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REGULAR ARTICLE

Chemical bonding in *oblatonido* ditantalaboranes and related compounds

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Abstract The recently discovered ditantalaboranes $Cp_2Ta_2B_nH_{n+6}$ ($n = 4, 5$) are isoelectronic with the previously discovered dimetallaboranes $Cp_2M_2B_nH_{n+4}$ of the group 6 metals Cr, Mo, and W where Cp = η^5-cyclopentadienyl or substituted cyclopentadienyl. Their *oblatonido* polyhedral structures can be derived from the oblate (flattened) deltahedra of the *oblatocloso* dirhenaboranes $Cp_2Re_2B_{n+1}H_{n+1}$ by removal of an equatorial BH vertex with adjustment of the skeletal electron count by changing the metal atoms and adding hydrogen atoms. In these *oblatocloso* dirhenaborane deltahedra, the approximately antipodal rhenium atoms are close enough together to form a formal Re=Re double bond with lengths in the range 2.69–2.82 Å. Similarly, short M=M distances are maintained in the related *oblatonido* derivatives $Cp_2Ta_2B_nH_{n+6}$ ($n = 4, 5$) and $Cp_2M_2B_nH_{n+4}$ (M=Cr, Mo, W). However, the synthesis of $Cp_2Ta_2B_nH_{n+6}$ ($n = 4, 5$) from $CpTaCl_4 + LiBH_4/BH_3$ also gives a less-reduced product $Cp_2Ta_2Cl_2B_5H_{11}$ with a longer Ta–Ta distance of ~3.2 Å. This may be regarded as a formal single bond bridged by one of the hydrogen atoms. Vertices of degree 5 (excluding terminal atoms/groups but not edge-bridging hydrogens) are sites of highest stability/lowest chemical reactivity not only in metal-free boranes but also in the dimetallaboranes discussed in this paper. For example, all four boron vertices in $Cp_2Ta_2B_4H_{10}$ have the favorable degree or 5.

Keywords Dimetallaboranes · Boranes · Tantalum · Oblate polyhedra · Chemical bonding

1 Introduction

The basic building blocks of metal-free polyhedral boranes and isoelectronic carboranes have long been recognized to be the most spherical deltahedra, also known as *closo* deltahedra (Fig. 1) [1, 2]. The vertices in such deltahedra are as nearly similar as possible so that such deltahedra with 6–12 vertices have either degree 4 or 5 vertices with the exception of the 11-vertex *closo* deltahedron, which has a single degree 6 vertex. 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 prototypical examples of such *closo* deltahedral boranes are the dianions $B_nH_n^{2-}$ ($6 \leq n \leq 12$) as well as the isoelectronic carborane monoanions $CB_{n-1}H_n^-$ and particularly the neutral dicarbaboranes $C_2B_{n-2}H_n$.

Shortly after the discovery of the *closo* boranes and carboranes, Hawthorne et al. [3] showed that the boron and/or carbon vertices can be replaced by isolobal and isoelectronic transition metal vertices, typically units of the type CpM or $M(CO)_3$ (Cp = η^5-cyclopentadienyl or substituted 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 *closo* deltahedral geometry. Thus, 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

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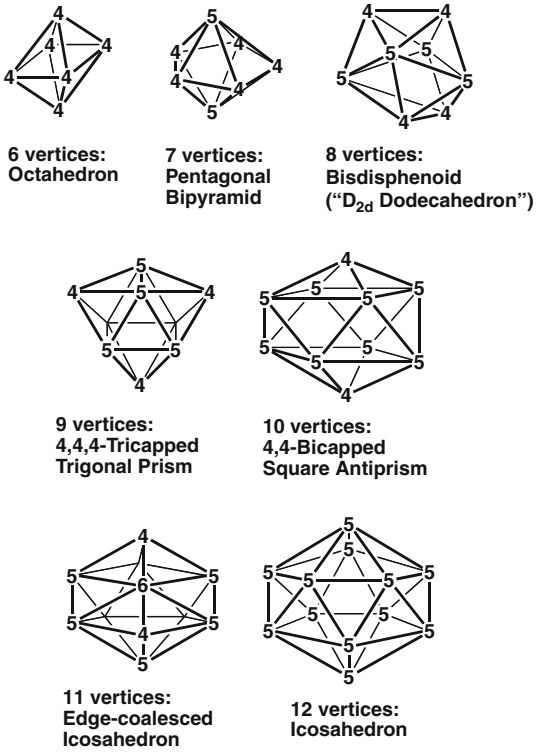

Fig. 1 The "most spherical" borane deltahedra. The *numbers* on the vertices indicate their degrees

was subsequently developed involving polyhedra other than the icosahedron, particularly by Kennedy et al. [4–7], metallaborane structures with nine and ten vertices were discovered based on deltahedra topologically different from the *closo* deltahedra (Fig. 2). These anomalous metallaborane deltahedra have been called either *isocloso* [8] or *hypercloso* deltahedra; the former designation will be used in this paper [9–11]. These nine- and ten-vertex *isocloso* deltahedra provide a single degree 6 vertex for the metal atom (Fig. 2), whereas the corresponding nine- and ten-vertex *closo* deltahedra (Fig. 1) have only degree 4 and 5 vertices.

