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Hypoelectronic Dirhenaboranes Having Eight to Twelve Vertices: Internal Versus Surface Rhenium−Rhenium Bonding

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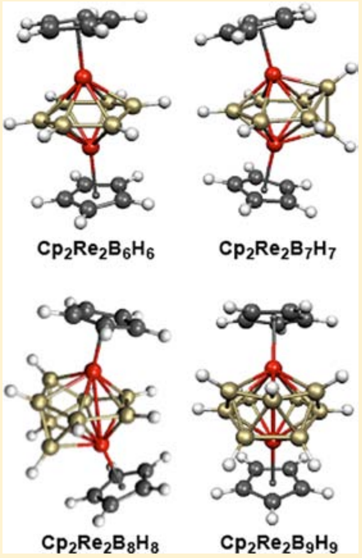
S *Supporting Information*

ABSTRACT: Fehlner, Ghosh, and their co-workers have synthesized a series of dirhenaboranes $Cp_2Re_2B_{n-2}H_{n-2}$ (n = 8, 9, 10, 11, 12) exhibiting unprecedented oblate (flattened) deltahedral structures. These structures have degree 6 and/or 7 rhenium vertices at the flattest regions on opposite sides of an axially compressed deltahedron thereby leading to Re═Re distances in the range 2.69 to 2.94 Å suggesting internal formal double bonds. These experimental oblate (flattened) deltahedral structures are shown by density functional theory to be the lowest energy structures for these dirhenaboranes. In some cases the energy differences between such oblate deltahedral structures and the next higher energy structures are quite considerable, that is, up to 25 kcal/mol for the nine-vertex $Cp_2Re_2B_7H_7$ structures. The higher energy $Cp_2Re_2B_{n-2}H_{n-2}$ structures are of the two types: (1) Most spherical (*closo*) deltahedra having unusually short 2.28 to 2.39 Å Re−Re edges with unusually high Wiberg bond indices suggesting formal multiple bonds on the deltahedral surface; (2) Deltahedra having one or two degree 3 vertices and 2.6 to 2.9 Å Re−Re edges. The latter deltahedra are derived from smaller deltahedra by capping Re_2B faces with the degree 3 vertices.



1. INTRODUCTION

The most stable polyhedral boranes and isoelectronic carboranes have structures based on the so-called most spherical deltahedra, also known as *closo* deltahedra.[1,2] Such polyhedra have all triangular faces and vertices as nearly similar as possible. This means that the six- to twelve-vertex *closo* deltahedra have only degree 4 or 5 vertices except for the 11-vertex *closo* deltahedron, required by polyhedral topology[3] to have a single degree 6 vertex in addition to its degree 4 and 5 vertices (Figure 1). The number of skeletal electrons in such structures is generally determined by the Wade−Mingos rules[4−6] which state that n-vertex *closo* deltahedral boranes are particularly stable if they contain $2n + 2$ skeletal electrons. This special stability has been ascribed to three-dimensional aromaticity.[7−9] In accord with the Wade−Mingos rules the so-called *closo* borane anions $B_nH_n^{2-}$ ($6 \leq n \leq 12$) as well as the isoelectronic *closo* carboranes $CB_{n-1}H_n^-$ and $C_2B_{n-2}H_n$ exhibit special stability.

The vertices in the *closo* deltahedral boranes and related carboranes were first shown by Hawthorne and co-workers[10] to be replaceable by isolobal transition metal vertices. The initial work used moieties of the type CpM or $M(CO)_3$ (Cp = η^5-cyclopentadienyl; M = transition metal) to replace BH vertices in icosahedral borane structures. Initially it was assumed that such substitution did not affect the underlying *closo* deltahedral geometry. However, as metallaborane chemistry was subsequently developed using polyhedra other than the icosahedron, particularly by Kennedy and co-workers,[11−14] a variety of nonicosahedral metallaborane structures were discovered based on deltahedra topologically distinct from the *closo* deltahedra. Such polyhedra have been called either *isocloso*[15] or *hypercloso*[16−18] deltahedra; they will be called *isocloso* deltahedra in this paper. A characteristic feature of these *isocloso* metallaborane deltahedra is the presence of a single degree 6 vertex for the metal atom (Figure 2). This unique degree 6 vertex is surrounded by 4, 3, and 2 degree 4 vertices for the 9-, 10-, and 11-vertex metallaboranes, respectively. Distinct *isocloso* metallaboranes are found for metallaboranes having 9 and 10 vertices. The 11-vertex *isocloso* deltahedron is topologically identical to the 11-vertex *closo* deltahedron since the latter already has a single degree 6 vertex (Figures 1 and 2). Such *isocloso* metallaboranes were found to have $2n$ skeletal electrons rather than the $2n + 2$ skeletal electrons predicted by the Wade−Mingos rules[4−6] for metal-free deltahedral boranes and carboranes.

Further development of metallaborane chemistry led to the synthesis of some interesting dimetallaboranes. The early work

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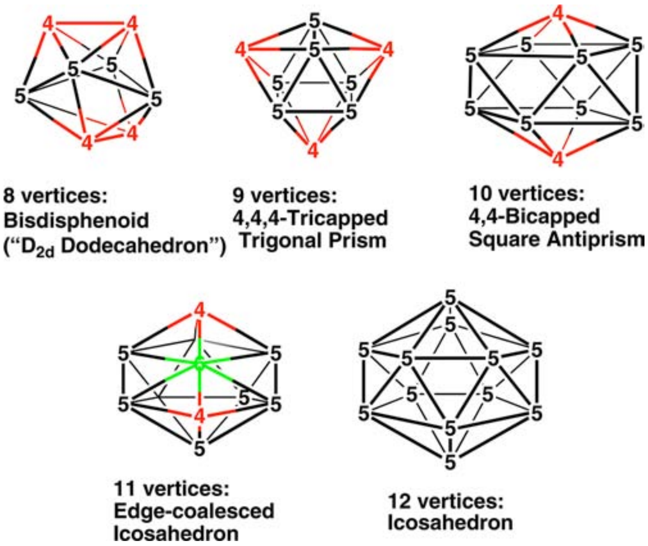

