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Conference paper

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Metal–metal bonding in deltahedral dimetallaboranes and trimetallaboranes: a density functional theory study

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Abstract: The skeletal bonding topology as well as the Re=Re distances and Wiberg bond indices in the experimentally known *oblatocloso* dirhenaboranes $Cp^{*}_2Re_2B_{n-2}H_{n-2}$ ($Cp^{*} = \eta^5Me_5C_5$, $n = 8$–12) suggest formal Re=Re double bonds through the center of a flattened Re_2B_{n-2} deltahedron. Removal of a boron vertex from these *oblatocloso* structures leads to *oblatonido* structures such as $Cp_2W_2B_5H_9$ and $Cp_2W_2B_6H_{10}$. Similar removal of two boron vertices from the $Cp_2Re_2B_{n-2}H_{n-2}$ ($n = 8$–12) structures generates *oblatoarachno* structures such as $Cp_2Re_2B_4H_8$ and $Cp_2Re_2B_7H_{11}$. Higher energy $Cp_2Re_2B_{n-2}H_{n-2}$ ($Cp = \eta^5$-C_5H_5, $n = 8$–12) structures exhibit *closo* deltahedral structures similar to the deltahedral borane dianions $B_nH_n^{2-}$. The rhenium atoms in these structures are located at adjacent vertices with ultrashort Re≣Re distances similar to the formal quadruple bond found in $Re_2Cl_8^{2-}$ by X-ray crystallography. Such surface Re≣Re quadruple bonds are found in the lowest energy $PnRe_2B_{n-2}H_{n-2}$ structures ($Pn = \eta^5,\eta^5$-pentalene) in which the pentalene ligand forces the rhenium atoms to occupy adjacent deltahedral vertices. The low-energy structures of the tritungstaboranes $Cp_3W_3(H)B_{n-3}H_{n-3}$ ($n = 5$–12), related to the experimentally known $Cp^{*}_3W_3(H)B_8H_8$, have central W_3B_{n-3} deltahedra with imbedded bonded W_3 triangles. Similar structures are found for the isoelectronic trirhenaboranes $Cp_3Re_3B_{n-3}H_{n-3}$. The metal atoms are located at degree 6 and 7 vertices in regions of relatively low surface curvature whereas the boron atoms are located at degree 3–5 vertices in regions of relatively high surface curvature. The five lowest-energy structures for the 11-vertex tritungstaborane $Cp_3W_3(H)B_8H_8$ all have the same central W_3B_8 deltahedron and differ only by the location of the "extra" hydrogen atom. The isosceles W_3 triangles in these structures have two long ~3.0 Å W–W edges through the inside of the deltahedron with the third shorter W–W edge of ~2.7 to ~2.8 Å corresponding to a surface deltahedral edge.

Keywords: cyclopentadienylmetal complexes; deltahedral boranes; density functional theory (DFT); dimetallaboranes; IMEBORON-16; metal–metal bonding; metal–metal quadruple bonds; pentalene metal complexes; rhenium; trimetallaboranes; tungsten.

Introduction

Imbedding transition metal vertices into a borane polyhedron leads to an interesting variety of metallaborane structures first studied by Hawthorne [1], Grimes [2], and their coworkers approximately a half-century ago. Using external cyclopentadienyl ($Cp = \eta^5$-C_5H_5) or pentamethylcyclopentadienyl ($Cp^{*} = \eta^5$-Me_5C_5) groups

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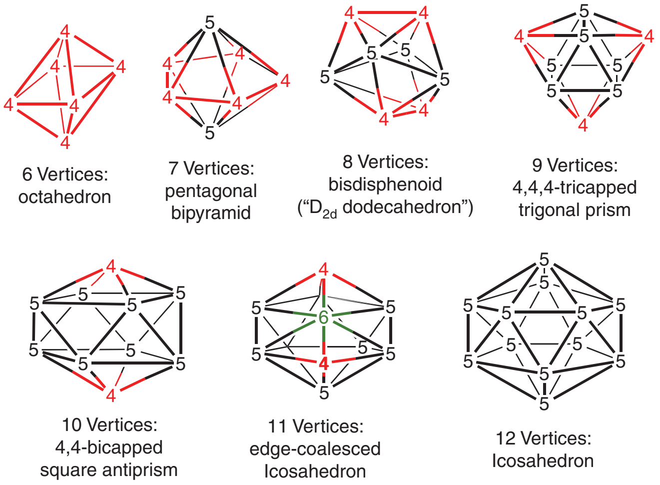
bonded to the transition metal vertices provides robust Cp–M or Cp*–M bonds to complete the coordination sphere of the transition metal vertices. This leads to dimetallaboranes of the types $Cp_2M_2B_{n-2}H_{n-2}$ and $Cp^*_2M_2B_{n-2}H_{n-2}$ exhibiting considerable thermodynamic and kinetic stability.