The further development of metallaborane chemistry, particularly in the laboratory of Fehlner et al. [12, 13], led to the discovery of dimetallaboranes exhibiting structures based on deltahedra different from either the *closo* or *isocloso* deltahedra (Fig. 3). This new family of deltahedra

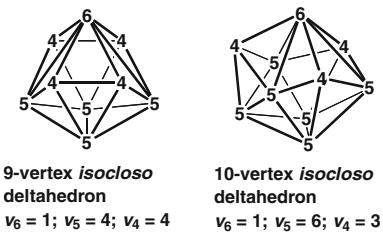

Fig. 2 The *isocloso* metallaborane deltahedra with nine and ten vertices. The numbers on the vertices indicate their degrees

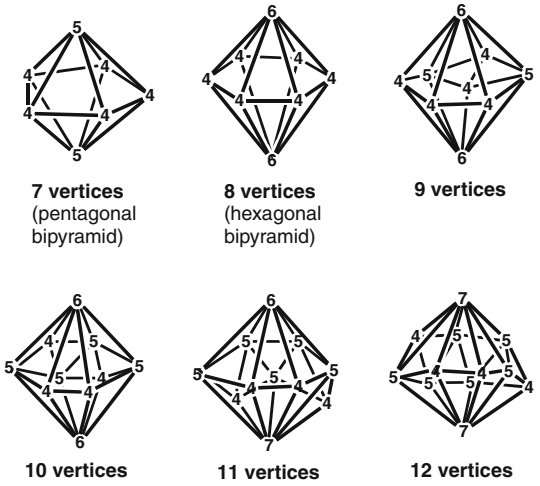

Fig. 3 The *oblatocloso* deltahedra found in the dirhenaboranes $Cp_2Re_2B_{n-2}H_{n-2}$ ($8 \leq n \leq 12$). The *numbers* on the vertices indicate their degrees. The rhenium atoms are located on the approximately antipodal vertices of degrees 6 and 7

is characterized by highly oblate (flattened) structures with two approximately antipodal degree 6 or 7 vertices for the metal atom and lower degree vertices for the boron atoms. The "*closo* nomenclature" has been extended to call these dimetallaborane deltahedra *oblatocloso* deltahedra suggestive of their flattened nature [14]. The two high degree metal vertices in such polyhedra are located at approximately antipodal "flat spots" on the polyhedral surface. The flattening of the *oblatocloso* dimetallaboranes is sufficient to place the two approximately antipodal metal atoms within bonding distance. The prototypical examples are the dirhenaboranes $Cp_2Re_2B_{n-2}H_{n-2}$ ($8 \leq n \leq 12$; Cp = pentamethylcyclopentadienyl) [15–17]. In addition, an isoelectronic hexagonal bipyramidal *oblatocloso* dimetalladicarbaborane $Cp_2Cr_2B_4H_4C_2(CH_2)_3$ is known with two equatorial carbon vertices bridged by a trimethylene group [18].

Removal of vertices from closed deltahedral boranes and metallaboranes leads to more open structures. Thus, *nido* structures are derived from *closo* structures by removal of one vertex. Similarly, *arachno* structures are derived from *closo* structures by removal of two vertices. Such open structures are hydrogen-rich relative to the *closo* structures from which they are derived. The metal-free *nido* and *arachno* boranes include the original binary boron hydrides discovered by Alfred Stock [19] many years before the discovery of the *closo* deltahedral borane dianions $B_nH_n^{2-}$ (Fig. 4). Thus, long-known *nido* B_nH_{n+4} derivatives include B_5H_9 with a B_5 square pyramid obtained by removal of one vertex from a B_6 octahedron and the very stable $B_{10}H_{14}$ obtained by removal of the unique degree 6 vertex from the B_{11} *closo* deltahedron (Fig. 1). Similarly, long-known *arachno* B_nH_{n+6} derivatives include B_4H_{10} obtained by