8 vertices: Bisdisphenoid ("D_{2d} Dodecahedron")

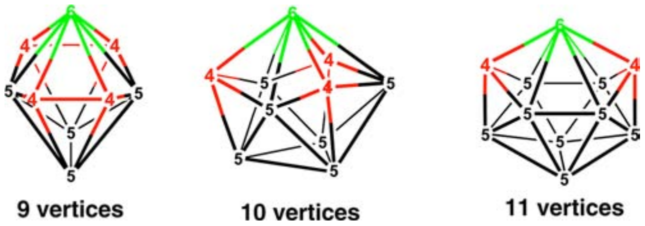
9 vertices: 4,4,4-Tricapped Trigonal Prism

10 vertices: 4,4-Bicapped Square Antiprism

11 vertices: Edge-coalesced Icosahedron

12 vertices: Icosahedron

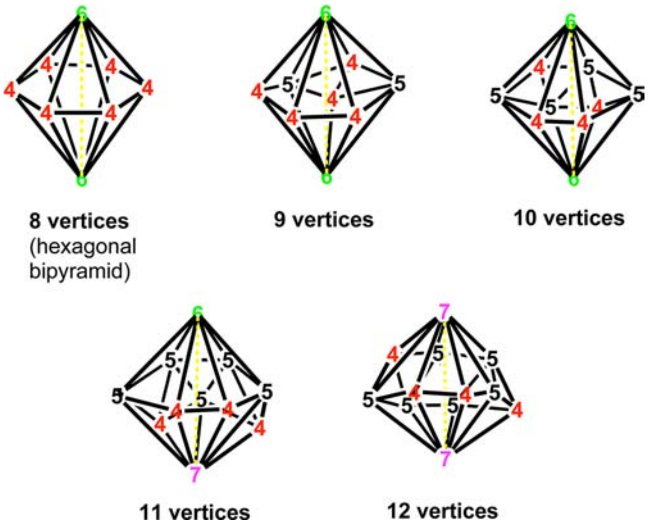
Figure 1. Most spherical deltahedra with 8 to 12 vertices. In both this figure and Figure 2 the vertices are labeled with their degrees. In addition degree 4, 5, and 6 vertices are shown in red, black, and green, respectively.


9 vertices

10 vertices

11 vertices

Figure 2. *Isocloso* metallaborane deltahedra with 9, 10, and 11 vertices. The metal atoms in these structures are located at the unique degree 6 vertex (green). The 11-vertex *isocloso* deltahedron is the same as the 11-vertex *closo* deltahedron (Figure 1) but is shown in a different view in this figure.


8 vertices (hexagonal bipyramid)

9 vertices

10 vertices

11 vertices

12 vertices

Figure 3. Oblate (flattened) *n*-vertex deltahedra found in the dirhenaboranes $Cp^*_2Re_2B_{n-2}H_{n-2}$ ($8 \leq n \leq 12$), which have been synthesized and structurally characterized by X-ray crystallography. The rhenium atoms are located at the degree 6 (green) and degree 7 (pink) vertices.

of Hawthorne and co-workers included the discovery of the interesting pair of dimetallaboranes $Cp_2M_2C_2B_6H_8$ (M = Co,[19] Fe[20]). The cobalt derivative, with $2n + 2$ skeletal electrons (= 22 for $n = 10$), has the expected *closo* bicapped square antiprism structure (Figure 1). However, the iron derivative with two less skeletal electrons ($2n = 20$ for $n = 10$) was found to have the *isocloso* structure (Figure 2) with one of the iron atoms at the unique degree 6 vertex.

The most unusual dimetallaboranes are a series of dirhenaboranes discovered by Fehlner, Ghosh, and their co-workers.[21−24] They found that cluster expansion of $(Cp^*ReH_2)_2B_4H_4$ ($Cp^* = \eta^5\text{-}Me_5C_5$) with monoborane derivatives under various conditions led to the sequential formation of a series of compounds $Cp^*_2Re_2B_{n-2}H_{n-2}$ (n = 9, 10, 11, 12) having structures based on unusual previously unknown *n*-vertex deltahedra (Figure 3). The related 8-vertex hexagonal bipyramidal derivative $Cp^*_2Re_2B_6H_4Cl_2$ was also synthesized. This new family of deltahedra is characterized by highly oblate (flattened) structures having the two metal atoms on opposite sides in the flattened direction so that the metal−metal distances are short enough for direct metal−metal bonding through the center of the deltahedron. Furthermore, the metal atoms are generally located at degree 6 or even degree 7 vertices with a corresponding reduction to 4 of the degrees of many of the boron vertices. The Wade−Mingos procedure for counting skeletal electrons[4−6] in these species arrives at $2n - 4$ skeletal electrons, which is six skeletal electrons short of the $2n + 2$ suggested to be optimal for deltahedral structures. However, such a Wadean skeletal electron count artificially assumes that the two rhenium vertices provide the typical three internal orbitals for skeletal bonding. Thus the Cp*Re vertices are considered to be donors of zero skeletal electrons. Several years ago one of the authors suggested an alternative model for the skeletal bonding in such rhenaboranes in which the Cp*Re vertices provide five rather than three internal orbitals for skeletal bonding.[25] Then the Cp*Re vertices become donors of four skeletal electrons so that the *n*-vertex $Cp^*_2Re_2B_{n-2}H_{n-2}$ systems now have $2n + 4$ skeletal electrons. These $2n + 4$ skeletal electrons provide for a formal Re═Re double bond through the center of the flattened deltahedron in addition to the usual surface bonding.

The experimental data on the $Cp^*_2Re_2B_{n-2}H_{n-2}$ derivatives indicate preference for highly oblate deltahedra having a rhenium atom at each mutually opposite flattest point. Such structures are apparently highly hypoelectronic relative to the Wadean $2n + 2$ skeletal electrons[4−6] for *n*-vertex deltahedral boranes and carboranes. These deltahedra are squashed (flattened) to the extent that the two rhenium atoms are within bonding distance for the formal internal double bond suggested by the topological bonding model.[25] Alternative possible structures for these $Cp^*_2Re_2B_{n-2}H_{n-2}$ derivatives could be more closely related to the most spherical deltahedra with the pair of rhenium atoms at one of the edges forming a surface rhenium−rhenium bond. The significantly greater radius of rhenium in such structures relative to the boron vertices would necessarily lead to distortion from sphericity.

