Some Examples of Unusual Skeletal Bonding Topologies in Metallaboranes Containing Two or Three Early Transition Metal Vertices

R. B. King

Department of Chemistry, University of Georgia, Athens, Georgia

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The metallaboranes $(CpM)_2B_nH_{n+4}$ (M = Cr, Mo, W; n = 4, 5; Cp = η^5-C_5H_5, η^5-C_5Me_5), $(CpW)_2B_7H_9$, $(CpRe)_2B_7H_7$, and $(CpW)_3B_8H_9$ have the $2v$ or $2v + 2$ skeletal electrons for *closo* or *isocloso* deltahedra (v = number of polyhedral vertices) if the early transition metal vertices are assumed to contribute four or more internal orbitals rather than the usual three internal orbitals for BH vertices. The polyhedra for the metallaboranes $(CpM)_2B_nH_{n+4}$ (M = Cr, Mo, W; n = 4, 5) are derived from (n + 1)-gonal bipyramids by removal of an equatorial vertex. The deltahedra for the larger metallaboranes $(CpW)_2B_7H_9$, $(CpRe)_2B_7H_7$, and $(CpW)_3B_8H_9$ are derived from the corresponding $B_nH_n^{2-}$ deltahedra (n = 9 and 11 in these cases) by sufficient diamond−square−diamond processes to provide vertices of degrees ≥ 6 for each of the CpM vertices. Reasonable skeletal bonding topologies in accord with the availability of skeletal electrons and orbitals consist of surface 2c−2e and 3c−2e bonds supplemented by metal−metal bonding through the center of the polyhedron.

Introduction

One of the distinctive features of borane chemistry is the special stability of molecules and ions based on the so-called “most spherical deltahedra,” namely polyhedra in which all faces are triangles and the vertices are as uniformly connected as possible.[1,2] Thus, the anions $B_nH_n^{2-}$ ($6 \leq n \leq 12$) all have structures based on deltahedra with only degree 4 and 5 vertices except for a single degree 6 vertex in $B_{11}H_{11}^{2-}$. Wade[3] and Mingos[4] recognized the special stability of such deltahedra with $2n + 2$ skeletal electrons in which BH and CH vertices contribute two and three skeletal electrons, respectively, as well as three internal orbitals to the skeletal bonding. This led to the development of polyhedral skeletal pair theory and the Wade−Mingos rules.[5] The special stability of the borane deltahedra also led Aihara[6] to the first explicit suggestion of three-dimensional aromaticity in the deltahedral boranes. At about the same time King and Rouvray[7] provided a graph-theory-derived model for the skeletal bonding in deltahedral boranes consisting of a multicenter core bond using orbitals from all of the deltahedral vertex atoms supplemented by surface bonding using an electron pair from each deltahedral vertex atom. These topology-based concepts provided further support for the consideration of deltahedral boranes as the three-dimensional analogues of the more familiar planar two-dimensional aromatic hydrocarbons such as benzene and the isoelectronic $C_5H_5^-$ and $C_7H_7^+$.

The introduction of transition metal vertices into borane deltahedra was first achieved by Hawthorne and co-workers[8] in the 1960s. The first metallaboranes were icosahedral carboranes in which one or occasionally two of the boron vertices were replaced by transition metal vertices following isolobal and isoelectronic rules, first suggested by Wade[3] and later developed by Hoffmann.[9] The transition metal vertices, like the corresponding boron and carbon vertices, were assumed to contribute three internal orbitals so that, for example, a C_5H_5-Co vertex was considered to be a donor of two skeletal electrons analogous to the isolobal and isoelectronic BH vertex.

Initially it was assumed that the polyhedra in metallaboranes would be the same as the polyhedra in isoelectronic metal-free boranes. However, as metallaborane chemistry was extended further to nonicosahedral structures, particularly by Kennedy and co-workers,[10,11] a variety of deltahedral metallaborane structures were discovered based on deltahedra topologically distinct from the deltahedra found in the metal-free boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$). Of particular interest were the so-called “isocloso” 9- and 10-vertex structures based on a deltahedron with the transition metal at a degree 6 vertex in contrast to the corresponding metal-free deltahedral boranes, which have only degree 4 and 5 vertices. What was even more interesting was the observation that such “anomalous” metallaborane deltahedra also violated the Wade−Mingos rules[5] by having only $2n$ rather than $2n + 2$ skeletal electrons for a deltahedral structure. Recently the author showed how the anomalous electron counts of the “isocloso” metallaborane deltahedra could be rationalized by assuming skeletal bonding consisting exclusively of three-center two-electron (3c−2e) bonds in n of the $2n - 4$ faces of an n-vertex deltahedron.[12,13] Thus the skeletal bonding in such “isocloso” metallaboranes was suggested to consist solely of surface bonding with no core bonding in contrast to the metal-free deltahedral boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$).