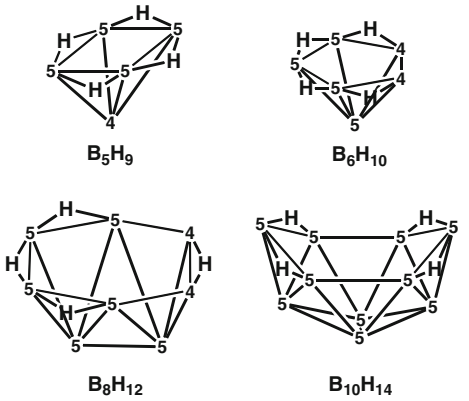

Fig. 4 The *nido* boranes B_nH_{n+4} ($n = 5, 6, 8, 10$). The *numbers* on the vertices indicate the vertex degrees including the B–H bonds

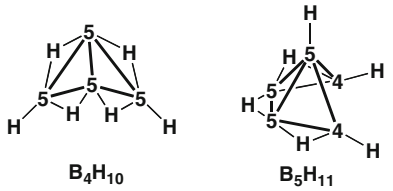

Fig. 5 The *arachno* boranes B_nH_{n+6} ($n = 4, 5$). One hydrogen on each boron atom is omitted so that the borons with an indicated terminal hydrogen are actually BH_2 groups. The *numbers* on the vertices indicate the vertex degrees including the B–H bonds

removal of two adjacent vertices from a B_6 octahedron and B_5H_{11} obtained by removal of an axial and an equatorial vertex from a B_7 pentagonal bipyramid (Fig. 5).

Vertex removal to give more open structures can also be applied to the *oblatocloso* dimetallaboranes (Fig. 6). In this case, however, the possibility of varying the transition metal atoms affords some flexibility of adjusting the skeletal electron count. Examples of *oblatonido* dimetallaboranes include $Cp_2M_2B_4H_8$ (M=Cr [20–22], Mo [23], and W) and $Cp_2Cr_2B_5H_9$ having structures derived from a pentagonal bipyramid and a hexagonal bipyramid, respectively, by removal of an equatorial vertex. Similarly, the structure of the *oblatoarachno* dirhenaborane [24] $Cp_2Re_2B_4H_8$ is derived from a hexagonal bipyramid by removal of two adjacent equatorial vertices.

Approximately 5 years ago, one of the authors (RBK) explored in some detail the unusual polyhedral geometries and chemical bonding in the *oblatocloso* dimetallaboranes and related *oblatonido* and *oblatoarachno* dimetallaboranes [14]. Since that time developments in the laboratory of the other author (SG) have led to the discovery of a new series of relatively hydrogen-rich ditantalaboranes [25], which possess interesting structures related to the *oblatonido* dimetallaboranes. This paper discusses the structure and bonding of these new ditantalaboranes in some detail.

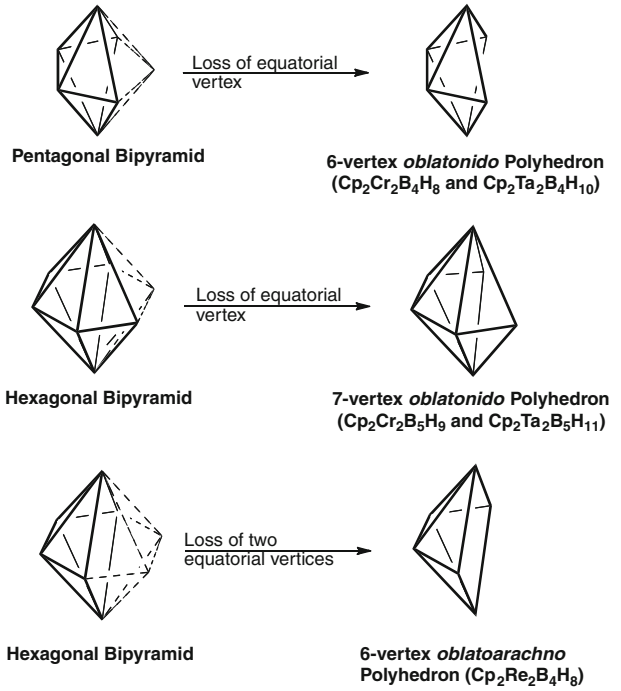

Fig. 6 Generation of *oblatonido* and *oblatoarachno* structures by removal of equatorial vertices from bipyramids

