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Oblate Deltahedra in Dimetallaboranes: Geometry and Chemical Bonding

R. B. King*

Department of Chemistry, University of Georgia, Athens, Georgia 30602

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A new series of nonspherical and very oblate deltahedra, conveniently called the oblatocloso deltahedra, is found in dimetallaboranes among which the dirhenaboranes $Cp_2Re_2B_{n-2}H_{n-2}$ ($8 \leq n \leq 12$) are the prototypes. The D_{6h} hexagonal bipyramid is the first member of this series ($n = 8$). However, the higher members of the series are not bipyramids but are derivable from them by a number of diamond–square–diamond processes. A viable model for the skeletal bonding in the oblatocloso dimetallaboranes can be developed if the two metal vertices, typically degree 6 or 7 vertices, are assumed each to contribute five internal orbitals rather than the three internal orbitals assumed by the Wade–Mingos rules. This leads to $2n + 4$ actual skeletal electrons for an n vertex oblatocloso dimetallaborane rather than the Wadean $2n - 4$ skeletal electrons. The surface bonding of an n vertex oblatocloso dimetallaborane then consists of n three-center two-electron bonds similar to that in corresponding isocloso metallaboranes thereby leaving four orbitals and four electrons for a metal–metal double bond inside the deltahedron. Removal of one or two boron vertices from oblatocloso deltahedra leads to oblatonido and oblatoarachno dimetallaboranes, respectively, having the same number of skeletal electrons as the oblatocloso deltahedra from which they are derived.

1. Introduction

The structures of metal-free polyhedral boranes and isoelectronic carboranes are long known to be derived from the so-called most spherical deltahedra, also known as closo deltahedra.[1,2] The vertices in these closo deltahedra are as nearly similar as possible so that the 6−12-vertex closo deltahedra generally have either degree 4 or 5 vertices. The only exception is 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. Note that a deltahedron is a polyhedron in which all faces are triangles and the degree of a vertex is the number of polyhedral edges meeting at the vertex in question.

The number of skeletal electrons in polyhedral boranes and isoelectronic carboranes 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 $C_2B_{n-2}H_n$, are particularly stable.

The vertices in the closo deltahedral boranes and related carboranes were shown by Hawthorne and co-workers[10] to be replaceable by isolobal transition metal vertices, typically units of the type CpM or $M(CO)_3$ (Cp = η^5-cyclopentadienyl; M = transition metal). Initially, it was assumed that such substitution of a light atom vertex (boron or carbon) by a transition metal vertex did not affect the underlying closo deltahedral geometry since the initially discovered derivatives were metallaboranes based on MC_2B_9 icosahedra, in which all vertices have the same degree, namely 5. However, as metallaborane chemistry was subsequently developed involving polyhedra other than the icosahedron, particularly by Kennedy and co-workers,[11−14] a variety of deltahedral

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* E-mail: rbking@chem.uga.edu.

(1) Williams, R. E *Inorg. Chem.* **1971**, *10*, 210.
(2) Williams, R. E. *Chem. Rev.* **1992**, *92*, 177.
(3) King, R. B.; Duijvestijn, A. J. W. *Inorg. Chim. Acta* **1990**, *178*, 55.
(4) Wade, K. *Chem. Commun.* **1971**, 792.
(5) Mingos, D. M. P. *Nature Phys. Sci.* **1972**, *99*, 236.
(6) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.
(7) Aihara, J.-I. *J. Am. Chem. Soc.* **1978**, *100*, 3339.
(8) King, R. B.; Rouvray, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 7834.
(9) King, R. B. *Chem. Rev.* **2001**, *101*, 1119.
(10) Callahan, K. P.; Hawthorne, M. F. *Adv. Organomet. Chem.* **1976**, *14*, 145.
(11) Bould, J.; Kennedy, J. D.; Thornton-Pett, M., *J. Chem. Soc., Dalton*, **1992**, 563.

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metallaborane structures were discovered based on deltahedra topologically distinct from the closo deltahedra. This led to the identification of a new class of less-spherical deltahedra for metallaboranes and metallacarboranes called either isocloso[15] or hypercloso[16−18] deltahedra; they will be called isocloso deltahedra in this paper. These isocloso metallaborane deltahedra are derived from the closo metal-free borane deltahedra by a diamond−square−diamond (dsd) process, typically generating a degree 6 vertex for the metal atom. The driving force behind this rearrangement is the preference of transition metals for higher-degree vertices than carbon or boron atoms. Whereas metal-free boranes and carboranes are known for all of the closo deltahedra between the octahedron and icosahedron, namely those with 6−12 vertices, distinctive isocloso deltahedra are known only for a more limited vertex range, namely 9−12 vertices.