The “isocloso” metallaboranes studied by Kennedy and co-workers[10,11] typically have a single metal vertex and $2n$ skeletal

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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[14,15,16] have reported a variety of deltahedral metallaboranes containing two or three 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 for borane deltahedra assuming that the CpM vertices (Cp = η^5-cyclopentadienyl ligands such as η^5-C_5H_5 or η^5-Me_5C_5) like the BH vertices contribute the usual three internal orbitals. 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 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 (e.g., $(CpCr)_2B_4H_8$ and $(CpCrCO)_2B_4H_6$) or a hexagonal bipyramid (e.g., $(CpCr)_2B_5H_9$); (2) Deltahedra with nine (e.g., $(CpRe)_2B_7H_7$ and $(CpW)_2B_7H_9$) or 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. This paper explains how the ideas presented previously[12,13] to rationalize the anomalous electron counts in the "isocloso" metallaboranes containing a single transition metal vertex can be extended to dimetallaboranes and trimetallaboranes containing early transition metal vertices with very low apparent skeletal electron counts.

Metallaboranes Derived from Bipyramids. In recent years Fehlner and co-workers have prepared metallaboranes of the type $(CpM)_2B_nH_{n+4}$ (M = Cr, Mo, W; n = 4, 5).[14,15,16] The chromium compounds have been studied in the greatest detail and will be used as examples in this discussion; analogous principles, of course, apply to the corresponding molybdenum and tungsten derivatives. If direct M−M interactions are ignored in the $(CpM)_2B_nH_{n+4}$ derivatives, the M_2B_n polyhedra can then be derived from an $(n + 1)$-gonal bipyramid by loss of an equatorial vertex (Figure 1). The six-vertex polyhedron has been called a "diagonally deficient cube" by the author mainly because he could not think of a better name at the time.[17,18] Introduction of an M−M bond across the diagonal connecting the degree 4 vertices of the quadrilateral face of the diagonally deficient cube converts it to a bicapped tetrahedron (Figure 2), a deltahedron first encountered in the structure of $Os_6(CO)_{18}$ nearly 30 years ago.[19] The diagonally deficient cube may also be regarded as the "square" intermediate in a single diamond−square−diamond process converting an octahedron into a bicapped tetrahedron.

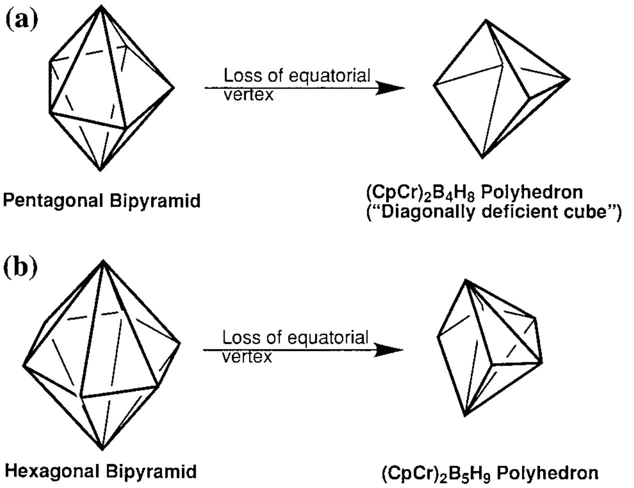

Figure 1. (a) Conversion of a pentagonal bipyramid to the $(CpCr)_2B_4H_8$ "diagonally deficient cube" by loss of an equatorial vertex and associated edges. (b) Conversion of a hexagonal bipyramid to the $(CpCr)_2B_5H_9$ polyhedron by loss of an equatorial vertex and associated edges.