The basic building blocks of the borane anions $B_nH_n^{2-}$ and isoelectronic carboranes $CB_{n-1}H_n^-$ and $C_2B_{n-2}H_n$ as well as their substitution products are the most spherical *closo* deltahedra in which all faces are triangles and the vertices are as nearly equal as possible (Fig. 1) [3, 4] For structures typically encountered experimentally having from 6 to 12 vertices such deltahedra have only degree 4 and 5 vertices except for the 11-vertex *closo* deltahedron, which is required by topology to have a single degree 6 vertex [5].

The electron bookkeeping in polyhedral borane derivatives follows the Wade–Mingos rules [6–8] which assume that each vertex atom contributes three orbitals to the skeletal bonding. Using this approach a B–H vertex contributes two electrons to the skeletal bonding and a C–H vertex contributes three electrons to the skeletal bonding. Skeletal electron counts obtained by this procedure are conveniently called Wadean skeletal electrons. The most spherical *closo* deltahedra (Fig. 1) are favored for *n*-vertex structures containing $2n+2$ Wadean skeletal electrons.

The early work on metallaboranes frequently resulted in structures containing CpCo vertices, which are donors of two Wadean skeletal electrons similar to B-H vertices. However, in other cases introduction of transition metal vertices into borane polyhedra, especially those of early transition metals with fewer valence electrons, can lead to deviations from the sphericity of the *closo* deltahedra. This arises from the preference of transition metals for vertices of larger degrees than carbon and boron vertices. For example *isocloso* deltahedra [9] providing a degree 6 vertex for the transition metal atom (Fig. 2) are found in metallaboranes having only $2n$ Wadean skeletal electrons [10–13].


6 Vertices: octahedron

7 Vertices: pentagonal bipyramid

8 Vertices: bisdisphenoid ("D_{2d} dodecahedron")

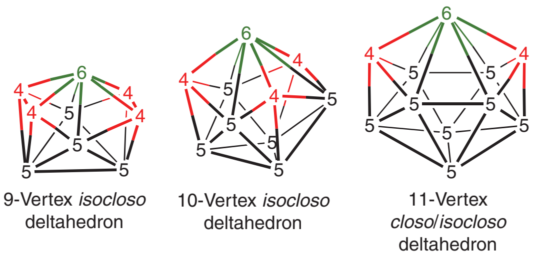
9 Vertices: 4,4,4-tricapped trigonal prism

10 Vertices: 4,4-bicapped square antiprism

11 Vertices: edge-coalesced Icosahedron

12 Vertices: Icosahedron

Fig. 1: The most spherical *closo* deltahedra found in boranes and carboranes showing the vertex degrees with degree 4, 5, and 6 vertices in red, black, and green, respectively.


9-Vertex *isocloso* deltahedron

10-Vertex *isocloso* deltahedron

11-Vertex *closo*/*isocloso* deltahedron

Fig. 2: The *isocloso* deltahedra providing a degree 6 vertex for a transition metal atom. Since the 11-vertex *closo* deltahedron already has a degree 6 vertex, the *closo* and *isocloso* 11-vertex deltahedra are the same.

In order to explore the extent of metallaborane chemistry, particularly metallaboranes containing two or more transition metal vertices, we have undertaken an extensive theoretical study on possible such structures. Our protocol involves the initial screening of a large number of possible isomers using a relatively rapid density functional theory method with the B3LYP functional, a 6-31g(d) double zeta basis set for light atoms, and an SDD basis set for heavy atoms [14–17]. In many cases we are able to examine hundreds of possible isomers for a given metallaborane stoichiometry to find a relatively small number of low-energy structures. We then refine the relative energies and geometries for this relatively small number of lowest energy isomers using the M06-L function with a larger 6-311G(d,p) triple zeta basis set for light atoms and the same SDD basis set for heavy atoms [18]. In some critical cases we also use the more computationally intensive single point coupled cluster DLPNO-CCSD(T) method [19].

Dimetallaboranes

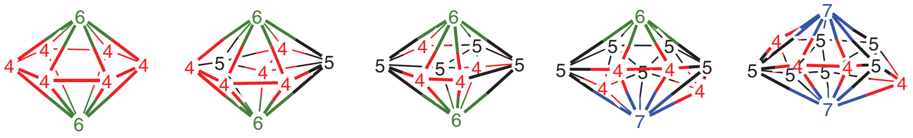
The first dimetallaboranes prepared by Hawthorne and co-workers [1] included species such as $Cp_2Co_2C_2B_6H_8$ with the correct $2n+2$ skeletal electrons (=22 for $n=10$) for the 10-vertex *closo* deltahedron, namely the bicapped square antiprism (Fig. 1) [20]. In the early studies the Hawthorne group also synthesized the iron derivative $Cp_2Fe_2C_2B_6H_8$ having only $2n$ skeletal electrons shown by X-ray crystallography to have a central $Fe_2C_2B_6$ deltahedron later interpreted as the 10-vertex *isocloso* deltahedron (Fig. 2) with a degree 6 vertex for the iron atom [21].