An initially unexpected property of the isocloso metallaboranes was their failure to obey the Wade−Mingos rules,[4−6] which were derived from consideration of metal-free borane and carborane polyhedra. Thus, the isocloso metallaborane deltahedra with n vertices are found to have $2n$ skeletal electrons rather than the $2n + 2$ skeletal electrons of the generally metal-free closo borane and carborane deltahedra predicted by the Wade−Mingos rules.

The further development of metallaborane chemistry, particularly in the laboratory of Fehlner and co-workers,[19] led to the discovery of dimetallaboranes exhibiting structures based on previously unknown deltahedra. This new family of deltahedra is characterized by highly oblate (flattened) structures with the two metal atoms 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 four of the degrees of many of the remaining vertices for the boron atoms. These highly oblate deltahedra, found so far only in dimetallaboranes of Group 6 and Group 7 transition metals, are conveniently called oblatocloso deltahedra to differentiate them from the closo and isocloso deltahedra discussed above. The most complete set of stable compounds exhibiting oblatocloso deltahedral structures are found in the cyclopentadienylrhenium dimetallaboranes $Cp_2Re_2B_{n-2}H_{n-2}$ ($8 \leq n \leq 12$; Cp = an η^5-cyclopentadienyl ligand, most commonly η^5-Me_5C_5).[20−22] These oblatocloso dirhenaboranes all have $2n - 4$ Wadean skeletal electrons. In this connection, Wadean skeletal electrons are defined as the skeletal electrons counted using the Wade−Mingos procedure,[4−6] which artificially assumes that the two rhenium vertices provide the typical three internal orbitals for skeletal bonding. Thus, the Wadean skeletal electron count may not necessarily correspond to the actual number of skeletal electrons. Because of their Wadean skeletal electron count, the oblatocloso structures appear even more hypoelectronic than expected by extrapolation beyond the metal-free closo deltahedral boranes with $2n + 2$ skeletal electrons and the isocloso deltahedral metallaboranes with $2n$ skeletal electrons

In 2001, the author attempted to analyze the skeletal bonding in such dimetallaborane structures when only a few such structures were known.[23] Thus, at that time the only known member of the $Cp_2Re_2B_{n-2}H_{n-2}$ series was the nine-vertex oblatocloso structure $Cp_2Re_2B_7H_7$, as well as the isoelectronic $Cp_2W_2B_7H_9$.[24,25] The 2001 paper[23] also discusses a number of other dimetallaboranes such as $Cp_2M_2B_nH_{n+4}$ (M = Cr,[26−28] Mo,[29] W;[30] n = 4, 5[31]), which are now seen to be oblatonido and oblatoarachno derivatives derived from a larger oblatocloso deltahedron by removal of one or two vertices. This paper revisits the geometry/topology of these dimetallaborane oblato polyhedra, as well as their skeletal bonding, in light of the subsequent discovery[20−22] of what might well be the complete set of oblatocloso polyhedra in the series $Cp_2Re_2B_{n-2}H_{n-2}$ ($8 \leq n \leq 12$).

2. Geometry and Topology of Oblato Polyhedra

2.1. The oblatocloso deltahedra. The oblatocloso deltahedra are depicted in Figure 1, and their important properties are listed in Table 1. All of the oblatocloso deltahedra are characterized by two antipodal or nearly antipodal vertices of higher degree than any of the other vertices (typically degrees 6 or 7). These two pseudoantipodal high-degree vertices are the metal vertices in the dimetallaboranes. The remaining vertices typically have degrees of 4 or 5 and are boron vertices in most of the known dimetallaboranes. However, a hexagonal bipyramidal oblatocloso dimetalladicarbaborane $(\eta^5\text{-}Me_5C_5)_2Cr_2B_4H_4C_2(CH_2)_3$ is known with two equatorial carbon vertices bridged by a trimethylene group.

The oblatocloso deltahedra can, of course, be characterized by the usual polyhedral properties such as the numbers of vertices of various degrees, typically from 4 to 7. However,

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(12) Kennedy, J. D.; Štibr, B. In *Current Topics in the Chemistry of Boron*; Kabalka, G. W., Ed.; Royal Society of Chemistry: Cambridge, 1994; pp 285−292.

(13) Kennedy, J. D. In *The Borane-Carborane-Carbocation Continuum*; Casanova, J., Ed.; Wiley: New York, 1998; Chapter 3, pp 85−116.

(14) Štibr, B.; Kennedy, J. D.; Drdáková, E.; Thornton-Pett, M., *J. Chem. Soc., Dalton Trans.* **1994**, 229.

(15) Kennedy, J. D. *Inorg. Chem.* **1986**, *25*, 111.

