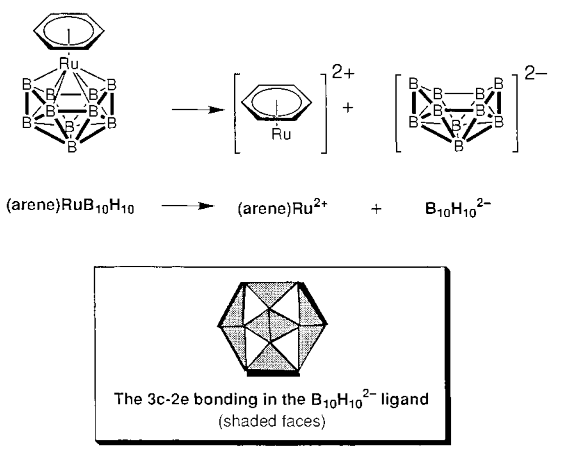


Fig. 7. (a) Dissection of (arene)$RuB_{10}H_{10}$ into (arene)Ru^{2+} and $B_{10}H_{10}^{2-}$. (b) Localized bonding in the open $B_{10}H_{10}^{2-}$ ligand in (arene)$RuB_{10}H_{10}$ indicating the eight 3c-2e B_3 bonds by shaded faces and the three 2c-2e B_2 bonds by alternating bold exterior edges around the outer hexagon.

4.2. Analogies between isocloso metallaboranes and olefin–metal complexes

The chemical bonding topology of the *isocloso* metallaboranes outlined above bears some resemblance to that in metal complexes of olefins and arenes. Thus consider the 11-vertex ruthenium complexes of the type (arene)$RuB_{10}H_{10}$ (arene = *p*-cymene, hexamethylbenzene, etc.) [45], which may be considered to have 22 skeletal electrons, namely two from each of the 11 vertices. The ruthenium atom in the (arene)Ru vertex may be considered to have a typical +2 formal oxidation state like the stable [(arene)$Ru^{II}Cl_2]_2$ compounds so that removal of this vertex as (arene)Ru^{2+} leaves behind a $B_{10}H_{10}^{2-}$ ligand with all of the 22 skeletal electrons (Fig. 7a). These skeletal electrons are used to form 3c-2e B_3 bonds in eight of the 12 triangular faces of the open $B_{10}H_{10}^{2-}$ unit and three 2c-2e B_2 bonds in alternating edges of the open hexagonal face similar to the alternating C=C double bonds in a Kekulé structure of benzene (Fig. 7b). Reconstituting the *isocloso* metallaborane (arene)$RuB_{10}H_{10}$ from the open $B_{10}H_{10}^{2-}$ ligand with this bonding topology and the (arene)Ru^{2+} vertex with three internal orbitals converts the 2c-2e bonds on the open hexagonal face of $B_{10}H_{10}^{2-}$ into 3c-2e bonds leading to 11 3c-2e bonds and no 2c-2e bonds in the skeletal bonding framework of the reconstituted (arene)$RuB_{10}H_{10}$ structure in accord with its 22 skeletal