The experimentally known dirhenaboranes of the type $Cp_2Re_2B_{n-2}H_{n-2}$ are even more hypoelectronic, having only $2n-4$ apparent Wadean skeletal electrons [22–25]. The central Re_2B_{n-2} deltahedra (Fig. 3) deviate strongly from sphericity with relatively low curvature at the two approximately polar degree 6 and/or 7 rhenium vertices and relatively high curvature at the remaining $n-2$ equatorial degree 4 and 5 boron vertices. They thus resemble oblate (flattened) ellipsoids rather than spheres and, for this reason, have been called *oblatocloso* deltahedra [26].

The dirhenaboranes $Cp_2Re_2B_{n-2}H_{n-2}$ have been the subject of theoretical studies owing to their unusual structures [27, 28]. Such studies gratifyingly show the experimentally known *oblatocloso* dirhenaborane structures to be the lowest energy structures (Fig. 4). However, higher energy isomers were found having central Re_2B_{n2} *closo* deltahedra with adjacent rhenium atoms and short Re–Re distances suggesting formal multiple bonds. Such structures become the lowest energy structures in related pentalenedirhenaboranes $PnRe_2B_{n-2}H_{n-2}$ (Pn = η^5,η^5-pentalene) in which the pentalene ligand uses each of its five-membered rings to bond to a rhenium atom so that the two rhenium atoms are forced to stay in adjacent positions (Fig. 5) [29].

The lowest energy $PnRe_2B_{n-2}H_{n-2}$ structures are seen to have central Re_2B_{n-2} *closo* deltahedra with short Re≡Re distances of 2.24–2.26 Å very similar to that of the formal Re≡Re quadruple bond length of 2.24 Å in $K_2Re_2Cl_8$ [30]. Such metal–metal multiple bonds provide a way of drawing otherwise non-bonding metal electrons into the skeletal bonding. This can be clarified by considering the skeletal bonding topology in polyhedral boranes and metallaboranes (Table 1).

Consider first *closo* boranes having n vertices. Two of the three internal (skeletal) orbitals of each vertex atom are used for the surface bonding leading to n two-center two-electron (2e–2c) bonds distributed on the polyhedral surface as a canonical structure. The actual surface bonding, requiring $2n$ skeletal electrons



8 Vertices (hexagonal bipyramid) 9 Vertices 10 Vertices 11 Vertices 12 Vertices

Fig. 3: The *oblatocloso* deltahedra found in the dirhenaboranes $Cp_2Re_2B_{n-2}H_{n-2}$.

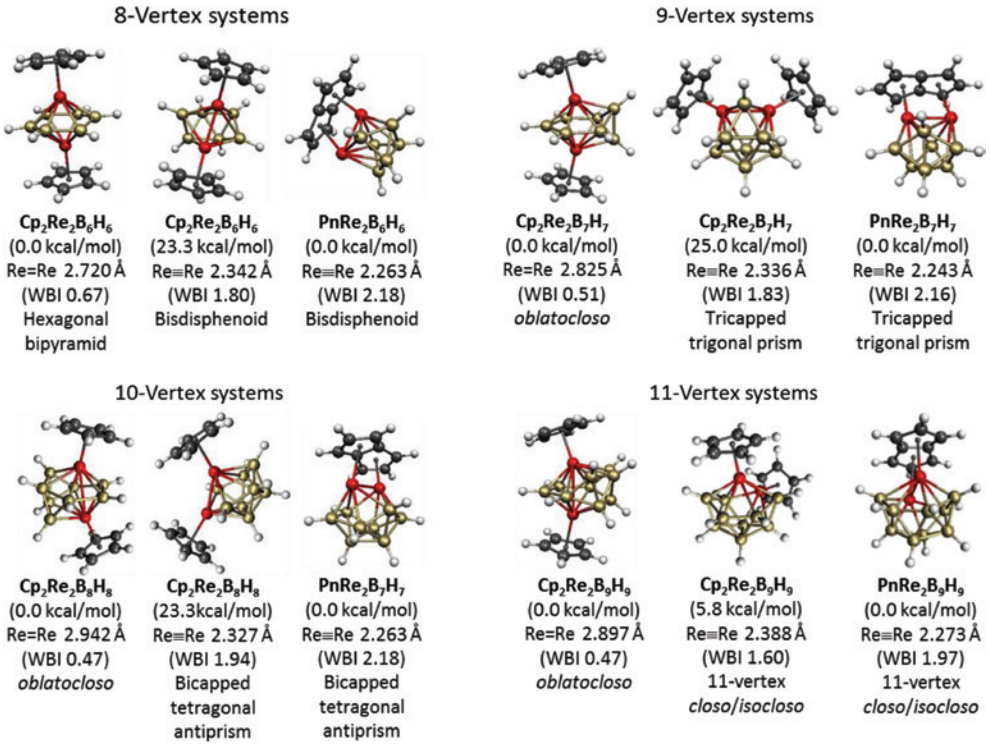


Fig. 4: Structures of the dirhenaboranes $Cp_2Re_2B_{n-2}H_{n-2}$ and $PnRe_2B_{n-2}H_{n-2}$.