The standard Wade−Mingos electron counting rules[3,4,5] 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 $2n - 2$ skeletal electron hypoelectronic structures. Using this approach a reasonable skeletal bonding model can be derived for $(CpCr)_2B_4H_8$ with 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. This skeletal bonding model uses the 10 apparent skeletal electrons in five skeletal bonds requiring the combined 18 available orbitals. However, a similar skeletal bonding scheme for $(CpCr)_2B_5H_9$ 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 3c−2e bond in violation of rules suggested by O'Neill and Wade[20] to determine 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 (skeletal) 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 nonbonding 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.) in which a CpCr unit is bonded to four other groups.

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 as illustrated by the following electron counting scheme for $(CpCr)_2B_4H_8$:

2 CpCr vertices contributing four internal orbitals each: 2 × 1 =	2 electrons
4 BH vertices: 4 × 2 =	8 electrons
4 "extra" hydrogen atoms: 4 × 1 =	4 electrons
total skeletal electrons	*14 electrons*

Skeletal bonding topologies for $(CpCr)_2B_4H_8$ and $(CpCr)_2B_5H_9$ closely related to those of the corresponding deltahedral boranes[7] $B_6H_6^{2-}$ and $B_7H_7^{2-}$ 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 corresponding to the $2n + 2$ skeletal electrons or $n + 1$ skeletal electron pairs. In the deltahedral boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$) the surface bonding

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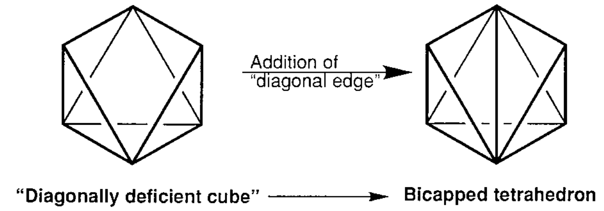

Figure 2. Conversion of a "diagonally deficient cube" to a bicapped tetrahedron by adding a diagonal across the degree 4 vertices of the quadrilateral face.

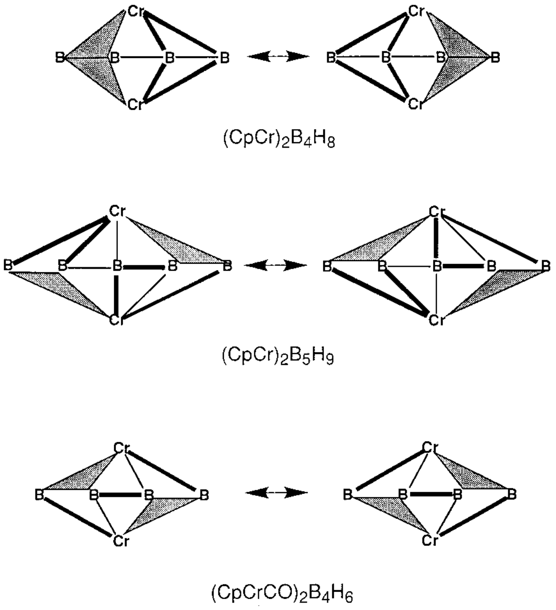

Figure 3. Possible surface bonding schemes for $(CpCr)_2B_4H_8$, $(CpCr)_2B_5H_9$, and $(CpCrCO)_2B_4H_6$. Two symmetry-equivalent "resonance structures" are shown for each of the three compounds. In figures 3, 6, and 8, 2c−2e surface bonds are shown by bold edges and 3c−2e surface bonds are shown by shading the (triangular) faces in which they occur.

is assumed to consist of n 2c−2e bonds.[7] However, in $(CpCr)_2B_4H_8$ and $(CpCr)_2B_5H_9$ two of the surface bonds must be 3c−2e rather than 2c−2e bonds to account for the two extra internal orbitals provided by the CpCr vertices contributing four rather than three internal orbitals. Distributions of the 2c−2e and 3c−2e skeletal bonds in $(CpCr)_2B_4H_8$ and $(CpCr)_2B_5H_9$ consistent with the electron counting and internal orbital availability are depicted in Figures 3a and 3b with the 3c−2e bonds being indicated by shading the faces containing the bonds and the 2c−2e bonds being indicated by bold edges. Note that each chromium atom is part of three surface bonds and each boron atom is part of two surface bonds in accord with the availability of orbitals for surface bonding The $(n + 2)$-vertex polyhedra for the $(CpCr)_2B_nH_{n+4}$ derivatives in Figure 3 are depicted as Schlegel diagrams[21,22] in which the base face is the quadrilateral face arising from loss of an equatorial vertices and the associated edges from the underlying $(n + 1)$-gonal bipyramid.[23] In each case two symmetry equivalent structures are shown in Figure 3.