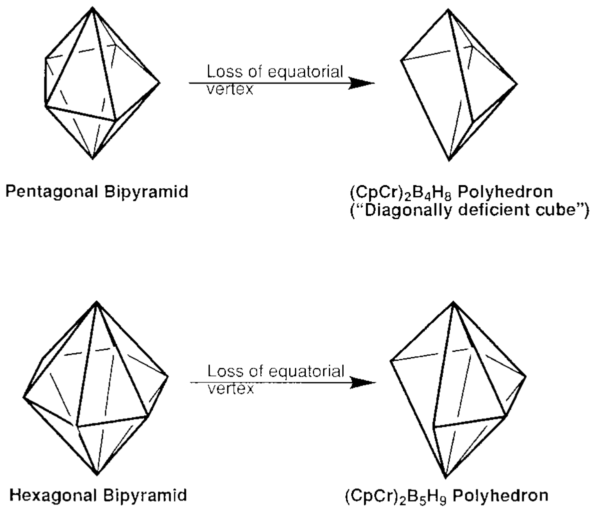


Fig. 8. (a) Conversion of a pentagonal bipyramid to the $(CpCr)_2B_4H_8$ 'diagonally deficient cube' by loss of an equatorial vertex and associated edges. (b) An analogous conversion of a hexagonal bipyramid to the $(CpCr)_2B_4H_8$ polyhedron by loss of an equatorial vertex and associated edges.

electrons provided by the 33 internal orbitals of the 11-vertex atoms. The $B_{10}H_{10}^{2-}$ dianion ligand in (arene)$RuB_{10}H_{10}$, which can be considered as a hexahapto ligand, can be seen to be analogous to an arene or triolefin ligand with the three 2c-2e B_2 bonds on alternating edges of the open hexagon of the $B_{10}H_{10}^{2-}$ ligand (Fig. 7b) functioning like the three alternating C=C double bonds of benzene in metal complexation.

4.3. Deltahedral dimetalla- and trimetallaboranes: role of metal–metal bonding

The *isocloso* metallaboranes discussed above have a single metal vertex and $2n$ skeletal electron counts for deltahedral structures with n vertices. The transition metals involved are relatively late transition metals, typically Groups 8 (Ru) or 9 (Rh, Ir). In recent years Fehlner and co-workers [46–48] have reported a variety of deltahedral metallaboranes containing two or three

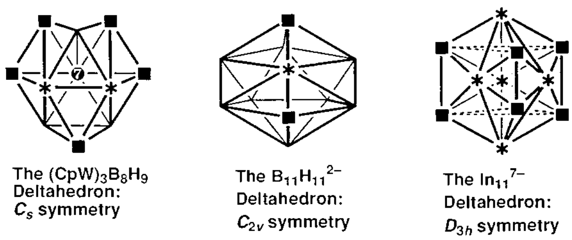


Fig. 10. A comparison of the 11-vertex deltahedra in $(CpW)_3B_8H_9$, $B_{11}H_{11}^{2-}$, and In_{11}^{7-}.

cyclopentadienylmetal vertices with Group 6 (Cr, Mo, W) or Group 7 (Re) metals. The apparent skeletal electron counts in the Fehlner early transition metal metallaboranes are generally very low relative to the Wade–Mingos $2n + 2$ skeletal electron rule [27,30,31] for borane deltahedra assuming that the CpM vertices, like the BH vertices, contribute the usual three internal orbitals and the transition metal atom has the favored 18-electron rare gas configuration. For example, the 11-vertex trimetallaborane $(CpW)_3B_8H_9$ has only 14 apparent skeletal electrons corresponding to $2n - 8$ for $n = 11$ in contrast to the 24 skeletal electrons expected for an 11-vertex *closo* deltahedron.

The polyhedra found in these early transition metallaboranes are of two types: (1) polyhedra derived by loss of an equatorial vertex from a pentagonal bipyramid (Fig. 8a) or a hexagonal bipyramid (Fig. 8b); and (2) deltahedra with nine (e.g. $(CpRe)_2B_7H_7$ and $(CpW)_2B_7H_9$) and 11 vertices (e.g. $(CpW)_3B_8H_9$), which are topologically different from the corresponding $B_nH_n^{2-}$ deltahedra because of the tendency for the transition metals to occupy vertices of high degrees (Figs. 9 and 10).