There are thus two possible general types of deltahedra for the $Cp^*_2Re_2B_{n-2}H_{n-2}$ derivatives:

(1) The experimentally observed oblate deltahedra with the rhenium atoms on opposite sides and flattened enough to bring the two rhenium atoms within bonding distance through the center of the deltahedron.[21,22] These structures can be considered to have an internal rhenium−rhenium bond, suggested to be a formal

Table 1. Optimized 8-Vertex $Cp_2Re_2B_6H_6$ Structures within 25 kcal/mol of the Global Minimum

	ΔE	vertex degrees					Re−Re				
structure (symmetry)	kcal/mol	v_3	v_4	v_5	v_6	v_7	BRe_2	BRe	Å	WBI	comments
B6Re2-1F (C_s)	0.0	0	6	0	2	0	6	0	2.720	0.67	hex bipyramid
B6Re2-2 (C_{2v})	8.4	2	2	2	2	0	4	2	2.593	0.85	bicap octahedron
B6Re2-3 (C_s)	21.2	1	4	1	2	0	4	2	2.638	0.57	bicap trig prism
B6Re2-4 (C_2)	23.3	0	4	4	0	0	2	4	2.342	1.80	bisdisphenoid

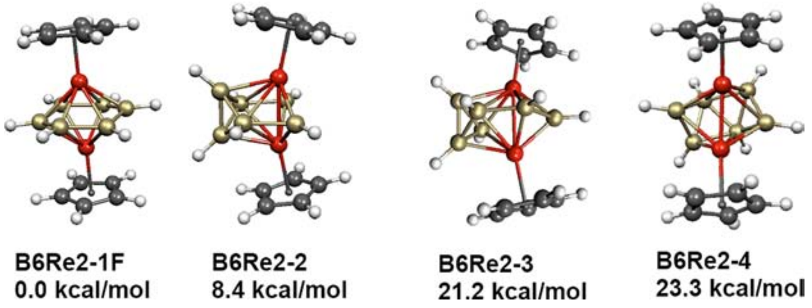


Figure 4. Four optimized 8-vertex $Cp_2Re_2B_6H_6$ structures within 25 kcal/mol of the global minimum.

double bond on the basis of the Re═Re distance and electron bookkeeping.[25] These deltahedra are of interest since they have not yet been found in other types of metallaborane derivatives.

(2) More familiar deltahedra with adjacent rhenium atoms forming a surface rhenium−rhenium bond leading to a distorted spherical deltahedron.

This paper reports a density functional theory study on these $Cp_2Re_2B_{n-2}H_{n-2}$ systems (n = 8, 9, 10, 11, 12) to assess the relative energies of these two types of structures. To facilitate the computational aspects of the work unsubstituted η^5-C_5H_5 derivatives were studied rather than the experimentally known η^5-Me_5C_5 derivatives.[22−24] This is not expected to have a major effect on the chemistry.

2. THEORETICAL METHODS

Full geometry optimizations were carried out on the $Cp_2Re_2B_{n-2}H_{n-2}$ systems at the B3LYP/6-31G(d)[26−29] level of theory for all atoms except Re for which the SDD[30] (Stuttgart−Dresden ECP plus DZ) basis set has been chosen. The initial structures were constructed by systematic substitution of two boron atoms from possible $B_nH_n^{2-}$ structures by CpRe units. This led to a large number of different starting structures. Thus 94 structures of the 8-vertex clusters $Cp_2Re_2B_6H_6$, 62 structures of the 9-vertex clusters $Cp_2Re_2B_7H_7$, 78 structures of the 10-vertex clusters $Cp_2Re_2B_8H_8$, 113 structures of the 11-vertex clusters $Cp_2Re_2B_9H_9$, and 46 structures of the 12-vertex clusters $Cp_2Re_2B_{10}H_{10}$ were chosen as starting points for the optimizations (see the Supporting Information). The nature of the stationary points after optimization was checked by calculations of the harmonic vibrational frequencies. If significant imaginary frequencies were found, the optimization was continued by following the normal mode corresponding to imaginary frequencies to ensure that genuine minima were obtained. Normally this resulted in reduction of the molecular symmetry. The Wiberg bond indices (WBIs) for the Re−Re interactions in the optimized $Cp_2Re_2B_{n-2}H_{n-2}$ structures were determined using natural bond orbital (NBO) analysis.[31] They are listed in Tables 1 to 5.

All calculations were performed using the Gaussian 09 package[32] with the default settings for the SCF cycles and geometry optimization, namely, the fine grid (75,302) for numerically evaluating the integrals, 10^{-8} hartree for the self-consistent field convergence, maximum force of 0.000450 hartree/bohr, rms force of 0.000300 hartree/bohr, maximum displacement of 0.001800 bohr, and rms displacement of 0.001200 bohr.

The $Cp_2Re_2B_{n-2}H_{n-2}$ structures are numbered as **B(*n*−2)Re2-*x*** where ***n*** is the total number of polyhedral vertices and ***x*** is the relative order of the structure on the energy scale. Structures based on oblate ("flattened") deltahedra with an internal rhenium−rhenium bond are designated by **F**. Tables 1 to 5 describing the optimized $Cp_2Re_2B_{n-2}H_{n-2}$ structures list the numbers of vertices of each degree d as v_d and the numbers of boron atoms bonded directly to one or two rhenium atoms as BRe and BRe_2, respectively. In all of the optimized structures the two rhenium atoms are consistently located at the two highest degree vertices.

Only the lowest energy and thus potentially chemically significant structures are considered in detail in this paper. More comprehensive lists of structures, including higher energy structures, are given in the Supporting Information. The energy cutoff points chosen depend upon the distribution of isomer structures and their energies and are indicated in the figure captions. The chosen energy cutoff points led to sets of 2 to 8 structures for a given cluster size discussed in detail in this paper.