The deltahedra observed experimentally for the boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$) are the most spherical deltahedra of Williams[1,2] in which the vertex degrees are as nearly similar as possible so that the numbers of degree 4 and 5 vertices are maximized. In the "isocloso" metallaborane deltahedra, particularly those with 9 and 10 vertices, the transition metals are found to prefer vertices of higher connectivity (degree) so that some deviations in shape from the $B_nH_n^{2-}$ deltahedra are found.[10,11] This effect should be even more pronounced for transition metal vertices contributing four rather than three internal orbitals such as the CpCr vertices in $(CpCr)_2B_4H_8$ and $(CpCr)_2B_5H_9$. The apical vertices in the bipyramids from which their polyhedral structures are derived have higher connectivities than the corresponding equatorial vertices so that they are natural sites for the CpCr vertices.

An important reaction of $(CpCr)_2B_4H_8$ is the addition of two molecules of carbon monoxide with hydrogen loss according to the following equation:[24,25]

$$(CpCr)_2B_4H_8 + 2\,CO \rightarrow (CpCrCO)_2B_4H_6 + H_2 \qquad (1)$$

In this reaction two hydrogen atoms corresponding to two electrons are replaced by two carbonyl groups corresponding to four electrons so that $(CpCrCO)_2B_4H_6$ has two more apparent skeletal electrons than $(CpCr)_2B_4H_8$. However, the Cr_2B_4 polyhedron is essentially unchanged in going from $(CpCr)_2B_4H_8$ to $(CpCrCO)_2B_4H_6$. Although it is reasonable to allow a CpCr vertex to contribute four internal orbitals to the skeletal bonding, addition of a CO group to such a vertex uses the "extra" internal orbital for bonding to the external CO group. For this reason a CpCrCO vertex can only contribute three internal orbitals and thus is a donor of +1 skeletal electron leading to a 12 skeletal electron system as follows:

2 CpCrCO vertices with 3 internal orbitals each: (2)(1) =	2 skeletal electrons
4 BH vertices: (4)(2) =	8 skeletal electrons
2 "extra" hydrogen atoms: (2)(1) =	2 skeletal electrons
total skeletal electrons	*12 skeletal electrons*

The 12 skeletal electrons in $(CpCrCO)_2B_4H_6$ correspond to 6 skeletal bonds. There are a total of 6 orbitals from the two chromium atoms and 12 orbitals from the four boron atoms to distribute among these six skeletal bonds. The following skeletal bonding scheme with one 6c−2e Cr_2B_4 core bond similar to that in $(CpCr)_2B_4H_8$ and a combination of 3c−2e and 2c−2e surface bonds uses these 18 available internal orbitals:

	Internal Orbitals	
bonds	Cr	B
one 6c−2e Cr_2B_4 core bond:	2	4
two 3c−2e CrB_2 surface bonds:	2	4
two 2c−2e Cr−B surface bonds	2	2
one 2c−2e B−B surface bond	0	2
total skeletal orbitals required	*6*	*12*

A possible arrangement of the 3c−2e and 2c−2e surface bonds compatible with the availability of internal orbitals is depicted in Figure 3c. An alternative skeletal bonding scheme for $Cp_2Cr_2(CO)_2B_4H_6$ using six 3c−2e CrB_2 bonds in the six triangular faces of the diagonally deficient cube (Figure 2) similar to bonding schemes previously suggested by the author for "isocloso" metallaboranes[12,13] does not work since such a bonding scheme requires the center two boron atoms to use four internal orbitals and the outer boron atoms to use only two

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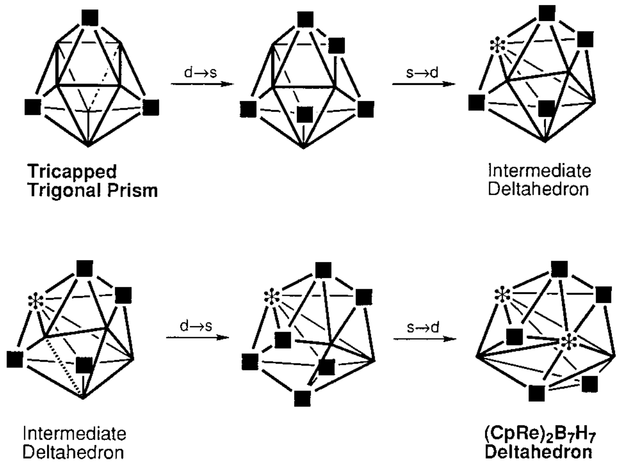