The standard Wade–Mingos electron counting rules [27,30,31] assume that the vertex atoms contribute three internal orbitals to the skeletal bonding. If such rules are applied to the CpCr vertices in $(CpCr)_2B_4H_8$ and $(CpCr)_2B_5H_9$, the CpCr vertices become -1 skeletal electron donors and these Cr_2B_n clusters become $2n - 2$

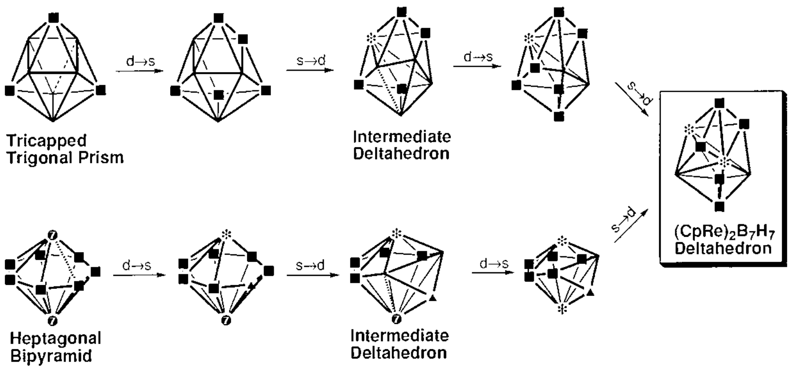


Fig. 9. Generation of the nine-vertex $(CpRe)_2B_7H_7$ deltahedron from the tricapped trigonal prism and from the heptagonal bipyramid by double diamond–square–diamond processes (d → s → d) in each case.

skeletal electron hypoelectronic structures assuming that the chromium atom has the favored 18-electron rare gas configuration. Using this approach a reasonable skeletal bonding model can be derived for $(CpCr)_2B_4H_8$ using a single six-center two-electron (6c-2e) Cr_2B_4 core bond and 3c-2e CrB_2 bonds in four of the polyhedral faces to use the ten apparent skeletal electrons in five skeletal bonds requiring the 18 available internal orbitals from the six-vertex atoms. However, a similar skeletal bonding scheme for the higher homologue $(CpCr)_2B_5H_9$ based on the CpCr vertices contributing three skeletal orbitals cannot be derived using the available vertex atom orbitals and with the six skeletal bonds corresponding to the 12 apparent skeletal electrons without having a pair of vertex atoms bonded both by a 2c-2e and a 3c-2e bond in violation of rules suggested by O'Neill and Wade [49] for feasible localized borane structures.

These problems can be avoided if the CpCr vertices in $(CpCr)_2B_4H_8$ and $(CpCr)_2B_5H_9$ are assumed to contribute four internal orbitals rather than only three internal orbitals. In this way a CpCr vertex becomes a donor of $+1$ skeletal electron rather than -1 skeletal electron. This arises from the fact that one of the non-bonding electron pairs in a CpCr vertex contributing three internal orbitals becomes an additional skeletal electron pair when the CpCr vertex contributes a fourth internal orbital. The feasibility of a CpCr vertex contributing four rather than three internal orbitals is suggested by the stability of many compounds of the type $CpCr(CO)_3X$ (X = H, halide, alkyl, etc.). If the CpCr vertices in $(CpCr)_2B_4H_8$ and $(CpCr)_2B_5H_9$ contribute four rather than three internal orbitals, they become $2n + 2$ skeletal electron systems. Skeletal bonding topologies for $(CpCr)_2B_4H_8$ and $(CpCr)_2B_5H_9$ closely related to those of the corresponding deltahedral boranes $B_6H_6^{2-}$ and $B_7H_7^{2-}$ [10] are then possible with a single multicenter two-electron core bond at the center of the polyhedron and one surface bond for each vertex atom.