The structures, total and relative energies, relevant interatomic distances, and relative energies with zero point energy and thermal corrections for all of the structures discussed in this paper systems are given in the Supporting Information. The zero point energy and thermal corrections were found to make relatively little difference in the relative energies of the structures. Therefore the uncorrected relative energies are discussed in the text and presented in the figures and tables.

3. RESULTS

3.1. 8-Vertex Structures $Cp_2Re_2B_6H_6$.

Four $Cp_2Re_2B_6H_6$ structures were found within 25 kcal/mol of the global minimum **B6Re2-1F** (Figure 4 and Table 1). The global minimum is the hexagonal bipyramid **B6Re2-1F** found in the experimentally known closely related $Cp^*_2Re_2B_6H_4Cl_2$.[24] The predicted Re−Re distance of 2.720 Å for $Cp_2Re_2B_6H_6$ is close to the experimental distance of 2.6889(5) Å for $Cp^*_2Re_2B_6H_4Cl_2$, determined by X-ray crystallography. Structure **B6Re2-1F** appears to be a very favorable structure since it lies more than 8 kcal/mol below any other $Cp_2Re_2B_6H_6$ structure.

Structure **B6Re2-1F** is the only oblate deltahedral $Cp_2Re_2B_6H_6$ structure where the Re−Re bond passes through the center of the deltahedron. Higher energy $Cp_2Re_2B_6H_6$ structures all have a surface Re−Re bond forming an edge of the deltahedron. The lowest energy such structure, namely, **B6Re2-2** lying 8.4 kcal/mol above **B6Re2-1F**, is a bicapped octahedron with BH groups capping both of the Re_2B faces sharing an edge. Structure **B6Re2-2** has two degree 3 vertices.

The next two $Cp_2Re_2B_6H_6$ structures lie at considerably higher energies (Figure 4 and Table 1). Structure **B6Re2-3**, lying 21.2 kcal/mol above **B6Re2-1F**, has a single degree 3 vertex. This vertex caps a BRe_2 face of an underlying capped trigonal prism.

The Re−Re edge lengths in the deltahedral structures **B6Re2-2** and **B6Re2-3** are approximately ∼2.6 Å. The still higher energy $Cp_2Re_2B_6H_6$ structure **B6Re2-4**, lying 23.3 kcal/mol above the global minimum **B6Re2-1F**, is of interest from two points of view:

(1) Its structure is the most spherical 8-vertex deltahedron, namely, the bisdisphenoid (Figure 1).

(2) The Re−Re edge is unusually short at ∼2.3 Å, suggesting a surface bond of multiple order. The high formal order of the Re−Re bond in **B6Re2-4** is supported by its high WBI of 1.80, which is more than twice as high as the WBIs of any other of the lowest energy $Cp_2Re_2B_6H_6$ structures listed in Table 1,

3.2. 9-Vertex Structures $Cp_2Re_2B_7H_7$.

The lowest energy $Cp_2Re_2B_7H_7$ structure **B7Re2-1F** is the experimentally known oblate structure with both rhenium atoms at degree 6 vertices. This is obviously a very favorable structure since it lies ∼25 kcal/mol below the next lowest energy structure. The predicted Re−Re distance of 2.825 Å through the center of the Re_2B_7 deltahedron is close to the experimental distance of 2.787 Å in $Cp^*{}_2Re_2B_7H_7$, determined by X-ray crystallography.

The only other $Cp_2Re_2B_7H_7$ structure within 25 kcal/mol of the global minimum **B7Re2-1F** is **B7Re2-2**, lying 25.0 kcal/mol above **B7Re2-1F** (Figure 5 and Table 2). The Re_2B_7 polyhedron in **B7Re2-2** is the tricapped trigonal prism, which is the most spherical 9-vertex deltahedron (Figure 1). The Re−Re distance in **B7Re2-2** is predicted to be very short at 2.336 Å, similar to that in the 8-vertex structure **B6Re2-4** (Figure 4 and Table 1), which is based on the most spherical 8-vertex deltahedron, namely, the bisdisphenoid. The high order of the Re−Re multiple bond in **B7Re2-2** is suggested by its high WBI of 1.83.

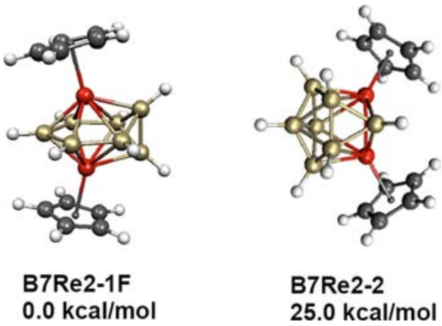

B7Re2-1F
0.0 kcal/mol
B7Re2-2
25.0 kcal/mol

Figure 5. Two optimized 9-vertex $Cp_2Re_2B_7H_7$ structures within 25 kcal/mol of the global minimum.

3.3. 10-Vertex Structures $Cp_2Re_2B_8H_8$.

The lowest energy $Cp_2Re_2B_8H_8$ structure is the experimentally known[24] oblate structure **B8Re2-1F** (Figure 6 and Table 3). This structure is obviously a highly favored structure since it lies ∼16 kcal/mol below the next lowest energy $Cp_2Re_2B_8H_8$ structure. In **B8Re2-1F** both rhenium atoms are located at degree 6 vertices, and all boron atoms are located at either degree 4 or degree 5 vertices. The predicted Re−Re distance of 2.942 Å through the cluster is ∼0.1 Å longer than the experimental Re−Re distance of 2.8345(8) Å,[24] determined by X-ray crystallography on $Cp^*{}_2Re_2B_8H_8$.

Two higher energy oblate deltahedral $Cp_2Re_2B_8H_8$ structures were found (Figure 6 and Table 3). Structure **B8Re2-3F**, lying 17.2 kcal/mol above **B8Re2-1F**, has both rhenium atoms at degree 6 vertices similar to **B8Re2-1F**. However, **B8Re2-3F** differs from **B8Re2-1F** by having a boron atom at an additional degree 6 vertex. The still higher energy oblate $Cp_2Re_2B_8H_8$ structure **B9Re2-5F**, lying 20.9 kcal/mol above **B8Re2-1F**, has one rhenium atom at a degree 6 vertex and the other rhenium atom at a degree 7 vertex.