Figure 4. Two successive diamond−square−diamond (d→s→d) processes converting a D_{3h} tricapped trigonal prism to the deltahedron found in (CpRe)$_2$B$_7$H$_7$ and (CpW)$_2$B$_7$H$_9$. For clarity the vertices of degrees 3, 4, 6, and 7 are labeled with the symbols ▲, ■, ∗, and ⑦, respectively, in Figures 4, 5, and 7. The vertices of degree 5 are not labeled in these figures.

internal orbitals in contradiction to the availability of exactly three internal orbitals from each boron vertex.

The pair of compounds Cp$_2$Cr$_2$B$_4$H$_8$ and Cp$_2$Cr$_2$(CO)$_2$B$_4$H$_6$ is of interest since their structures are based on the same Cr$_2$B$_4$ polyhedron even though they have different numbers of skeletal electrons and therefore different skeletal bonding schemes. Similar behavior has been observed in other types of transition metal cluster structures. For example, iron carbonyl phosphinidene clusters are known of the stoichiometries (RP)$_2$Fe$_4$(CO)$_{11}$ and (RP)$_2$Fe$_4$(CO)$_{12}$.[26] Both of these types of clusters contain Fe$_4$P$_2$ octahedra despite their different numbers of apparent skeletal electrons.[17,27] The Fe$_4$P$_2$ octahedra in the complexes (RP)$_2$Fe$_4$(CO)$_{11}$ can be considered to be globally delocalized with one 6c−2e Fe$_4$P$_2$ core bond and six 2c−2e surface bonds whereas the Fe$_4$P$_2$ octahedra in the complexes (RP)$_2$Fe$_4$(CO)$_{12}$ can be considered to be edge-localized with 12 2c−2e bonds along the 12 edges of the octahedron.[17,27]

The Nine-Vertex Metallaboranes (CpW)$_2$B$_7$H$_9$ and (CpRe)$_2$B$_7$H$_7$. It might appear that the metallaboranes (CpCr)$_2$B$_4$H$_8$ and (CpCr)$_2$B$_5$H$_9$ are the first two members of a (CpCr)$_2$B$_n$H$_{n+4}$ homologous series. However, no higher members of this series are known experimentally. Thus no eight-vertex (CpM)$_2$B$_6$H$_{10}$ derivatives are known. The nine-vertex derivatives do not have the stoichiometry (CpM)$_2$B$_7$H$_{11}$ (M = Cr, Mo, W) of the (CpM)$_2$B$_n$H$_{n+4}$ series for $n = 7$. Instead the dehydrogenation product (CpW)$_2$B$_7$H$_9$ and the isoelectronic and isostructural (CpRe)$_2$B$_7$H$_7$ are known.[28] The M$_2$B$_7$ units in these structures form a nine-vertex deltahedron (Figure 4) which can be derived from familiar nine-vertex deltahedra by either of the following processes: (1) The tricapped trigonal prism found in B$_9$H$_9$$^{2-}$ can undergo two successive diamond−square−diamond processes[29,30] to provide two vertices of degree 6 for the CpM units (Figure 4). Thus whereas the original tricapped trigonal prism has six degree 5 vertices and three degree 4 vertices, the final M$_2$B$_7$ deltahedron has five degree 4 vertices, two degree 5 vertices, and two degree 6 vertices. (2) The equatorial heptagonal "belt" of a heptagonal bipyramid can be "warped" so that each of the axial metal atoms is bonded to six rather than seven equatorial atoms (Figure 5). This equatorial belt warping corresponds to two successive diamond−square−diamond processes converting both degree 7 vertices of the heptagonal bipyramid to degree 6 vertices while concurrently increasing the degrees of two of the seven original equatorial vertices from four to five.