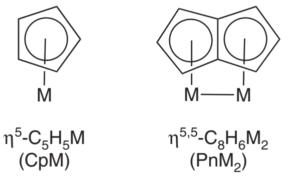


Fig. 5: Comparison of the bonding of a cyclopentadienyl (Cp) ligand to one rhenium atom with that of a pentalene (Pn) ligand to two rhenium atoms.

Table 1: Skeletal bonding topology in *closo*, *isocloso*, and *oblatocloso* boranes and metallaboranes.

Type	Surface bonding	Core bonding	Total electrons/orbitals	Wadean skeletal electrons
closo	$n\times 2c–2e$	$nc–2e$		
	$2n$ electrons	2 electrons	$2n+2$ electrons	$2n+2$ electrons
	$2n$ orbitals	n orbitals	$3n$ orbitals	
isocloso	$n\times 3c–2e$	None		
	$2n$ electrons	–	$2n$ electrons	$2n$ electrons
	$3n$ orbitals	–	$3n$ orbitals	
oblatocloso	$n\times 3c–2e$	M=M double bond		
	$2n$ electrons	4 electrons	$2n+4$ electrons	$2n-4$ electrons
	$3n$ orbitals	4 orbitals	$3n+4$ orbitals*	deg 5 M vertices

for these 2c–2e bonds, can then be considered as a resonance hybrid of all such canonical structures. The remaining internal orbitals on each vertex atom overlap in the center of the deltahedron to form a n-center two-electron bond. This bonding scheme accounts for the $2n+2$ Wadean skeletal electrons in *closo* deltahedral boranes [31–33].

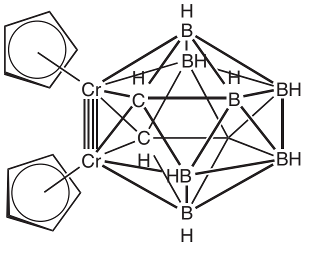
A related bonding topology for *isocloso* metallaboranes uses all three internal orbitals from each vertex atom to form n three-center two-electron surface bonds in a canonical structure [34]. Again the actual surface bonding, requiring $2n$ skeletal electrons for these 3c–2e bonds, can be considered as a resonance hybrid of all such canonical structures. This bonding scheme leaves no orbitals for any type of core bonding so that the *isocloso* metallaboranes have only $2n$ Wadean skeletal electrons.

A reasonable bonding topology for the *oblatocloso* dirhenaboranes deviates from the Wade–Mingos scheme [6–8] by assuming that the CpRe vertices use five rather than three orbitals for the skeletal bonding (Table 1) [27]. This is reasonable owing to the relatively low surface curvature at the rhenium vertices. Providing five skeletal orbitals makes each CpRe vertex a source of four skeletal electrons rather than the zero skeletal electrons that it would provide if using only three orbitals for skeletal bonding in the Wade–Mingos scheme [6–8]. Although the n-vertex *oblatocloso* dirhenaboranes appear to be highly hypoelectronic with only $2n-4$ Wadean skeletal electrons, they are best interpreted as $2n+4$ actual skeletal electron systems. Forming n surface 3c–2e bonds in the *oblatocloso* dirhenaboranes similar to those in the *isocloso* metallaboranes discussed above leaves four "extra" skeletal electrons for an internal Re=Re double bond. The two "extra" orbitals on each rhenium atom beyond the three required for the surface bonding are exactly the orbitals needed for such a Re=Re double bond.

The CpM (and Cp*M) vertices found in many metallaboranes use three metal orbitals for bonding to the Cp ring and another three orbitals for a Wadean skeletal electron bonding scheme [5–7]. Assuming that the metal atom has the favored 18-electron configuration, this leaves three of the nine orbitals in the sp^3d^5 metal valence orbital manifold with non-bonding lone pairs. Some of these lone pair electrons can be drawn into the skeletal bonding if the valence metal atoms form multiple bonds. Thus increasing the formal bond order of a surface metal–metal single bond to a quadruple bond draws six additional electrons into the skeletal bonding. In this way, $Cp_2Re_2B_{n-2}B_{n-2}$ and $PnRe_2B_{n-2}B_{n-2}$ systems with $2n-4$ Wadean skeletal electrons and a surface Re≣Re quadruple bond can have the actual $2n+2$ skeletal electrons required for a *closo* deltahedral structure.