(16) Baker, R. T. *Inorg. Chem.* **1986**, *25*, 109.

(17) Johnston, R. L.; Mingos, D. M. P. *Inorg. Chem.* **1986**, *25*, 3321.

(18) Johnston, R. L.; Mingos, D. M. P.; Sherwood, P. *New J. Chem.* **1991**, *15*, 831.

(19) For a review of much of the relevant chemistry from Fehlner's group, see Fehlner, T. P. In *Group 13 Chemistry: From Fundamentals to Applications*; Shapiro, P. J., Atwood, D. A., Eds; American Chemical Society: Washington, D. C., 2002; pp 49−67.

(20) Ghosh, S.; Shang, M.; Li, Y.; Fehlner, T. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 1125.

(21) Wadepohl, H. *Angew. Chem. int. Ed.* **2002**, *41*, 4220.

(22) Le Guennic, B.; Jiao, H.; Kahlal, S.; Saillard, J.-Y.; Halet, J.-F.; Ghosh, S.; Shang, M.; Beatty, A. M.; Rheingold, A. L.; Fehlner, T. P. *J. Am. Chem. Soc.* **2004**, *126*, 3203.

(23) King, R. B. *Inorg. Chem.* **2001**, *40*, 2699.

(24) Weller, A. S.; Shang, M.; Fehlner, T. P. *Chem. Commun.* **1998**, 1788.

(25) Weller, A. S.; Shang, M.; Fehlner, T. P. *Organometallics* **1999**, *18*, 853.

(26) Ho, J.; Deck, K. J.; Nishihara, Y.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1995**, *117*, 10292.

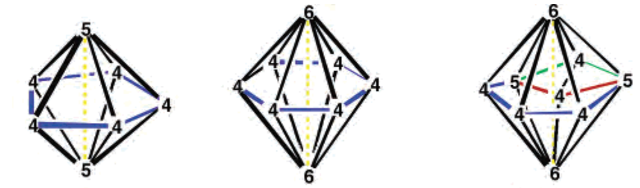
(27) Fehlner, T. P. *J. Organomet. Chem.* **1998**, *550*, 21.

(28) Aldridge, S.; Hashimoto, H.; Kawamura, K.; Shang, M.; Fehlner, T. P. *Inorg. Chem.* **1998**, *37*, 928.

(29) Aldridge, S.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1998**, *120*, 2586.

(30) Weller, A. S.; Shang, M.; Fehlner, T. P. *Organometallics* **1999**, *18*, 53.

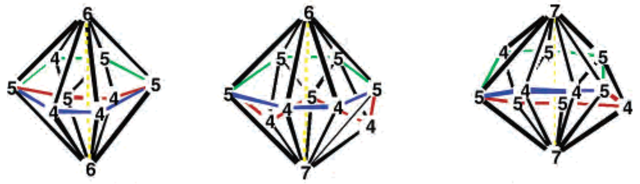
(31) Weller, A. S.; Fehlner, T. P. *Organometallics* **1999**, *18*, 447.



7 vertices (pentagonal bipyramid)

8 vertices (hexagonal bipyramid)

9 vertices



10 vertices

11 vertices

12 vertices

Figure 1. Oblatocloso deltahedra having from 7 to 12 vertices. The edges of the polygonal fences are colored, and the metal−metal bond inside the deltahedron is indicated by a yellow dashed line. In Figures 1, 2, and 4, the vertices are numbered according to their degrees.

Table 1. Some Properties of the Oblatocloso Deltahedra Found in the $Cp_2Re_2B_nH_n$ Derivatives

no. of vertices	vertex degrees				BM_2	BM	Re−Re in $Cp_2Re_2B_nH_n$, Å
	v_4	v_5	v_6	v_7			
7	5	2	0	0	5	0	
8	6	0	2	0	6	0	2.689
9	5	2	2	0	5	2	2.787
10	4	4	2	0	4	4	2.835
11	4	5	1	1	5	4	2.860
12	4	6	0	2	6	4	2.819

because of their unusual nature with two pseudoantipodal vertices of uniquely relatively high degrees (conveniently called the metal vertices), there are some unusual ways of characterizing and visualizing these deltahedra. Thus, the lower-degree vertices in these oblatocloso deltahedra (conveniently called the boron vertices) can be partitioned into two types designated as BM and BM_2 vertices depending on whether they share edges with one or two metal vertices, respectively. No boron vertices are found in the known oblatocloso deltahedra that do not share at least one edge with a metal vertex, probably since the existence of such boron vertices would leave the two metal vertices too far apart to form a strong metal−metal bond inside the deltahedron.