Two deltahedral $Cp_2Re_2B_8H_8$ structures, namely, **B8Re2-2** and **B8Re2-6**, were found having the pair of rhenium atoms forming an unusually short Re−Re edge of length 2.3 to 2.4 Å (Figure 6 and Table 3). In **B8Re2-2**, lying 16.4 kcal/mol above **B8Re2-1F**, the deltahedron is the 10-vertex *isocloso* deltahedron (Figure 2) with one of the rhenium atoms at the unique degree 6 vertex and the other rhenium atom at an adjacent degree 5 vertex. In **B8Re2-6**, lying 23.3 kcal/mol above **B8Re2-1F**, the deltahedron is the most spherical 10-vertex *closo* deltahedron, namely, the bicapped square antiprism (Figure 1). In **B8Re2-6** the rhenium atoms are located at a pair of adjacent degree 5 vertices. The high orders of the Re−Re multiple bonds in **B8Re2-2** and **B8Re2-6** are supported by their unusually big WBIs of 1.61 and 1.94, respectively.

The remaining two $Cp_2Re_2B_8H_8$ structures lying within 25 kcal/mol in energy of **B8Re2-1F**, namely, **B8Re2-4** and **B8Re2-7**, have the pair of rhenium atoms forming a Re−Re edge of length ∼2.7 Å. Structure **B8Re2-4**, lying 18.5 kcal/mol above **B8Re2-1F**, has a Re_2B_8 tetracapped trigonal prism with a single degree 3 vertex. Structure **B8Re2-7**, lying 24.1 kcal/mol above **B8Re2-1F**, has a bicapped bisdisphenoid structure with two degree 3 vertices. In both structures all of the degree 3 vertices cap Re_2B faces of a smaller underlying deltahedron forming tetrahedral cavities.

3.4. 11-Vertex Structures $Cp_2Re_2B_9H_9$.

The potential surface for the 11-vertex cluster $Cp_2Re_2B_9H_9$ is found to be more complicated than those of the smaller clusters $Cp_2Re_2B_{n-2}H_{n-2}$ (n = 8, 9, 10) with 13 structures lying within 25 kcal/mol of the global minimum. Only the eight $Cp_2Re_2B_9H_9$ structures lying with 15 kcal/mol of the global minimum are discussed in this paper (Figure 7 and Table 4).

Table 2. Optimized 9-Vertex $Cp_2Re_2B_7H_7$ Structures within 25 kcal/mol of the Global Minimum

	ΔE	vertex degrees							Re−Re		
structure (symmetry)	kcal/mol	ν_3	ν_4	ν_5	ν_6	ν_7	BRe_2	BRe	Å	WBI	comments
B7Re2-1F (C_{2v})	0.0	0	5	2	2	0	5	2	2.825	0.51	experiment
B7Re2-2 (C_s)	25.0	0	3	6	0	0	2	4	2.336	1.83	tricap trig prism

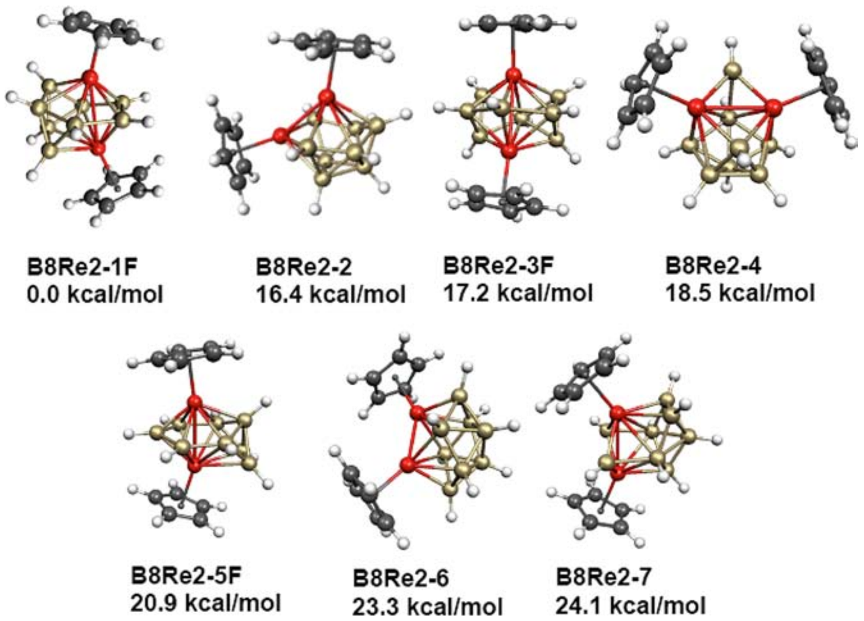


Figure 6. Seven optimized 10-vertex $Cp_2Re_2B_8H_8$ structures within 25 kcal/mol of the global minimum.

Table 3. Optimized 10-Vertex $Cp_2Re_2B_8H_8$ Structures within 25 kcal/mol of the Global Minimum

	ΔE	vertex degrees							Re−Re		
structure (symmetry)	kcal/mol	v_3	v_4	v_5	v_6	v_7	BRe_2	BRe	Å	WBI	comments
B8Re2-1F (C_2)	0.0	0	4	4	2	0	4	4	2.942	0.47	experiment
B8Re2-2 (C_s)	16.4	0	3	6	1	0	2	5	2.383	1.61	*isocloso*
B8Re2-3F (C_{2v})	17.2	0	5	2	3	0	4	4	2.950	0.43	
B8Re2-4 (C_s)	18.5	1	3	3	3	0	3	4	2.707	0.82	tetracap trigon prism
B8Re2-5F (C_s)	20.9	0	5	3	1	1	5	3	2.802	0.49	
B8Re2-6 (C_2)	23.3	0	8	2	0	0	2	4	2.327	1.94	bicap square antiprism
B8Re2-7 (C_s)	24.1	2	3	1	3	1	4	3	2.719	0.55	bicap bisdisphenoid