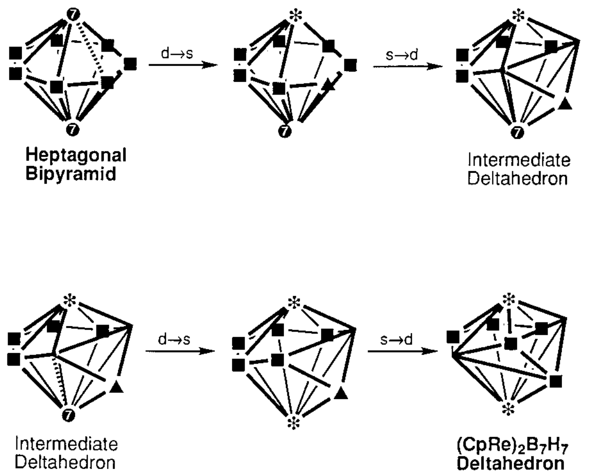

Figure 5. Two successive diamond−square processes resulting in the "warping" of the equatorial heptagon of a D_{7h} heptagonal bipyramid leading to the deltahedron found in (CpRe)$_2$B$_7$H$_7$ and (CpW)$_2$B$_7$H$_9$. Note that the latter deltahedron is in a different orientation than the same deltahedron produced by the process in Figure 4.

The M$_2$B$_7$ deltahedra in (CpW)$_2$B$_7$H$_9$ and (CpRe)$_2$B$_7$H$_7$ necessarily have 14 triangular faces and 21 edges such as the tricapped trigonal prism or any other nine-vertex deltahedra.

The electron counting in these nine-vertex derivatives is illustrated by (CpRe)$_2$B$_7$H$_7$ with the isoelectronic and isostructural (CpW)$_2$B$_7$H$_9$ following completely analogous principles. The CpRe vertices are assumed to provide five internal orbitals so that they each are donors of four skeletal electrons. This leads to formulation of these species as 22 skeletal electron systems as follows:

2 CpRe vertices with five internal orbitals: (2)(4) =	8 electrons
7 BH vertices with three internal orbitals: (7)(2) =	14 electrons
total skeletal electrons:	*22 electrons*

These 22 skeletal electrons in (CpRe)$_2$B$_7$H$_7$ correspond to 11 skeletal bonds. There are a total of 10 orbitals from the two rhenium atoms and 21 orbitals from the seven boron atoms to distribute among these 11 skeletal bonds suggesting the following skeletal bonding scheme:

	Internal Orbitals	
bonds	Re	B
one 2c−2e Re−Re bond through the center:	2	0
seven 3c−2e ReB$_2$ 3c−2e surface bonds:	7	14
two 3c−2e B−B−B surface bonds	0	6
one 2c−2e Re−B surface bond	1	1
total skeletal orbitals required	*10*	*21*

The nine-vertex polyhedron in (CpRe)$_2$B$_7$H$_7$ is sufficiently oblate (i.e., "squashed" or "flattened") so that the experimental Re−Re distance is 2.78 Å consistent with a single 2c−2e bond. A possible distribution of the remaining 10 bonds around the surface of the nine-vertex deltahedron is indicated in Figure 6 where the rhenium and boron atoms are numbered as in ref 28. For clarity the 14 faces of this deltahedron are separated into the following three groups: (1) The six faces surrounding Re1;

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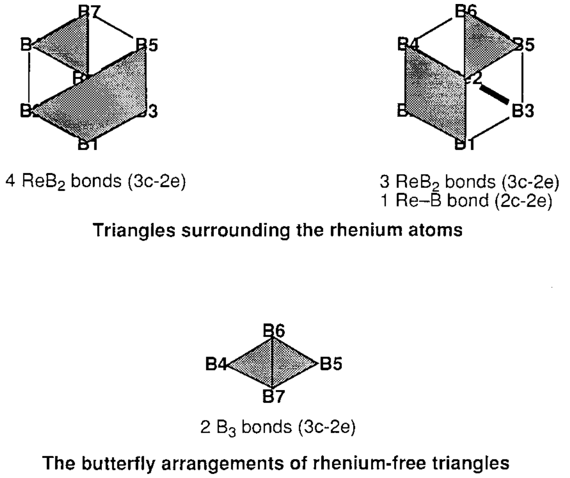

Figure 6. A possible scheme for the surface bonding in $(CpRe)_2B_7H_7$ and $(CpW)_2B_7H_9$.