At the time that we published our work on dimetallaboranes with metal–metal multiple bonds we were not aware of any experimental examples of such species. However, we subsequently found that we (as well as the reviewers of our papers) had overlooked the paper by Stone and coworkers in 1983 on the synthesis of an icosahedral dichromadicarbaborane $Cp_2Cr_2C_2B_8H_{10}$ by the reaction of chromocene with $C_2B_9H_{12}$ (Fig. 6). [35]. X-ray crystallography of $Cp_2Cr_2C_2B_8H_{10}$ shows an ultrashort Cr≣Cr distance of 2.272 Å very close to the Cr≣Cr distance of 2.288 Å for the chromium–chromium quadruple bond in anhydrous chromium(II) acetate dimer, $Cr_2(OAc)_4$ [36]. Note that $Cp_2Cr_2C_2B_8H_{10}$ is valence isoelectronic with $Cp_2Re_2B_{10}H_{10}$ exhibiting an albeit high-energy structure with a formal Re≣Re quadruple bond.

Removal of a high-degree vertex from a *closo* or *isocloso* deltahedron leads to a so-called *nido* structure with a pentagonal or hexagonal open face [3, 4]. The binary boranes of the type B_nH_{n+4} ($n=5$, 6, 8, 9 10) exhibit such structures (Fig. 7). Removal of a boron vertex from an *oblatocloso* dirhenaborane deltahedron can lead analogously to an *oblatonido* dimetallaborane deltahedron. Such *oblatonido* deltahedra are found in ditungstaboranes of the general type $Cp^{\star}_2M_2B_{n-2}H_{n+2}$ (M=W; $n=7$, 8: Fig. 8) [37–42]. The internal formal Re=Re double bond in the *oblatocloso* dirhenaborane structures $Cp_2Re_2B_{n-2}H_{n-2}$ becomes an external W=W double bond in these ditungstaboranes. This W=W bond has been the subject of a topological study using diverse methods



$Cp_2Cr_2C_2B_8H_{10}$

Fig. 6: The experimentally known dichromadicarbaborane suggested to have a formal Cr≣Cr quadruple bond.

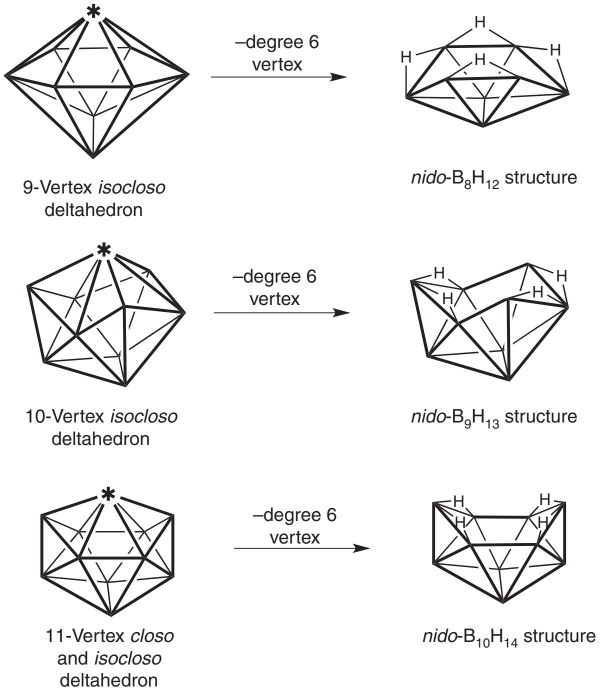


Fig. 7: Generation of structures for the binary *nido* boranes B_nH_{n+4} by vertex removal from *closo* and *isocloso* deltahedra.

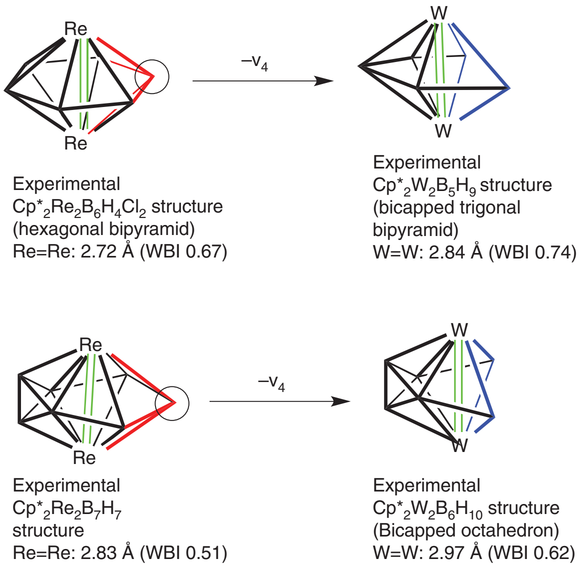
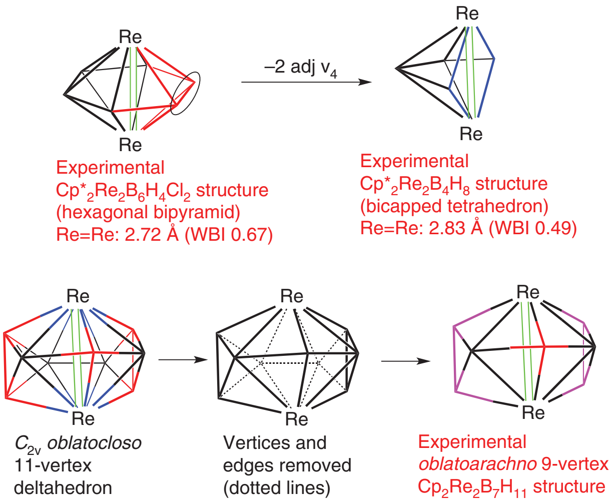