A related concept is that of a *polygonal fence* around the metal vertices in the oblatocloso deltahedra. In this connection, a polygonal fence is defined as the polygon formed by the boron vertices sharing an edge with the metal vertex in question. If the metal vertex is a degree 6 vertex, its polygonal fence is a hexagon. However, if the metal vertex is a degree 7 vertex, its polygonal fence is a heptagon. The locations of the two polygonal fences in the oblatocloso dimetallaborane deltahedra are a useful aid in visualizing these rather unfamiliar polyhedra. For this reason, the edges of the two polygonal fences are color-coded in Figure 1 as follows. Blue, edges common to the polygonal fences of both metal vertices; green, edges unique to the polygonal fence of the "top" metal vertex; red, edges unique to the polygonal fence of the "bottom" metal vertex; black, edges not part of any polygonal fence.

The simplest oblatocloso deltahedra are bipyramids in which the two metal vertices are axial vertices sharing the same polygonal fence (completely blue in Figure 1). The seven-vertex pentagonal bipyramid is the smallest deltahedron that meets the requirements of an oblatocloso deltahedron by having two antipodal vertices of distinctly higher degree than the remaining vertices. No pentagonal bipyramidal oblatocloso borane is known experimentally. The eight-vertex oblatocloso deltahedron is the hexagonal bipyramid with degree 6 metal vertices and degree 4 boron vertices. This is found in $Cp_2Re_2B_6H_4Cl_2$ (ref 22).

The remaining four oblatocloso deltahedra in Figure 1, namely those with 9−12 vertices, are all found in derivatives of the type $Cp_2Re_2B_{n-2}H_{n-2}$ ($9 \leq n \leq 12$).[20−22] The first two of these deltahedra, namely those with 9 and 10 vertices, are characterized by having two degree 6 metal vertices such as the hexagonal bipyramid. In the nine-vertex oblatocloso deltahedron, the two polygonal fences share four edges so there are five BM_2 and two BM vertices. In the 10-vertex oblatocloso deltahedron, the two polygonal fences share three edges so there are four BM_2 and four BM vertices. Note that for both the 9- and 10-vertex oblatocloso deltahedra the vertices common to the polygonal fences of both metal vertices (i.e., the BM_2 vertices) are connected by a linear path. Such a set of BM_2 vertices is called a set of *fully connected* BM_2 vertices.

Degree 7 metal vertices begin to appear in the oblatocloso deltahedron with 11 vertices (Figure 1), which has one degree 7 and one degree 6 metal vertex. In this polyhedron, the two polygonal fences share three edges so that there are four BM_2 and five BM vertices. In the 12-vertex oblatocloso deltahedron, both metal vertices are degree 7 vertices and the two polygonal fences again share three edges leading to four BM_2 and six BM vertices. For both the 11- and 12-vertex oblatocloso deltahedra, the BM_2 vertices are fully connected.

The smallest oblatocloso deltahedron, which is not a bipyramid, is the nine-vertex deltahedron. This deltahedron, which is found in $Cp_2Re_2B_7H_7$ and $Cp_2W_2B_7H_9$ (ref 25), is derived from the heptagonal bipyramid by two dsd rearrangements depicted in Figure 2 using the same color coding as in Figure 1. Each dsd rearrangement reduces the degree of one of the metal vertices from 7 to 6 and converts a BM_2 boron vertex into a BM boron vertex. Note that the BM_2 vertices remain fully connected throughout this process. Similar sequences of dsd processes keep the remaining BM_2 vertices fully connected while converting higher bipyramids to the oblatocloso deltahedra observed in the $Cp_2Re_2B_{n-2}H_{n-2}$ ($9 \leq n \leq 12$) structures.[20−22] Thus, fully connected BM_2 vertices appear to be a property of the oblatocloso deltahedra and allow such deltahedra to approximate as closely as possible the corresponding bipyramids while lowering to 6 or 7 the degrees of the metal vertices.

2.2. Oblatonido and oblatoarachno polyhedra. Removal of a vertex from an $n + 1$ vertex closo deltahedron generates a so-called nido polyhedron with n vertices and one non-triangular face where the vertex was removed. The num-