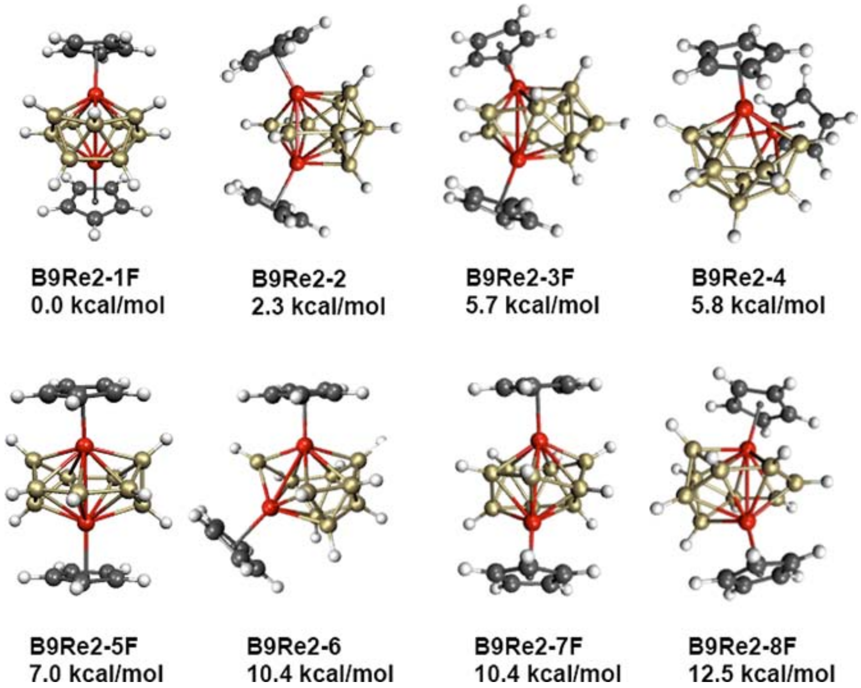


Figure 7. Eight optimized 11-vertex $Cp_2Re_2B_9H_9$ structures within 15 kcal/mol of the global minimum.

Table 4. Optimized 11-Vertex $Cp_2Re_2B_9H_9$ Structures within 15 kcal/mol of the Global Minimum

	ΔE	vertex degrees							Re−Re		
structure (symmetry)	kcal/mol	v_3	v_4	v_5	v_6	v_7	BRe_2	BRe	Å	WBI	comments
B9Re2-1F (C_s)	0.0	0	4	5	1	1	4	5	2.897	0.47	experiment
B9Re2-2 (C_s)	2.3	2	2	4	1	2	4	4	2.850	0.44	pentacap trig prism
B9Re2-3F (C_{2v})	5.7	0	3	6	2	0	4	4	2.946	0.50	
B9Re2-4 (C_1)	5.8	0	2	8	1	0	2	5	2.388	1.60	11-vertex *closo*
B9Re2-5F (C_{2v})	7.0	0	5	4	0	2	5	4	2.817	0.45	
B9Re2-6 (C_1)	10.4	0	3	6	2	0	3	6	2.711	0.84	cap 10-vertex *isocloso*
B9Re2-7F (C_2)	10.4	0	3	6	2	0	3	6	3.038	0.49	
B9Re2-8F (C_2)	12.5	0	5	4	0	2	5	4	2.830	0.48	

The lowest energy $Cp_2Re_2B_9H_9$ structure **B9Re2-1F** is the experimentally known oblate structure with one rhenium atom at a degree 6 vertex and the other rhenium atom at a degree 7 vertex (Figure 7 and Table 4). The optimized Re−Re distance of 2.897 Å for **B9Re2-1F** is somewhat longer than the experimental Re−Re distance of 2.8604(5) Å in $Cp^*_2Re_2B_9H_9$, found by X-ray crystallography.[24]

Four higher energy oblate deltahedral $Cp_2Re_2B_9H_9$ structures were found (Figure 7 and Table 4). Structures **B9Re2-3F** and **B9Re2-7F**, lying 5.7 and 10.4 kcal/mol, respectively, above **B9Re2-1F**, have both rhenium atoms located at degree 6 vertices and predicted Re−Re distances of 2.946 and 3.038 Å, respectively, through the center of the deltahedron. Structures **B9Re2-5F** and **B9Re2-8F**, lying 7.0 and 12.5 kcal/mol, respectively, above **B9Re2-1F**, have both rhenium atoms located at degree 7 vertices and predicted Re−Re distances of 2.817 and 2.830 Å, respectively, through the center of the deltahedron. In the five oblate deltahedral $Cp_2Re_2B_9H_9$ structures **B9Re2-1F**, **B9Re2-3F**, **B9Re2-5F**, **B9Re2-7F**, and **B9Re2-8F** the Re−Re distances through the center of the deltahedron are thus seen to decrease as the degrees of the rhenium vertices are increased.

Structure **B9Re2-4**, lying 5.8 kcal/mol above the global minimum **B9Re2-1F**, is the only low-energy $Cp_2Re_2B_9H_9$ structure having a short Re−Re deltahedral edge, namely, 2.388 Å (Figure 7 and Table 4). The underlying Re_2B_9 deltahedron is the most spherical 11-vertex deltahedron, namely, the edge-coalesced icosahedron (Figure 1). The high order of the Re−Re multiple bond in **B9Re2-4** is supported by its high WBI of 1.60.

The remaining two $Cp_2Re_2B_9H_9$ structures within 15 kcal/mol of the global minimum **B9Re2-1F**, both have degree 3 vertices capping Re_2B triangular faces of a smaller deltahedron (Figure 7 and Table 4). Structure **B9Re2-2**, lying 2.3 kcal/mol above **B9Re2-1F**, is a pentacapped trigonal prism with two degree 3 vertices and a predicted Re−Re distance of 2.850 Å. Structure **B9Re2-6**, lying 10.4 kcal/mol above **B9Re2-1F**, has a single degree 3 vertex capping an Re_2B triangular face of an underlying 10-vertex *isocloso* deltahedron (Figure 2). In **B9Re2−6** the Re−Re distance is 2.711 Å.