Fig. 8: Formation of the *oblatonido* ditungstaboranes $Cp^*_2W_2B_{n-2}H_{n+2}$ ($n = 7, 8$) structures by removal of a boron vertex from the *oblatocloso* dirhenaboranes $Cp_2Re_2B_{n2}H_{n-2}$.

[43]. Removal of two adjacent boron vertices from the hexagonal bipyramidal *oblatocloso* $Cp^*_2Re_2B_6H_4Cl_2$ structure leads to the *oblatoarachno* structure $Cp^*_2Re_2B_4H_8$ (Fig. 9) [44].

Trimetallaboranes

In 1998 Fehlner and co-workers [45] reported the synthesis of the unusual tritungstaborane $Cp^*_3W_3(\mu\text{-H})B_8H_8$ by the pyrolysis of $Cp^*WB_4H_{11}$. The central 11-vertex W_3B_8 deltahedron in $Cp^*_3W_3(\mu\text{-H})B_8H_8$ deviates



Experimental $Cp^*_2Re_2B_6H_4Cl_2$ structure (hexagonal bipyramid) Re=Re: 2.72 Å (WBI 0.67)

Experimental $Cp^*_2Re_2B_4H_8$ structure (bicapped tetrahedron) Re=Re: 2.83 Å (WBI 0.49)

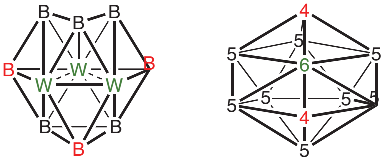
C_{2v} *oblatocloso* 11-vertex deltahedron

Vertices and edges removed (dotted lines)

Experimental *oblatoarachno* 9-vertex $Cp_2Re_2B_7H_{11}$ structure

Fig. 9: Formation of the *oblatoarachno* dirhenaborane $Cp^*_2Re_2B_{n-2}H_{n+2}$ ($n = 6, 9$) structures by removal of two adjacent boron vertices from *oblatocloso* dirhenaboranes.

considerably from sphericity in having degree 6 and 7 vertices for the tungsten atoms and degree 4 and 5 vertices for the boron atoms (Fig. 10). This structure can be considered as a bonded W_3 triangle imbedded into the 11-vertex W_3B_8 deltahedron. One of the W–W bonds in this W_3 triangle lies on the deltahedral surface whereas the remaining two W–W bonds are located inside the deltahedron. This W_3B_8 deltahedron is very different from the most spherical 11-vertex *closo* deltahedron (Fig. 1). Much later the molybdenum analog $Cp^*_3Mo_3(H)B_8H_8$ was synthesized by Ghosh and coworkers [46].



The $(CpW)_3B_8H_9$ deltahedron: C_s symmetry

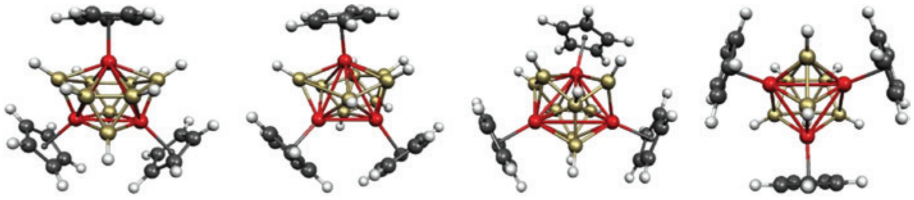
The $B_{11}H_{11}^{2-}$ deltahedron: C_{2v} symmetry

Fig. 10: Comparison of the W_3B_8 deltahedron in $Cp^*_3W_3(\mu\text{-}H)B_8H_8$ with the most spherical 11-vertex *closo* deltahedron found in $B_{11}H_{11}^{2-}$.