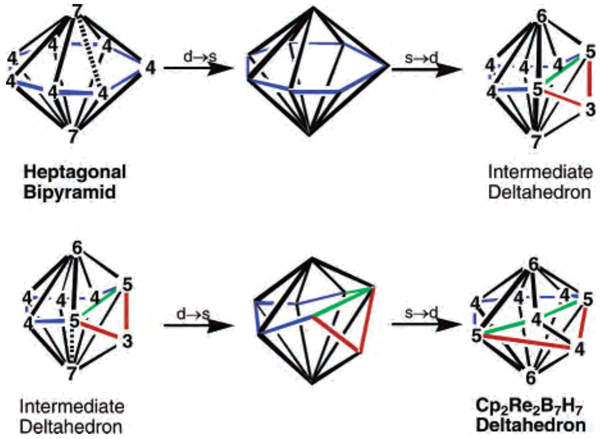


Figure 2. Sequence of diamond−square−diamond (dsd) processes converting the heptagonal bipyramid into the oblatocloso deltahedron found in $Cp_2Re_2B_7H_7$ with the same color coding as in Figure 1.

ber of skeletal electrons in a nido polyhedron with n vertices is the same as that in the closo deltahedron with $n + 1$ vertices from which the nido polyhedron is derived. Thus, the $2(n + 1) + 2$ skeletal electrons of the original $(n + 1)$-vertex closo polyhedron corresponds to $2n + 4$ skeletal electrons for the corresponding n-vertex nido polyhedron.

An analogous procedure can be used to generate arachno polyhedra with n vertices by removal of two vertices from a closo deltahedron with $n + 2$ vertices. If the two vertices removed from the closo deltahedron are adjacent vertices, a new single large hole will be found in the corresponding arachno polyhedron. However, if the two vertices removed from the closo deltahedron are nonadjacent vertices, then two new nontriangular faces will be generated in the arachno polyhedron. The arachno polyhedra with n vertices have the same number of skeletal electrons as the closo deltahedra with $n + 2$ vertices from which they are derived, i.e., $2(n + 2) + 2 = 2n + 6$.

Analogous procedures can be used to generate oblatonido and oblatoarachno polyhedra having n vertices from oblatocloso deltahedra having $n + 1$ and $n + 2$ vertices, respectively. Again, the number of Wadean skeletal electrons of the original oblatocloso deltahedron is maintained so that n-vertex oblatonido polyhedra have $2(n + 1) - 4 = 2n - 2$ Wadean skeletal electrons and oblatoarachno polyhedra n vertices have $2(n + 2) - 4 = 2n$ Wadean skeletal electrons.

The simplest oblatonido and oblatoarachno polyhedra are derived from the bipyramidal oblatocloso deltahedra. Thus, removal of a single equatorial vertex from the pentagonal and hexagonal bipyramids leads to the oblatonido polyhedra found in the cyclopentadienylchromium derivatives[26−28] $Cp_2Cr_2B_4H_8$ and $Cp_2Cr_2B_5H_9$, respectively, (Figure 3). These polyhedra have the 10 ($=2n - 4$ for $n = 7$) and 12 ($=2n - 4$ for $n = 8$) Wadean skeletal electrons, respectively, of the original bipyramids. Note that, in counting the Wadean skeletal electrons in these chromium derivatives, the CpCr vertices are "donors" of −1 skeletal electron each, reflecting the assumption of three internal orbitals for these vertices. Similarly the dirhenachloroborane[22] $Cp_2Re_2B_5Cl_5H_2$ has an oblatonido structure derived by removal of one equatorial vertex from a hexagonal bipyramid. This dirhenachloroborane also has the 12 Wadean skeletal electrons of the oblatocloso hexagonal bipyramid from which it is derived.

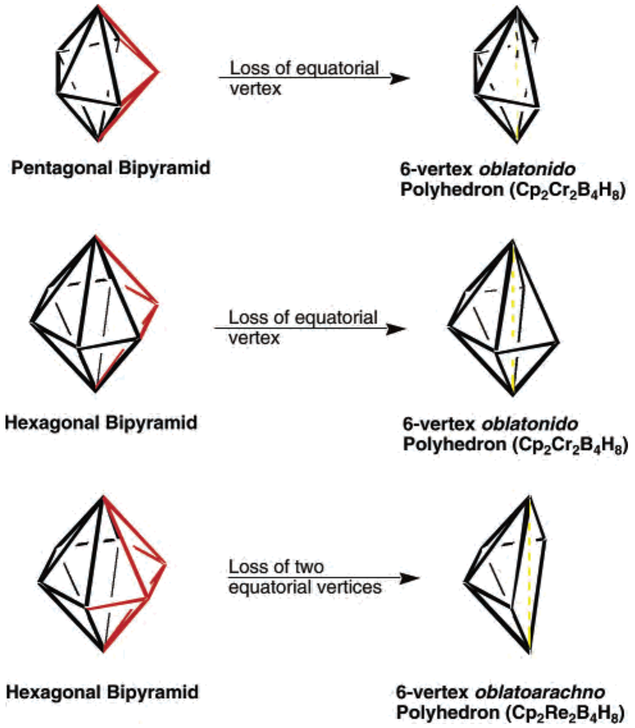


Figure 3. Generation of oblatonido and oblatoarachno polyhedra from bipyramids. The vertices and associated edges being removed from the bipyramid are shown in red and the endopolyhedral metal−metal bonds in the final oblatonido or oblatoarachno polyhedra are shown as yellow dashed lines.