3.5. 12-Vertex Structures $Cp_2Re_2B_{10}H_{10}$.

The lowest energy $Cp_2Re_2B_{10}H_{10}$ structure is the experimentally known oblate structure **B10Re2-1F** (Figure 8 and Table 5). In **B10Re2-1F** both rhenium atoms are located at degree 7 vertices, and all boron atoms are located at either degree 4 or degree 5 vertices. The predicted Re−Re distance through the cluster of 2.870 Å is somewhat longer than the experimental Re−Re distance of 2.8192(1) Å,[24] determined by X-ray crystallography in $Cp^*_2Re_2B_{10}H_{10}$.

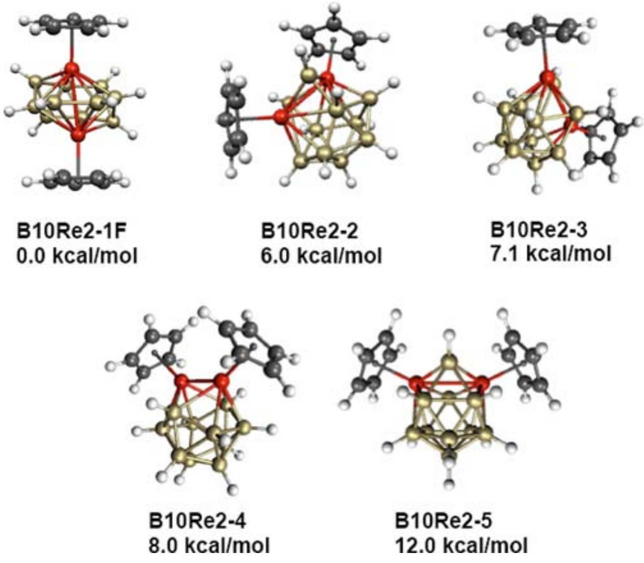


Figure 8. Five optimized 12-vertex $Cp_2Re_2B_{10}H_{10}$ structures within 20 kcal/mol of the global minimum.

Normally icosahedral structures are favored for 12-vertex borane deltahedra. The lowest energy icosahedral $Cp_2Re_2B_{10}H_{10}$ structure **B10Re2-4** lies 8.0 kcal/mol above the global minimum **B20Re2-1F** (Figure 8 and Table 5). The Re−Re edge of the Re_2B_{10} icosahedron in **B10Re2-4** is unusually short at 2.283 Å, and its WBI is a very high 2.15, suggesting a multiple surface bond for this hypoelectronic structure.

The remaining three $Cp_2Re_2B_{10}H_{10}$ structures within 18 kcal/mol of the global minimum **B10Re2-1F** all have Re−Re bonds of lengths ∼2.7 Å forming an edge of a 12-vertex deltahedron (Figure 8 and Table 5). In **B10Re2-5**, lying 12.0 kcal/mol above **B10Re2-1F**, the Re_2B_{10} deltahedron has two adjacent degree 6 vertices where the rhenium atoms are located. Structure **B10Re2-2**, lying 6.0 kcal/mol above **B10Re2-1F**, has two degree 3 vertices capping Re_2B faces of an underlying 10-vertex *isocloso* deltahedron (Figure 2). This capping pattern leads to two degree 7 vertices for the rhenium atoms. Similarly structure **B10Re2-3**, lying 7.1 kcal/mol above **B10Re2-1F**, has one degree 3 vertex capping an Re_2B face of an underlying 11-vertex *closo* deltahedron. In **B10Re2-3** one rhenium atom is located at a degree 7 vertex and the other at a degree 6 vertex.

4. DISCUSSION

The lowest energy $Cp_2Re_2B_{n-2}H_{n-2}$ structures (n = 8, 9, 10, 11, 12) found in this work were always oblate (flattened) deltahedral structures having degree 6 and/or 7 rhenium

Table 5. Optimized 12-Vertex $Cp_2Re_2B_{10}H_{10}$ Structures within 20 kcal/mol of the Global Minimum

	ΔE	vertex degrees							Re−Re		
structure (symmetry)	kcal/mol	v_3	v_4	v_5	v_6	v_7	BRe_2	BRe	Å	WBI	comments
B10Re2-1F (C_2)	0.0	0	4	6	0	2	4	6	2.870	0.48	experiment
B10Re2-2 (C_2)	6.0	2	2	4	2	2	4	4	2.740	0.58	bicap 10-vertex *isocloso*
B10Re2-3 (C_1)	7.1	1	2	6	2	1	3	5	2.721	0.79	cap 11-vertex *closo*
B10Re2-4 (C_{2v})	8.0	0	0	12	0	0	2	4	2.283	2.15	icosahedron
B10Re2-5 (C_{2v})	12.0	0	2	8	2	0	2	6	2.743	0.80	

vertices and degree 4 or 5 boron vertices. The rhenium atoms are located on opposite sides of the Re_2B_{n-2} deltahedron at the flattest parts of the deltahedral surfaces. The Re−Re distances through the deltahedra are bonding distances ranging from 2.72 to 2.94 Å. These oblate deltahedral structures are found experimentally for all of the $Cp^*_2Re_2B_{n-2}H_{n-2}$ structures,[22−24] consistent with their prediction as the lowest energy structures in our theoretical studies on $Cp_2Re_2B_{n-2}H_{n-2}$ derivatives. In some cases the oblate deltahedral structures are preferred by substantial energy margins over alternative $Cp_2Re_2B_{n-2}H_{n-2}$ structures. This is particularly true for the 9- and 10-vertex systems $Cp_2Re_2B_8H_8$, for which the oblate deltahedral structures **B7Re2-1F** and **B8Re2-1F** lie 25.0 and 16.4 kcal/mol below the next lowest energy structurea **B7Re2-2** and **B8Re2-2**, respectively (Figures 5 and 6 and Tables 2 and 3). Because of the small separation of only ~2 kcal/mol between **B9Re2-1F** and the next lowest lying isomers, the lowest energy $Cp_2Re_2B_9H_9$ structures were also optimized using the hybrid meta-GGA DFT method, M06-L, developed by Truhlar's group.[33] Again the oblate 11-vertex structure **B9Re2-1F** was found to be the lowest lying $Cp_2Re_2B_9H_9$ structure, this time by ~3 kcal/mol.