Table 2: Comparison of the electron bookkeeping for the isoelectronic systems $Cp_3Re_3B_8H_8$ and $Cp_3W_3(\mu H)B_8H_8$

Source of skeletal electrons for $Cp_3Re_3B_8H_8$:	
Three CpRe vertices with five internal orbitals: $3 \times 4 =$	12 electrons
Eight BH vertices: $8 \times 2 =$	16 electrons
Total skeletal electrons obtained:	28 electrons
Use of skeletal electrons:	
Deltahedral surface bonding: $11 \times 2 =$	22 electrons
Bonded Re–Re triangle (three 2c–2e bonds): $3 \times 2 =$	6 electrons
Total skeletal electrons required:	28 electrons
Source of skeletal electrons for $Cp_3W_3B_8H_8(H)$:	
Three CpW vertices with five internal orbitals: $3 \times 3 =$	9 electrons
Bridging μ-H atom brings external W lone pair into the skeletal bonding scheme:	3 electrons
Eight BH vertices: $8 \times 2 =$	16 electrons
Total skeletal electrons required:	28 electrons

A complication in the theoretical study of the $\mathrm{Cp^{*}_{3}W_{3}(\mu\text{-}H)B_{8}H_{8}}$ and related $\mathrm{Cp_{3}W_{3}B_{n-3}H_{n-2}}$ systems is the location of the "extra" hydrogen atom. Therefore we first studied the related trirhenaborane $\mathrm{Cp_{3}Re_{3}B_{8}H_{8}}$ without the extra hydrogen atom [47]. The $\mathrm{Cp_{3}W_{3}(\mu\text{-}H)B_{8}H_{8}}$ and $\mathrm{Cp_{3}Re_{3}B_{8}H_{8}}$ systems are isoelectronic (Table 2) since addition of the extra hydrogen atom as a deltahedral edge bridge brings an additional three electrons into the skeletal bonding. One of these three electrons is provided by the hydrogen atom. The remaining two



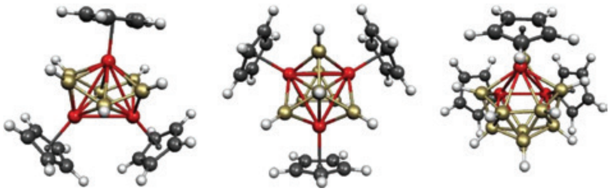
$\mathrm{B_8Re_{3\text{–}1}}$ (C_1)
0.0 kcal/mol

$\mathrm{B_8Re_{3\text{–}2}}$ (C_1)
13.9 kcal/mol

$\mathrm{B_8Re_{3\text{–}3}}$ (C_1)
18.2 kcal/mol

$\mathrm{B_8Re_{3\text{–}4}}$ (C_s)
18.3 kcal/mol

Fig. 11: The four lowest-energy $\mathrm{Cp_3Re_3B_8H_8}$ structures.

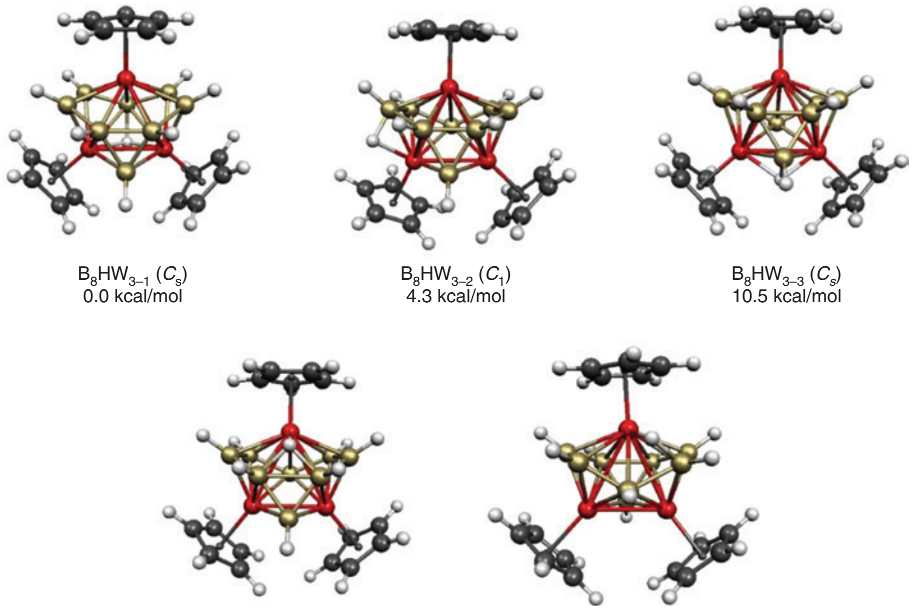


$\mathrm{Cp_3Re_3B_6H_6}$
9-Vertex *isocloso*

$\mathrm{Cp_3Re_3B_7H_7}$
Tetracapped
octahedron

$\mathrm{Cp_3Re_3B_8H_8}$
Icosahedron

Fig. 12: The lowest energy $\mathrm{Cp_3Re_3B_{n-3}H_{n-3}}$ ($n = 9$, 10, 12) structures.