2 Chemical bonding in polyhedral boranes and metallaboranes

The Wade–Mingos rules [26–28], which are traditionally used to count skeletal electrons in polyhedral borane structures, assume the involvement of three internal orbitals from each vertex atom in the skeletal bonding. For the "light" vertex atoms boron and carbon, which use only s and p orbitals in their four-orbital sp^3 manifolds, the fourth valence orbital is clearly an external orbital, typically bonded to a monovalent atom or group such as hydrogen, fluorine, alkyl, or cyano. However, the transition metals use d orbitals as well as s and p orbitals for their chemical bonding leading to a nine-orbital sp^3d^5 manifold. Filling each of these nine orbitals with an electron pair leads to the familiar 18-electron rule corresponding to the electronic configurations of the most stable transition metal complexes. The use of only three of these nine orbitals of a transition metal vertex in a metallaborane polyhedron for internal skeletal bonding leaves six orbitals remaining for bonding to external ligands and for "non-bonding" lone pairs. In most of the metallaboranes and dimetallaboranes discussed in this paper, the external ligand is a cyclopentadienyl ring, requiring only three of the metal orbitals for the metal-ring bond. In a transition metal vertex with a closed-shell 18-electron configuration using three orbitals for skeletal bonding and three orbitals for bonding to an external cyclopentadienyl ring, three "non-bonding"

electron pairs remain. In some cases, the transition metal vertex can use more than three internal orbitals for bonding in a metallaborane structure so that originally non-bonding electron pairs become involved in the skeletal bonding.

These ideas can be illustrated by the number of skeletal electrons contributed by various vertex units. Thus, BH and CH vertices clearly contribute 2 and 3 skeletal electrons each, respectively, to the skeletal bonding after using one of the three or four valence electrons of the boron or carbon, respectively, for bonding to the external hydrogen atom. Similarly, a CpRe vertex contributes zero skeletal electrons if the rhenium atom uses only three of its valence orbitals for the skeletal bonding. However, in the extensive series of *oblatocloso* dirhenaboranes $Cp_2Re_2B_{n-2}H_{n-2}$, the rhenium atoms, which are both located in the "flat" region of the surface of the oblate deltahedron, can be assumed to use five rather than three internal orbitals. This draws two otherwise non-bonding electron pairs into the skeletal bonding. Thus, a CpRe vertex using five rather than only three internal orbitals is a donor of four skeletal electrons in these dirhenaboranes. However, in order to compare skeletal electron counts of metal-free polyhedral boranes and polyhedral metallaboranes, it is sometimes instructive to introduce the concept of "Wadean skeletal electrons," where each vertex of a polyhedron is assumed to use artificially three of their orbitals for the skeletal bonding whether or not that leads to a correct and/or useful model.

The stable metal-free deltahedral borane anions have the stoichiometry $B_nH_n^{2-}$ corresponding to $2n + 2$ skeletal electrons. The special significance of $2n + 2$ skeletal electrons in the Wade–Mingos rules [26–28] for determining special stability of deltahedral boranes and carboranes can be rationalized by an approach originating from graph theory [29]. Thus, consider a deltahedral borane $B_nH_n^{2-}$ or isoelectronic carborane with n vertices. The sp^3 valence orbital manifold of each vertex atom is partitioned into one external orbital and three internal orbitals. The three internal orbitals of each vertex atom are then partitioned further into two equivalent twin internal orbitals and a unique internal orbital. The twin internal orbitals are p orbitals that participate in surface bonding through pairwise overlap in the surface of the deltahedron. This leads to n surface or tangential bonding orbitals as well as n surface antibonding orbitals. Each unique internal orbital on a vertex atom is one part of a linear pair of sp hybrid orbitals and points toward the center of the deltahedron. The other component of the sp hybrid pair is the external orbital of the vertex atom, which overlaps with an orbital of an external group, such as hydrogen in $B_nH_n^{2-}$. The unique internal orbitals of the boron atoms in a $B_nH_n^{2-}$ derivative are radial orbitals pointing to the center or core of the deltahedron. The n radial orbitals from the n vertex atoms in a $B_nH_n^{2-}$ deltahedron overlap in the center of the deltahedron to form an n-center bond. This n-center bond generates only one new bonding orbital but $n - 1$ new antibonding orbitals. This analysis indicates that there are $n+1$ skeletal bonding orbitals with n of them arising from the surface bonding and the remaining orbital arising from the core bonding. Filling each of these $n+1$ bonding orbitals with an electron pair leads to the $2n + 2$ skeletal electrons suggested by the Wade–Mingos rules [26–28] for a closed deltahedral borane.