It might appear that the metallaboranes $(CpCr)_2B_4H_8$ and $(CpCr)_2B_5H_9$ are the first two members of a $(CpCr)_2B_nH_{n+4}$ homologous series. However, no higher members of this series are known experimentally. Thus no eight-vertex derivatives are currently known and the nine-vertex derivatives do not have the stoichiometry $(CpM)_2B_7H_{11}$ (M = Cr, Mo, W) of the $(CpM)_2B_nH_{n+4}$ series for $n = 7$. Instead the nine-vertex dehydrogenation product $(CpW)_2B_7H_9$ and the isoelectronic and isostructural $(CpRe)_2B_7H_7$ are known [50]. The M_2B_7 units in these structures form a nine-vertex deltahedron having two degree 6 vertices for the transition metal atoms (W or Re). This deltahedron can be derived from either the tricapped trigonal prism (the $B_9H_9^{2-}$ deltahedron in Fig. 2) or the heptagonal bipyramid by two diamond–square–diamond processes in each case (Fig. 9). The CpRe vertices can each be assumed to provide five internal orbitals but one of these internal orbitals is used to form a 2c-2e Re–Re bond through the center of the deltahedron. This leaves four internal orbitals from each CpRe vertex for the surface bonding. Since a CpRe vertex using five internal orbitals is a donor of four skeletal electrons, the $(CpRe)_2B_7H_7$ cluster (as well as the isoelectronic and isostructural $(CpW)_2B_7H_9$ cluster) is a 22 skeletal electron system corresponding to 11 skeletal bonds. The available orbitals allow for the Re–Re bond through the center of the deltahedron, seven 3c-2e ReB_2 surface bonds, two 3c-2e B_3 surface bonds, and one 2c-2e ReB surface bond. The skeletal bonding of $(CpRe)_2B_7H_7$ thus appears to be similar to that of the *isocloso* metallaboranes containing a single metal vertex (e.g. $(arene)RuB_{10}H_{10}$ in Fig. 7) except for the added feature of a 2c-2e Re–Re bond through the center of the deltahedron.

The largest early transition metallaborane reported by Fehlner and coworkers is $(CpW)_3B_8H_9$ [50], which has been shown by X-ray diffraction to have an 11-vertex W_3B_8 deltahedron (Fig. 10) topologically distinct from the 11-vertex deltahedra found in either $B_{11}H_{11}^{2-}$ (Fig. 2) or In_{11}^{7-} [51–53]. In the $(CpW)_3B_8H_9$ deltahedron two of the tungsten atoms are located at the degree 6 vertices and the third tungsten atom is located at a degree 7 vertex. If the CpW groups at the degree 6 vertices are assumed to use five internal orbitals and the CpW group at the degree 7 vertex is assumed to use six internal orbitals, then $(CpW)_3B_8H_9$ is a 28 skeletal electron system. The skeletal bonding can involve two 2c-2e W–W bonds through the center of the deltahedron. The tungsten atom at the degree 7 vertex participates in both of these 2c-2e bonds leaving four of its six internal orbitals for the remaining skeletal bonding. Enough electrons and orbitals then remain for 3c-2e surface bonds in 12 of the 18 faces of the 11-vertex deltahedron. This analysis suggests that the skeletal bonding of $(CpW)_3B_8H_9$ is closely related to that discussed above for $(arene)RuB_{10}H_{10}$ (Fig. 7) except for the added feature of two 2c-2e metal–metal bonds through the center of the deltahedron.

5. Summary

Three-center two-electron (3c-2e) interactions are found both in the C_2M σ-bonding in the Dewar–Chatt model of the olefin–metal bond and in the B_2H and B_3 bonding in borane structures based on deltahedra or deltahedral fragments. Incorporation of metals as vertices of boron deltahedra frequently changes their shapes to provide degree 6 and even degree 7 vertices for the metal atoms. In addition metal incorporation frequently modifies the core + surface skeletal bonding of the original $B_nH_n^{2-}$ to pure surface bonding consisting mainly or entirely of 3c-2e bonds. In such structures the resulting 3c-2e B_2M surface bonds are related to the C_2M σ-bonding in the Dewar–Chatt model. The skeletal bonding of deltahedral metallaboranes containing two or more metal vertices can also include 2c-2e metal–metal bonding through the center of the deltahedron.

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