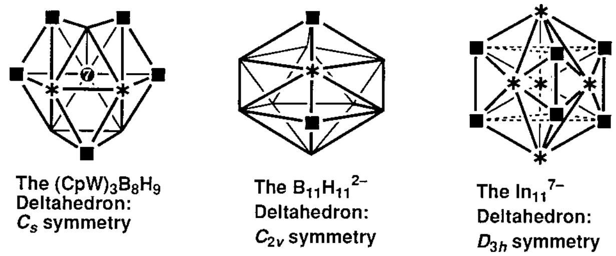

Figure 7. Comparison of the 11-vertex deltahedra found in $(CpW)_3B_8H_9$, $B_{11}H_{11}^{2-}$, and In_{11}^{7-}.

(2) The six faces surrounding Re2; (3) The two faces containing only boron atoms, which share an edge to form a "butterfly-like" configuration. The faces containing 3c−2e bonds are shaded and the 2c−2e bond is indicated by a bold edge. Note that each of the boron vertices is associated with exactly three surface bonds in accord with its contribution of three internal orbitals. Furthermore, each rhenium atom is associated with four surface bonds since the fifth internal orbital on each rhenium atom is used for the 2c−2e Re−Re bond through the center of the deltahedron.

The chemical bonding model implied by this skeletal bonding topology for $(CpRe)_2B_7H_7$ is distinctly different from either the globally delocalized bonding topology for the deltahedral borane $B_9H_9^{2-}$ (ref 7) or from the 3c−2e surface bonding topology of the "isocloso" metallaboranes.[12] It bears some resemblance to that of binuclear cyclopentadienylmetal carbonyls such as $[CpM(CO)_3]_2$ (M = Cr, Mo, W) or $[CpM'(CO)_2]_2$ (M′ = Fe, Ru, Os), each of which has a strong 2c−2e metal−metal bond in addition to the metal−ligand bonds. In this sense the rhenium−boron surface bonding interactions in $(CpRe)_2B_7H_7$ correspond to the metal−carbonyl interactions in these binuclear cyclopentadienylmetal carbonyls.

The Eleven-Vertex Metallaborane $(CpW)_3B_8H_9$. The largest early transition metallaborane reported by Fehlner and coworkers is $(CpW)_3B_8H_9$.[28] The structure of $(CpW)_3B_8H_9$ (Figure 7) is based on an 11-vertex W_3B_8 deltahedron topologically different from the 11-vertex deltahedra found in $B_{11}H_{11}^{2-}$ (ref 31) or In_{11}^{7-} (refs 32,33,34,). However, all three of these topologically distinct 11-vertex deltahedra necessarily have the 27 edges and 18 faces required by Euler's theorem.[35]

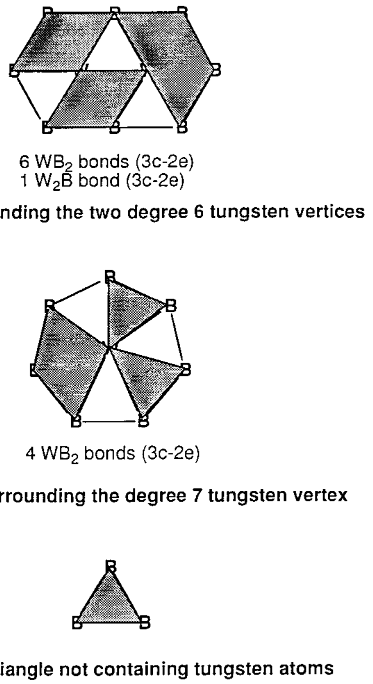

Figure 8. A possible scheme for the surface bonding in $(CpW)_3B_8H_9$.

Table 1. Comparison of the Vertex Degree Distributions in the 11-Vertex Deltahedra Found in $(CpW)_3B_8H_9$, $B_{11}H_{11}^{2-}$, and In_{11}^{7-}

	vertex degree distributions		
vertex degree	$(CpW)_3B_8H_9$	$B_{11}H_{11}^{2-}$	In_{11}^{7-}
3	0	0	2
4	5	2	3
5	3	8	0
6	2	1	6
7	1	0	0