The chemical bonding topology for the *isocloso* metallaboranes is rather different from that of the metal-free *closo* boranes [30]. Thus, a suitable skeletal bonding model for the *isocloso* metallaboranes has no core bonding but instead three-center two-electron (3c–2e) bonds in selected deltahedral faces. Thus, if each BH vertex or isolobal/isoelectronic equivalent contributes three skeletal (internal) orbitals and two skeletal electrons (i.e., a $2n$ skeletal electron system), then the numbers of skeletal orbitals and electrons are correct for 3c–2e bonds in n of the $2n - 4$ faces of the deltahedron leaving $n - 4$ faces without 3c–2e bonds.

Now consider the chemical bonding topology in the *oblatocloso* dimetallaboranes [14]. Skeletal electron counting by the Wade–Mingos rules [26–28] leads to $2n - 4$ skeletal electrons for a $Cp_2Re_2B_{n-2}H_{n-2}$ dirhenaborane [17] with n vertices. However, this somewhat artificial $2n - 4$ Wadean skeletal electron count assumes that each rhenium atom uses three of its nine orbitals in its sp^3d^5 manifold for skeletal bonding so that each CpRe unit is a formal donor of zero skeletal electrons. A more realistic chemical bonding scheme for these *oblatocloso* dimetallaboranes has each rhenium vertex using five rather than only three of the nine orbitals in its sp^3d^5 manifold, thereby drawing two otherwise "external" lone electron pairs into the skeletal bonding. The introduction of these "extra" two lone pairs from each CpRe vertex into the skeletal bonding makes these vertices donors of four rather than zero skeletal electrons. The $Cp_2Re_2B_{n-2}H_{n-2}$ dirhenaboranes thus become $2n + 4$ actual skeletal electron systems rather than the $2n - 4$ apparent skeletal electron systems by the Wade–Mingos rules [26–28]. The involvement of five rather than three orbitals from each CpRe vertex into the skeletal bonding of the $Cp_2Re_2B_{n-2}H_{n-2}$ dirhenaboranes is reasonable because the oblate nature of the relevant deltahedra leads to a relatively low local curvature at the sites of the metal vertices. This facilitates the introduction of otherwise non-bonding rhenium lone pairs into the skeletal bonding.

The recognition of the $Cp_2Re_2B_{n-2}H_{n-2}$ dirhenaboranes as $2n+4$ actual skeletal electron systems implies that the underlying *oblatocloso* 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 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 discussed above, namely n 3c–2e bonds requiring $2n$ skeletal electrons and $3n$ skeletal orbitals. The "extra" skeletal electrons and internal orbitals remaining after this surface bonding, namely four skeletal electrons and four internal orbitals, correspond to a formal metal=metal double bond inside the deltahedron. In this connection, the Re=Re distance of 2.723 Å found by X-ray crystallography [31] in $(\eta^5\text{-}Me_5C_5)_2Re_2(CO)_4$, which is required to have a Re=Re double bond for each atom to have the favored 18-electron configuration, is within the observed range of 2.69–2.82 Å of Re=Re distances found in the $Cp_2Re_2B_{n-2}H_{n-2}$ dirhenaboranes (Table 1) [15–17].

We thus see an interesting progression in the series of *closo* → *isocloso* → *oblatocloso* deltahedra for metal-free boranes, metallaboranes, and dimetallaboranes, respectively. 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 metal-free *closo* deltahedra supplement their surface bonding with an n-center two-electron 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.

3 Oblatonido dimetallaboranes: skeletal electron counting and placement of the hydrogen atoms

The ditantalaboranes of interest can be considered to be *oblatonido* dimetallaboranes with the general formula $Cp_2Ta_2B_{n-2}H_{n+4}$ and thus are isoelectronic with the corresponding dichromaboranes and dimolybdaboranes $Cp_2M_2B_{n-2}H_{n+2}$ (M=Cr, Mo). Thus, the two valence electrons lost by replacing two group 6 metals with the group 5 metal tantalum are balanced by the presence of two extra hydrogen atoms. If the metal vertices can be assumed to contribute five internal orbitals, then CpTa vertices are two-electron donors and CpM (M=Cr, Mo, W) vertices are three-electron donors. These *oblatonido* dimetallaboranes thus become $2n+6$ skeletal electron systems. These *oblatonido* structures thus have two more skeletal electrons for a given number of vertices than the related *oblatocloso* structures as exemplified by the rhenium compounds $Cp_2Re_2B_{n-2}H_{n-2}$ ($6 \leq n \leq 12$).