The dirhenaborane[32] $Cp_2Re_2B_4H_8$ has the same skeletal topology as $Cp_2Cr_2B_4H_8$ but two more skeletal electrons. It may thus be considered as an oblatoarachno derivative obtained by removal of two adjacent vertices from a hexagonal bipyramid (Figure 3). Note that the oblatoarachno "hole" in $Cp_2Re_2B_4H_8$ obtained by removal of two adjacent equatorial vertices from a hexagonal bipyramid is very similar to the oblatonido open face obtained by removal of one equatorial vertex from a pentagonal bipyramid $Cp_2Cr_2B_4H_4$. This is very similar to the long-known similar non-hydrogen atom topology[33] in *nido*-$B_{10}H_{14}$ and *arachno*-$B_{10}H_{14}^{2-}$.

An interesting oblatoarachno derivative is the nine-vertex dirhenaborane[34] $Cp_2Re_2B_7H_{11}$, whose structure can be derived from an 11-vertex oblatocloso deltahedron by removal of two adjacent degree 5 vertices to give a hexagonal open face (Figure 4). However, the starting oblatocloso 11-vertex deltahedron before removal of the two vertices is different from the oblatocloso 11-vertex deltahedron found in $Cp_2Re_2B_9H_9$ in the following ways: (1) It has higher symmetry (C_{2v}) than the C_s symmetry of $Cp_2Re_2B_9H_9$. (2) The two metal vertices have degree 7, whereas in $Cp_2Re_2B_9H_9$, one metal vertex has degree 6 and the other degree 7. (3) Its five BM_2 vertices are disconnected into one set of three and

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(32) Ghosh, S.; Shang, M.; Fehlner, T. P. *J. Organomet. Chem.* **2000**, *614−615*, 92.

(33) King, R. B. *Inorg. Chem.* **2003**, *42*, 3412.

(34) Ghosh, S.; Rheingold, A. L.; Fehlner, T. P. *Chem. Commun.* **2001**, 895.

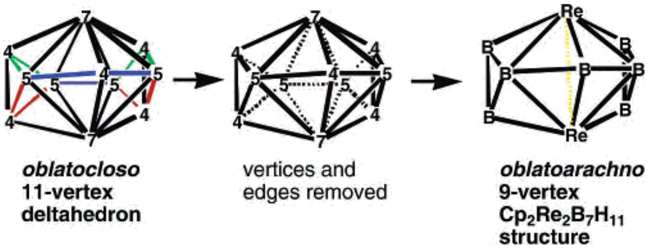

Figure 4. Generation of the oblatoarachno $Cp_2Re_2B_7H_{11}$ structure by removing two adjacent degree 5 vertices from an 11-vertex oblatocloso deltahedron different from that found in $Cp_2Re_2B_9H_9$.

one set of two, whereas the five BM_2 vertices in $Cp_2Re_2B_9H_9$ are fully connected as in the other $Cp_2Re_2B_{n-2}H_{n-2}$ derivatives (Figure 1, $n = 8-12$). Note that $Cp_2Re_2B_7H_{11}$ and $Cp_2Re_2B_9H_9$ have the same number of apparent skeletal electrons, namely 18 ($=2n - 4$ for $n = 11$).

3. Chemical Bonding

First consider a closo borane or isoelectronic carborane deltahedron with n vertices in which all of the vertices are boron or carbon atoms having four-orbital sp^3 valence manifolds. Using one of the four valence orbitals on each vertex atom for external bonding leaves three internal orbitals per vertex atom for a total of $3n$ orbitals for the internal skeletal bonding of the deltahedron. These $3n$ internal orbitals are partitioned into two twin internal or tangential orbitals per vertex atom and a single unique internal or radial orbital per vertex atom for a total of $2n$ tangential orbitals and n radial orbitals. Pairwise overlap between the $2n$ tangential orbitals is responsible for the surface bonding of the deltahedron and splits these $2n$ tangential orbitals into n bonding and n antibonding orbitals corresponding to n two-center two-electron (2c−2e) bonds along a Hamiltonian circuit in the surface of the deltahedron. In this connection, a Hamiltonian circuit in a polyhedron starts at a given vertex and goes to all of the other vertices without visiting any vertex twice. This surface-bonding model is a localized model; the actual surface bonding is a resonance hybrid using all of the possible Hamiltonian circuits on the closo deltahedron.