For the 10-vertex $Cp_2Re_2B_8H_8$ and the 11-vertex $Cp_2Re_2B_9H_9$ systems, several oblate deltahedral structures were found in addition to the lowest energy such structures. For $Cp_2Re_2B_8H_8$ the oblate deltahedral structures with a degree 6 boron vertex (**B8Re2-3F**) and with a degree 7 rhenium vertex (**B8Re2-5F**) both lie at higher energies than structure **B8Re2-1F** with two degree 6 rhenium vertices and all boron vertices of degrees 4 and 5 (Figure 6 and Table 3). For $Cp_2Re_2B_9H_9$ four additional oblate deltahedral structures (**B9Re2-3F, B9Re2-5F, B9Re2-7F,** and **B9Re2-8F**) lie within 13 kcal/mol of the lowest energy oblate deltahedral structure **B9Re2-1F**. In this case the lowest energy deltahedral structure **B9Re2-1F** has one degree 6 and one degree 7 rhenium vertex whereas the higher energy oblate deltahedral structures have either two degree 6 rhenium vertices (**B9Re2-3F** and **B9Re2-7F**) or two degree 7 rhenium vertices (**B9Re2-5F** and **B9Re2-8F**). In this group of five oblate deltahedral $Cp_2Re_2B_9H_9$ structures, the Re−Re distances through the deltahedron decrease with increasing rhenium vertex degrees.

The remaining $Cp_2Re_2B_{n-2}H_{n-2}$ structures (n = 8, 9, 10, 11, 12) are based on deltahedra in which the pair of rhenium atoms forms one of the edges. Of particular interest is the series of structures **B6Re2-4**, **B7Re2-2**, **B8Re2-6**, **B9Re2-4**, and **B10Re2-4** based on the corresponding most spherical *closo* deltahedra (Figure 1), namely, the bisdisphenoid, tricapped trigonal prism, bicapped square antiprism, "edge-coalesced icosahedron" (the 11-vertex *closo* deltahedron), and the icosahedron, respectively. A related structure is the 10-vertex *isocloso* deltahedral $Cp_2Re_2B_8H_8$ structure **B8Re2-2**. The Re−Re edges in these most spherical deltahedral structures are unusually short ranging from 2.283 Å in the icosahedral structure **B10Re2-4** to 2.388 Å in the 11-vertex *closo* deltahedral structure **B9Re2-4**. The unusually short Re−Re edges in these structures clearly indicate a high order multiple bond. This is supported by high WBIs for these structures ranging from 1.6 to 2.2.

The remaining $Cp_2Re_2B_{n-2}H_{n-2}$ structures found in this work are based on deltahedra having Re−Re edge lengths ranging from 2.6 to 2.9 Å, Re−Re WBIs ranging from 0.4 to 0.8, and one or two degree 3 vertices. Removal of the degree 3 vertices from these structures leads to smaller deltahedra. Structures of this type have long been known for transition metal carbonyl clusters having fewer than $2n + 2$ Wadean skeletal electrons such as the bicapped tetrahedral[34] $Os_6(CO)_{18}$ and the capped octahedral[35] $Os_7(CO)_{21}$. Dirhenaborane structures of this type include the bicapped octahedral structure **B6Re2-2** and bicapped trigonal prismatic structure **B6Re2-3** for $Cp_2Re_2B_6H_6$ (Figure 4 and Table 1) as well as the tetracapped trigonal prismatic structure **B8Re2-4** and the bicapped bisdisphenoid structure **B8Re2-7** for $Cp_2Re_2B_8H_8$ (Figure 6 and Table 3). Structures of this type for the 11-vertex rhenaborane $Cp_2Re_2B_9H_9$ include the pentacapped trigonal prismatic structure **B9Re2-2** and the capped 10-vertex *isocloso* structure **B9Re2-6**. For the 12-vertex rhenaborane $Cp_2Re_2B_{10}H_{10}$ such structures include the bicapped 10-vertex *isocloso* structure **B10Re2-2** and the capped 11-vertex *closo* structure **B10Re2-3**.

5. CONCLUSIONS

The experimentally known oblate (flattened) deltahedral structures[22−24] are found by density functional theory to be the lowest energy structures for the dirhenaboranes $Cp_2Re_2B_{n-2}H_{n-2}$ (n = 8, 9, 10, 11, 12). These structures have degree 6 and/or 7 rhenium vertices at the flattest regions on opposite sides of an axially compressed deltahedron. This leads to bonding Re=Re distances ranging from 2.69 to 2.94 Å, which have been interpreted[25] as internal double bonds. In some cases the energy differences between such oblate deltahedral structures and the next highest energy structures are quite considerable, that is, up to 25 kcal/mol for the nine-vertex $Cp_2Re_2B_7H_7$ structures. This suggests that in this size range the oblate deltahedral structures are particularly favorable relative to other possible such structures.

The higher energy $Cp_2Re_2B_{n-2}H_{n-2}$ structures are of the following two types: (1) Most spherical (*closo*) deltahedra (Figure 1) having unusually short 2.28 to 2.39 Å Re−Re edges with unusually high WBIs of 1.6 to 2.2 suggesting high order multiple bonds on the deltahedral surface; (2) Deltahedra having one or two degree 3 vertices and 2.6 to 2.9 Å Re−Re edges. The latter deltahedra are derived from smaller deltahedra by capping Re_2B faces with the degree 3 boron vertices, thereby forming Re_2B_2 tetrahedral cavities.

■ ASSOCIATED CONTENT

Supporting Information

Table S1, the $Cp_2Re_2B_6H_6$ structures; Table S2, the $Cp_2Re_2B_7H_7$ structures; Table S3, the $Cp_2Re_2B_8H_8$ structures; Table S4, the $Cp_2Re_2B_9H_9$ structures; Table S5, the $Cp_2Re_2B_{10}H_{10}$ structures; complete Gaussian09 Reference (reference 32). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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