The chemical bonding model for the *oblatocloso* $Cp_2Re_2B_{n-2}H_{n-2}$ dirhenaboranes discussed above predicts a formal Re=Re double bond through the center of the oblate Re_2B_{n-2} deltahedron. This is consistent with the 2.69–2.82 Å range of distances found experimentally [15–17]. The *oblatonido* derivatives mentioned above can be assumed to have similar M=M formal double bonds. Thus, the experimental Cr=Cr distances of 2.87 Å in $Cp_2Cr_2B_4H_8$ and 2.63 Å in $Cp_2Cr_2B_5H_9$ lie between the experimental [32] Cr–Cr single bond distance of 3.28 Å in $Cp_2Cr_2(CO)_6$ and the experimental [33] Cr≡Cr triple bond distance of 2.28 Å in $Cp_2Cr_2(CO)_4$. For the ditantalaboranes $Cp_2Ta_2B_{n-2}H_{n+4}$ ($n = 6, 7$), the Ta=Ta distances of ~2.9 Å can also correspond to formal double bonds.

Now consider the skeletal electron counting in this series of *oblatonido* dimetallaboranes using $Cp_2Ta_2B_5H_{11}$ as an example. The *oblatonido* structure of $Cp_2Ta_2B_5H_{11}$ is derived from a hypothetical Ta_2B_6 hexagonal bipyramid by removal of one of the equatorial boron vertices (Fig. 6). The CpTa vertices in $Cp_2Ta_2B_5H_{11}$, like the CpRe vertices in the *oblatocloso* $Cp_2Re_2B_nH_n$ discussed above, can be assumed to contribute five internal orbitals and thus are

Table 1 Some properties of the *oblatocloso* deltahedra found in the $Cp_2Re_2B_{n-2}H_{n-2}$ derivatives

Number of vertices	Vertex degrees				Experimental Re=Re in $Cp_2Re_2B_{n-2}H_{n-2}$, Å
	v_4	v_5	v_6	v_7	
7	5	2	0	0	
8	6	0	2	0	2.689
9	5	2	2	0	2.787
10	4	4	2	0	2.835
11	4	5	1	1	2.860
12	4	6	0	2	2.819

donors of two skeletal electrons each. Then, $Cp_2Ta_2B_5H_{11}$ is a 20 skeletal electron system as follows:

2 CpTa vertices using 5 internal orbitals: $2 \times 2 = 4$ electrons
5 BH vertices: $5 \times 2 = 10$ electrons
6 "extra" hydrogen atoms: $6 \times 1 = 6$ electrons
Total skeletal electrons: 20 electrons

From these 20 skeletal electrons in $Cp_2Ta_2B_5H_{11}$, 16 of them can be used to form eight surface bonds in the *oblatonido* polyhedron derived from the hexagonal bipyramid. This leaves the 4 skeletal electrons for the Ta=Ta double bond through the center of the $Cp_2Ta_2B_5H_{11}$ polyhedron.

The structures of both types of *oblatonido* derivatives, namely $Cp_2Ta_2B_{n-2}H_{n+4}$ and $Cp_2M_2B_{n-2}H_{n+2}$ (M=Cr, Mo), have one terminal hydrogen atom bonded to each boron atom. The remaining hydrogens form M–H–B bridges along some of the M–B edges of the *oblatonido* polyhedron (Fig. 7). In such systems, the vertex degrees of the boron atoms are of interest. Boron vertices of degree 5 are the most stable/least reactive as exemplified by icosahedral borane structures, for example, $B_{12}H_{12}^{2-}$(Fig. 1), in which all of the vertices have degree 5 [34]. In this connection, the degree of a vertex counts "internal connections" within the polyhedron, including those to any hydrogens bridging edges of the polyhedron as well as the B–B and B–M edges themselves, but not the "external" B-H bonds. An example of a very stable binary boron hydride is the long-known decaborane $B_{10}H_{14}$, in which all of the vertices have degree 5 (Fig. 4). Decaborane is the most stable of the simple binary boranes and is a significant product from the simple pyrolysis of diborane.

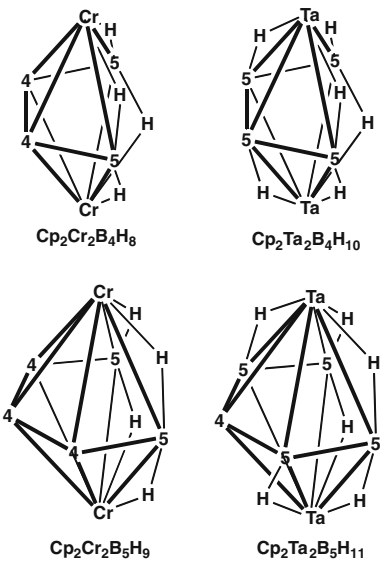

Fig. 7 Placement of the bridging hydrogen atoms in the *oblatonido* dimetallaboranes $Cp_2Ta_2B_{n-2}H_{n+4}$ and $Cp_2Cr_2B_{n-2}H_{n+4}$. For clarity, the Cp rings and the terminal BH hydrogens are omitted. The *numbers* on the boron vertices indicate their degrees