$\mathrm{B_8HW_{3\text{–}1}}$ (C_s)
0.0 kcal/mol

$\mathrm{B_8HW_{3\text{–}2}}$ (C_1)
4.3 kcal/mol

$\mathrm{B_8HW_{3\text{–}3}}$ (C_s)
10.5 kcal/mol

$\mathrm{B_8HW_{3\text{–}4}}$ (C_s)
10.9 kcal/mol

$\mathrm{B_8HW_{3\text{–}5}}$ (C_s)
14.4 kcal/mol

Fig. 13: The five lowest energy $\mathrm{Cp_3W_3(H)B_8H_8}$ structures.

electrons arise when an otherwise non-bonding metal lone pair is drawn into the skeletal bonding by the hydrogen bridge.

Figure 11 shows the four lowest-energy structures for the trirhenaborane $Cp_3Re_3B_8H_8$ [47]. The lowest energy structure is seen to have the same M_3B_8 deltahedron as the experimental $Cp^*_3W_3(\mu H)B_8H_8$ deltahedron consistent with the isoelectronicity of the two structures. The lowest energy structures for the $Cp_3Re_3B_{n-3}H_{n-3}$ systems of other sizes ($n = 9$, 10, 12) are shown in Fig. 12. These structures can all be considered to contain an Re_3 triangle imbedded into an Re_3B_{n-3} deltahedron. The interior Re–Re bonds in these Re_3 triangles range from 2.8 to 3.0 Å. The surface Re–Re bonds are significantly shorter at 2.6–2.7 Å because of their partial double bond character combining with the overall delocalized surface bonding of the deltahedron (Table 1).

The lowest energy structures for the $Cp_3W_3(\mu\text{-}H)B_{n-3}H_{n-3}$ ($n = 9$–12) were determined using the same density functional theory methods [48]. All of the five lowest energy structures for the experimentally known 11-vertex $Cp_3W_3(\mu H)B_8H_8$ system were found to have the same 11-vertex central W_3B_8 deltahedron as the experimental $Cp^*_3W_3(\mu H)B_8H_8$ structure (Fig. 13). They differ only in the location of the "extra" bridging hydrogen atom. The lengths of the interior W–W bonds were found to be ~3.0 Å, whereas those of the surface bonds were found to be significantly shorter at ~2.7 to ~2.8 Å. This is consistent with the observations on the $Cp_3Re_3B_{n-3}H_{n-3}$ systems as noted above.

Conclusions

The lowest energy structures for the dirhenaboranes $Cp_2Re_2B_{n-2}H_{n-2}$ correspond to the *oblatocloso* structures found experimentally by Fehlner, Ghosh, and their coworkers. Such structures have Re=Re distances ranging from 2.69 to 2.94 Å suggested by their skeletal bonding topology and Re=Re Wiberg bond indices to be formal double bonds. Higher energy structures for the dirhenaboranes $Cp_2Re_2B_{n-2}H_{n-2}$ have the same *closo* deltahedra as found in the corresponding $B_nH_n^{2-}$ anions. In these structures the rhenium atoms are located at adjacent vertices with ultrashort Re≣Re distances of 2.28–2.39 Å similar to the experimental Re≣Re distance of 2.24 Å for the formal quadruple bond in $K_2Re_2Cl_8$. A formal Cr≣Cr quadruple bond of length 2.272 Å is found experimentally in the icosahedral $Cp_2Cr_2C_2B_{10}H_{10}$ isoelectronic with $Cp_2Re_2B_{10}H_{10}$. Replacement of the Cp_2Re_2 unit with a $PnRe_2$ ($Pn = \eta^5,\eta^5$-pentalene) unit forces the rhenium atoms to remain in adjacent positions so that the *closo* deltahedral structures with surface Re≣Re quadruple bonds become the lowest energy structures.

The lowest energy structures for the trimetallaboranes $Cp_3Re_3B_{n-3}H_{n-3}$ and $Cp_3W_3(\mu\text{-}H)B_{n-3}H_{n-3}$ related to the experimentally known $Cp_3W_3(\mu\text{-}H)B_8H_8$ have a central M_3B_{n-3} deltahedron typically containing a bonded M_3 triangle. This central M_3B_{n3} deltahedron is not the most spherical *closo* deltahedron since the metal atoms prefer degree 6 and 7 vertices whereas the boron atoms prefer degree 4 and degree 5 vertices. The metal–metal bonds in the central M_3 triangle are ~3.0 Å if they go through the center of the M_3B_{n-3} deltahedron but shorter at ~2.7 to ~2.8 Å if they lie on the surface of the M_3B_{n-3} deltahedron.

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