This surface bonding in closo deltahedra is supplemented by an n-center core bond formed by mutual overlap of the n radial bonding orbitals leading to one additional bonding orbital and $n - 1$ antibonding orbitals. The combination of the surface and core bonding thus leads to a total of $n + 1$ bonding orbitals. Filling each of these bonding orbitals with an electron pair leads to the $2n + 2$ skeletal electrons required by the Wade−Mingos rules[4−6] for a globally delocalized three-dimensional aromatic[7−9] closo deltahedron.

Now consider an isocloso metallaborane deltahedron having n vertices and only $2n$ Wadean skeletal electrons. Such an isocloso metallaborane with $2n$ Wadean skeletal electrons can at least formally be derived from a *closo* metallaborane with $2n + 2$ Wadean skeletal electrons by a two-electron oxidation. Such a two-electron oxidation is actually known experimentally in the reported[35] reaction of the [*closo*-(η^6-arene)RuB_9H_9]$^{2-}$ dianion with dioxygen to give neutral *isocloso*-(η^6-arene)RuB_9H_9. Now assume that each vertex atom in an isocloso metallaborane uses three internal orbitals for the bonding in the deltahedral skeleton. Transition metal vertices with a nine-orbital sp^3d^5 manifold then have six external orbitals in contrast to a boron or carbon vertex without accessible d orbitals having only a four-orbital sp^3 manifold. Some of the six assumed external orbitals of a transition metal vertex are involved in bonding to external ligands, typically cyclopentadienyl or arene rings in many of the isocloso metallaboranes including *isocloso*-(η^6-arene)-RuB_9H_9 mentioned above. If the metal vertex has the favored 18-electron configuration, the external orbitals not involved in metal−ligand bonding contain lone pairs of electrons.

An n-vertex isocloso metallaborane thus has $3n$ internal orbitals but only $2n$ skeletal electrons, which is exactly what is needed for n three-center two-electron (3c−2e) bonds in n of the $2n - 4$ faces of the deltahedron. Such bonding models for isocloso metallaboranes, discussed in detail in previous papers,[36,37] suggest that the bonding in isocloso metallaboranes is exclusively surface bonding composed of 3c−2e bonds. Thus conversion of a closo deltahedral metallaborane to an isocloso deltahedral metallaborane with the same number of vertices by a two-electron oxidation has the overall effect of removing the electrons of the n-center core bond of the closo structure leaving only the surface bonding. The n extra internal orbitals released upon removal of the core bonding electrons in the closo → isocloso metallaborane oxidation are now available for surface bonding, thereby converting the n formal 2c−2e surface bonds of the closo deltahedron into the n formal 3c−2e bonds of the corresponding isocloso deltahedron.

Now consider an n-vertex oblatocloso deltahedral dimetallaborane having $2n - 4$ Wadean skeletal electrons of which the $Cp_2Re_2B_{n-2}H_{n-2}$ derivatives[20−22] (Figure 1) can be considered as the prototypes. This $2n - 4$ Wadean skeletal electron count artificially assumes that each rhenium vertex uses three of the nine orbitals of its sp^3d^5 manifold for skeletal bonding so that each CpRe vertex is a formal donor of zero skeletal electrons. A more realistic chemical bonding scheme for these oblatocloso deltahedral dimetallaboranes has each rhenium vertex using five rather than only three of the nine orbitals of its sp^3d^5 manifold, thereby drawing two otherwise external lone pairs into the skeletal bonding. The introduction of these “extra” two lone pairs from each CpRe vertex into the skeletal bonding makes these vertices four skeletal electron donors rather than zero skeletal electron donors. This is reasonable because the oblate nature of the relevant deltahedra leads to a relatively low curvature at the sites of the metal vertices, thereby facilitating introduction of otherwise nonbonding lone pairs into the skeletal bonding.

Introduction of two otherwise nonbonding lone pairs from each CpRe vertex in the oblatocloso $Cp_2Re_2B_{n-2}H_{n-2}$ dimetallaboranes into the skeletal bonding adds eight skeletal electrons to the Wadean skeletal electron count. These apparently hypoelectronic deltahedra with $2n - 4$ Wadean

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(35) Littger, R.; Englich, U.; Ruhlandt-Senge, K.; Spencer, J. T. *Angew. Chem., Int. Ed.* **2000**, *39*, 1472.

(36) King, R. B. *Inorg. Chem.* **1996**, *35*, 5151.