First consider the group 6 metal derivatives $Cp_2M_2B_{n-2}H_{n+2}$ ($n = 6$ and 7; M=Cr, Mo, W). The "end" borons in the equatorial chain of $n-2$ boron atoms are connected to a bridging hydrogen atom to each of the metal atoms and thus have the favorable degree 5 (Fig. 7). However, the $n - 4$ "internal" borons in the equatorial chain are not connected to any bridging hydrogen atoms and thus are only of degree 4. Moving from a group 6 metal to tantalum creates the need for two more hydrogens to compensate for the lost two valence electrons. These hydrogens can bridge from a tantalum atom to an interior boron atom in the B_{n-2} chain thereby increasing that boron vertex degree from 4 in $Cp_2Cr_2B_{n-2}H_{n+2}$ to the more favorable 5 in $Cp_2Ta_2B_{n-2}H_{n+4}$. Thus in $Cp_2Ta_2B_4H_{10}$, all four boron vertices have the favorable degree of 5 and in $Cp_2Ta_2B_5H_{11}$ only the central boron atom in the B_5 chain has the less favorable degree of 4. This simple analysis predicts the non-existence of a stable hafnium derivative $Cp_2Hf_2B_4H_{12}$ isoelectronic with $Cp_2Ta_2B_4H_{10}$ and with a similar Hf_2B_4 framework. In such a $Cp_2Hf_2B_4H_{12}$ structure, there is simply not room enough for the eight bridging hydrogen atoms without exceeding the favorable degree of 5 for at least one boron vertex.

4 Formal addition to the metal–metal double bond in an *oblatonido* ditantalaborane

The chemical bonding model discussed above for the *oblato* dimetallaboranes leads to a formal double bond between the metal atoms through the polyhedral cavity. In the complicated reaction between (η^5-Me_5C_5)$TaCl_4$ and $LiBH_4/BH_3$-THF used to synthesize the ditantalaboranes discussed in this paper [25], two interesting products with central Ta_2B_5 polyhedra are observed (Fig. 8). The first product, $Cp_2Ta_2B_5H_{11}$, is the *oblatonido* derivative, also depicted in Fig. 7. The experimental Ta=Ta distance of 2.925 Å can correspond to the formal double bond required by the chemical bonding model for *oblato* dimetallaboranes discussed above. The second product $Cp_2Ta_2Cl_2B_5H_{11}$ contains two extra chlorine atoms and thus arises from incomplete removal of the chlorine atoms from $CpTaCl_4$ with the borane reagents. Formally, however, the product $Cp_2Ta_2Cl_2B_5H_{11}$ can arise from the addition of chlorine to the Ta=Ta double bond in $Cp_2Ta_2B_5H_{11}$. In accord with this interpretation, the tantalum–tantalum distance lengthens from the Ta=Ta double bond distance of 2.926 Å in $Cp_2Ta_2B_5H_{11}$ to a Ta–Ta single bond distance of 3.222 Å in $Cp_2Ta_2Cl_2$. The six bridging hydrogen atoms in $Cp_2Ta_2B_5H_{11}$ reorganize in

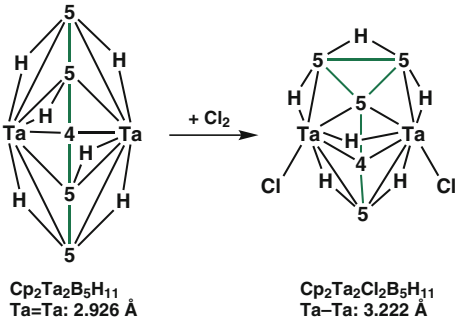

Fig. 8 Formal addition of Cl_2 to the formal Ta=Ta double bond in the *oblatonido* ditantalaborane to give another *oblatonido* borane with a formal internal protonated Ta–Ta single bond. Cyclopentadienyl rings and terminal hydrogen atoms are omitted for clarity. The numbered vertices are the boron vertices with the *numbers* indicating their degrees counting direct B–B, B–H, and B–Ta linkages but not "external" B–H bonds to terminal hydrogen atoms

$Cp_2Ta_2Cl_2B_5H_{11}$ so that one of the six hydrogen atoms bridges the Ta–Ta single bond in the latter species. Furthermore, spreading the tantalum atoms further apart in $Cp_2Ta_2Cl_2B_5H_{11}$ because of the longer Ta–Ta single bond reorganizes the five boron atoms. Thus in $Cp_2Ta_2B_5H_{11}$, the five boron atoms form a straight chain with no B_n cycles. However, in $Cp_2Ta_2Cl_2B_5H_{11}$, three of the five boron atoms form a B_3 triangle with the remaining two boron atom attached to one of the B_3 triangle vertices as a chain. However, in both structures, four of the five boron atoms have the favored degree of 5, whereas the fifth boron atom has a degree of only four (Fig. 8).