A comparison of the 11-vertex polyhedra of $B_{11}H_{11}^{2-}$ and $(CpW)_3B_8H_9$ is most instructive (Table 1). The 11-vertex $B_{11}H_{11}^{2-}$ polyhedron, sometimes called the edge-coalesced icosahedron, has all degree 4 and 5 vertices except for the single topologically required degree 6 vertex.[36] However, the 11-vertex $(CpW)_3B_8H_9$ deltahedron has two degree 6 vertices and one degree 7 vertex for the tungsten atoms leaving five degree 4 and three degree 5 vertices for the eight boron atoms. In the $(CpW)_3B_8H_9$ deltahedron the 27 edges are partitioned into one W−W edge, 17 W−B edges, and 9 B−B edges and the 18 faces are partitioned into 2 W_2B faces, 15 WB_2 faces, and one B_3 face. Figure 8 dissects the 18 faces into the set of 10 faces surrounding the pair of degree 6 tungsten vertices, the set of seven faces surrounding the degree 7 tungsten vertex, and the single face not associated with any of the tungsten atoms. Note that the degree 6 tungsten vertices share two of their six associated faces, namely the 2 W_2B faces, whereas none of the seven faces associated with the degree 7 tungsten vertex is shared with either degree 6 tungsten vertex.

A viable electron counting scheme for $(CpW)_3B_8H_9$ assumes that the degree 6 CpW vertices use 5 internal orbitals and the single degree 7 CpW vertex uses 6 internal orbitals making them donors of three and five skeletal electrons, respectively. The three tungsten atoms form an isosceles triangle with two 3.06 Å edges and one 2.80 Å edge corresponding to tungsten−tungsten bonding distances. Therefore it is reasonable for each

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of these three edges of the W_3 isosceles triangle to be either a 2c−2e W−W bond or part of a multicenter bond involving two tungsten atoms. The 2.80 Å edge between the two tungsten atoms at degree 6 vertices is located in the surface of the deltahedron so that this tungsten−tungsten interaction is assumed to be part of the surface bonding. The two 3.06 Å edges between the a degree 6 tungsten atom and the degree 7 tungsten atom pass through the deltahedron. They correspond to internal 2c−2e W−W bonds, which supplement the surface bonding. The following allocation of skeletal electrons and orbitals is consistent with these considerations:

sources of skeletal electrons and orbitals	electrons	orbitals
one degree 7 CpW vertex using 6 internal orbitals: 1 × 5 =	5	6 (W)
two degree 6 CpW vertices using 5 internal orbitals: 2 × 3 =	6	10 (W)
eight BH vertices using 3 internal orbitals: 8 × 2 =	16	24 (B)
“extra” hydrogen atoms: 1 × 1 =	1	0
total available skeletal electrons and orbitals:	*28*	*40*

use of skeletal electrons and orbitals	electrons	W orbitals	B orbitals
2 internal W−W 2c−2e bonds:	4	4	0
10 3c−2e WB_2 surface bonds:	20	10	20
1 3c−2e W_2B surface bonds:	2	2	1
1 3c−2e B_3 surface bonds	2	0	3
total skeletal electrons and orbitals required:	*28*	*16*	*24*

This skeletal bonding scheme for $(CpW)_3B_8H_9$ is shown in Figure 8.

Summary

The apparently hypoelectronic metallaboranes $(CpM)_2B_nH_{n+4}$ (M = Cr, Mo, W; $n = 4, 5$), $(CpW)_2B_7H_9$, $(CpRe)_2B_7H_7$, and $(CpW)_3B_8H_9$ exhibit skeletal electron counts closer to $2n$ or $2n + 2$ if the early transition metal vertices are assumed to contribute four or more internal orbitals rather than the usual three internal orbitals for BH vertices. The polyhedra for the metallaboranes $(CpM)_2B_nH_{n+4}$ (M = Cr, Mo, W; $n = 4, 5$) are derived from $(n + 1)$-gonal bipyramids by removal of an equatorial vertex. The deltahedra for the larger metallaboranes $(CpW)_2B_7H_9$, $(CpRe)_2B_7H_7$, and $(CpW)_3B_8H_9$ are derived from the corresponding $B_nH_n^{2-}$ deltahedra ($n = 9$ and 11 in these cases) by sufficient diamond−square−diamond processes to provide vertices of degrees ≥ 6 for each of the CpM vertices. Reasonable skeletal bonding topologies in accord with the availability of skeletal electrons and internal orbitals consist of surface 2c−2e and 3c−2e bonds supplemented by metal−metal bonding through the center of the polyhedron. The surface bonding in such structures appears to be closely related to that of the “isocloso” metallaboranes with a single transition metal atom discussed in a previous paper.[12]

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