(37) King, R. B. *Inorg. Chim. Acta* **2000**, *300−302*, 537.

skeletal electrons now become deltahedra having $(2n - 4) + 8 = 2n + 4$ *actual* skeletal electrons, implying that such deltahedra should contain $n + 2$ skeletal bonds of some type. Furthermore, there are $3(n - 2)$ internal orbitals from the $n - 2$ boron vertices and $2 \times 5 = 10$ internal orbitals from the two rhenium vertices for a total of $3n + 4$ internal orbitals. This corresponds to a skeletal bonding topology with n 3c−2e bonds and two 2c−2e bonds.

Assume now that the surface bonding in the oblatocloso dimetallaboranes with n vertices is the same as that in the isocloso metallaboranes, namely n 3c−2e bonds requiring $2n$ skeletal electrons and $3n$ skeletal orbitals.[36,37] The "extra" skeletal electrons and internal orbitals left over after this surface bonding, namely four skeletal electrons and four internal orbitals, correspond to a metal═metal double bond inside the deltahedron. In this connection the Re═Re distance of 2.723 Å found by X-ray crystallography[38] in $(\eta^5\text{-}Me_5C_5)_2Re_2(CO)_4$, which is required to have a Re═Re double bond for each rhenium atom to have the favored 18-electron configuration, is within the observed range of 2.69−2.82 Å of rhenium−rhenium distances found in the $Cp_2Re_2B_{n-2}H_{n-2}$ derivatives.[20−22]

We thus see an interesting progression in the series of closo → isocloso → oblatocloso/borane → metallaborane → dimetallaborane deltahedra. All of these three types of n vertex deltahedra have n formal surface bonds, which may be either two-center or three-center bonds depending on the available number of internal orbitals. The closo deltahedra supplement their surface bonding with an n-center two-electron (nc−2e) core bond. The two electrons removed from a closo deltahedron upon oxidation to give the corresponding isocloso deltahedron come ultimately from the nc−2e core bond, thereby breaking this bond. This leaves only the n surface bonds in the isocloso deltahedron, but now as 3c−2e rather than 2c−2e bonds because of the release of n empty internal orbitals upon breaking the core bond. Bringing two additional lone pairs from each of the two metal atoms to give the oblatocloso dimetallaborane deltahedra can retain the n surface bonds as 3c−2e bonds but adds a new metal−metal double bond inside the deltahedron using the extra four skeletal electrons and the extra four internal orbitals.

This model for the skeletal bonding in n vertex oblatocloso deltahedra differs from a model discussed in a previous paper[23] for $Cp_2Re_2B_7H_7$ in which the n 3c−2e surface bonds are supplemented by one of the two 2c−2e bonds so that there are a total of $n + 1$ surface bonds. The metal−metal bond inside the deltahedron is then only a single 2c−2e bond rather than a double bond. Although this model cannot be rigorously excluded, it appears less likely since it requires the surface bonding in oblatocloso n vertex dimetallaboranes with n 3c−2e bonds and one 2c−2e bond to be fundamentally different from that of the isocloso n vertex metallaboranes with only the n 3c−2e bonds.

4. Summary

A new series of nonspherical and very oblate deltahedra, conveniently called the oblatocloso deltahedra, is found in dimetallaboranes among which the dirhenaboranes $Cp_2Re_2B_{n-2}H_{n-2}$ ($8 \leq n \leq 12$) are the prototypes. The D_{6h} hexagonal bipyramid is the first member of this series ($n = 8$) with the two metal atoms at the degree 6 vertices in antipodal positions on the C_6 axis. The higher members of the series are not bipyramids. However, they can be derived from n-vertex bipyramids by a sequence of dsd processes reducing the degrees of the axial vertices of the original bipyramid. In all of these n-vertex oblatocloso deltahedra with ($8 \leq n \leq 12$), the two nearly antipodal metal vertices have degrees 6 or 7 and the remaining boron vertices have degrees 4 or 5. Removal of one or two boron vertices from oblatocloso deltahedra leads to oblatonido and oblatoarachno dimetallaboranes, respectively, having the same number of skeletal electrons as the deltahedra from which they are derived.

A viable model for the skeletal bonding in the oblatocloso dimetallaboranes can be developed if each of the two metal vertices is assumed to contribute five internal orbitals rather than the three internal orbitals assumed by the Wade−Mingos rules.[4−6] This leads to $2n + 4$ actual skeletal electrons for an n vertex oblatocloso dimetallaborane rather than the Wadean $2n - 4$ skeletal electron count for these structures. The surface bonding of an n-vertex oblatocloso dimetallaborane then consists of n 3c−2e bonds similar to that in corresponding isocloso metallaboranes. This leaves four orbitals and four electrons for a metal−metal double bond inside the oblatocloso deltahedron.

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[38] Casey, C. P.; Sakaba, H.; Hazin, P. N.; Powell, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 8165.