Now consider the skeletal electron counting in the *oblatonido* compound $Cp_2Ta_2Cl_2B_5H_{11}$. Since the internal tantalum–tantalum bond is only a single bond, the CpTa vertices can be assumed to use only four rather than five of their orbitals for the skeletal bonding thereby making them donors of zero skeletal electrons. Thus, $Cp_2Ta_2Cl_2B_5H_{11}$ has 18 skeletal electrons as follows:

2 CpTa vertices using 4 internal orbitals: $2 \times 0 = 0$ electrons
2 external chlorine atoms: $2 \times 1 = 2$ electrons
5 BH vertices: $5 \times 2 = 10$ electrons
6 "extra" hydrogen atoms: $6 \times 1 = 6$ electrons
Total skeletal electrons: 18 electrons

Now consider the 8-vertex *oblatocloso* polyhedron from which the 7-vertex Ta_2B_5 *oblatonido* polyhedron is derived by removal of a vertex. However, this 8-vertex *oblatocloso* polyhedron cannot be the hexagonal bipyramid in Fig. 3 because of the arrangement of the five boron atoms in $Cp_2Ta_2Cl_2B_5H_{11}$. The 18 skeletal electrons can be used to form 8 surface bonds plus the Ta–Ta single bond through the center of the $Cp_2Ta_2Cl_2B_5H_{11}$ polyhedron.

5 Summary

The recently discovered ditantalaboranes $Cp_2Ta_2B_nH_{n+6}$ ($n = 4, 5$) are isoelectronic with the previously discovered dimetallaboranes $Cp_2M_2B_nH_{n+4}$ of the group 6 metals Cr, Mo, and W where Cp = η^5-cyclopentadienyl or substituted cyclopentadienyl (mainly η^5-pentamethylcyclopentadienyl in the compounds discussed here). Their *oblatonido* polyhedral structures can be derived from the structures of the deltahedral *oblatocloso* dirhenaboranes $Cp_2Re_2B_{n+1}H_{n+1}$ by removal of an equatorial BH vertex with adjustment of the skeletal electron count by changing the metal atoms and adding hydrogen atoms. The dirhenaborane deltahedra are not the most spherical deltahedra found in the metal-free boranes $B_nH_n^{2-}$ but instead are oblate (flattened) deltahedra with the approximately antipodal rhenium atoms close enough together to form a formal Re=Re double bond with lengths in the range 2.69–2.82 Å. Similarly, short M=M distances are maintained in the *oblatonido* derivatives $Cp_2Ta_2B_nH_{n+6}$ ($n = 4, 5$) and $Cp_2M_2B_nH_{n+4}$ (M=Cr, Mo, W). However, the synthesis of $Cp_2Ta_2B_nH_{n+6}$ ($n = 4, 5$) from $CpTaCl_4 + LiBH_4/BH_3$ also gives a less-reduced product $Cp_2Ta_2Cl_2B_5H_{11}$ with a longer Ta–Ta distance of $\sim$3.2 Å. This may be regarded as a formal single bond bridged by one of the hydrogen atoms. Thus, the hypothetical conversion of $Cp_2Ta_2B_5H_{11}$ to $Cp_2Ta_2Cl_2B_5H_{11}$ can formally be regarded as adding Cl_2 to a Ta=Ta double bond with concurrent adjustment of the bridging hydrogen atoms.

The vertex degrees of the boron atoms in polyhedral boranes and metallaboranes are important in determining their stabilities and chemical reactivities. Vertices of degree 5 (excluding terminal atoms/groups but not edge-bridging hydrogens) are sites of highest stability/lowest chemical reactivity as exemplified by the stability and low reactivity of the icosahedral boranes $B_{12}H_{12}^{2-}$ and the stability of decaborane, $B_{10}H_{14}$, relative to other binary neutral boron hydrides. Similar ideas appear to apply in metallaborane chemistry including the *oblato* derivatives discussed in this paper. Thus in $Cp_2Ta_2B_4H_{10}$, all of the boron vertices have the favorable degree of 5. Similarly in $Cp_2Ta_2B_5H_{11}$ and $Cp_2Ta_2Cl_2B_5H_{11}$, all but one of the boron vertices have the favorable degree of 5.

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