



Geometry and chemical bonding in polyhedral boranes, metallaboranes, and dimetallaboranes: From *closo* to *isocloso* to *oblatocloso* polyhedra

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ABSTRACT

The geometry and chemical bonding in the *closo* metal-free boranes $B_nH_n^{2-}$ and the isoelectronic carboranes $CB_{n-1}H_n$ and $C_2B_{n-2}H_n$ with $2n + 2$ skeletal electrons are based on the most spherical deltahedra with a preference for degree 5 vertices, particularly for the boron atoms. Such deltahedral boranes can be considered to be three-dimensional aromatic systems, as indicated by strongly diatropic nucleus independent chemical shift values for $B_nH_n^{2-}$ ($n = 6, 8, 9, 12$). Metallaborane structures, particularly those with 9–11 vertices and only $2n$ rather than $2n + 2$ apparent skeletal electrons, are often based on *isocloso* deltahedra with the metal atom at a degree 6 vertex. Dimetallaborane structures, particularly the rhenium derivatives $Cp_2Re_2B_{n-2}H_{n-2}$ ($8 \leq n \leq 12$), are based on highly non-spherical and very oblate deltahedra with the metal atoms typically at degree 6 or 7 vertices, which are the lowest curvature sites of the deltahedra. A viable model for the skeletal bonding in such dimetallaboranes can be developed if each of the two metal vertices is assumed to contribute five internal orbitals to the skeletal bonding. This leads to $2n + 4$ skeletal electrons, which are partitioned into n surface bonds and a formal metal–metal double bond inside the oblate deltahedron.

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1. Introduction

The vertices in the *closo* deltahedral boranes and related carboranes [1,2] were first shown by Hawthorne and co-workers [3] to be replaceable by isolobal transition metal vertices, typically units of the type CpM or $M(CO)_3$ ($Cp = \eta^5$ -cyclopentadienyl; $M =$ transition metal). The initially discovered metallaboranes were dicarbaboranes having structures based on MC_2B_9 icosahedra so it was initially assumed that substitution of a boron vertex with an isoelectronic metal vertex did not affect the cluster geometry. However, as metallaborane chemistry was subsequently developed involving polyhedra other than the icosahedron, particularly by Kennedy and co-workers [4–7], a variety of deltahedral 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* [8] or *hypercloso* [9–11] deltahedra; the former terminology will be used in this paper. These *isocloso* metallaborane deltahedra are derived from the *closo* metal-free borane deltahedra by one or more diamond-square-diamond processes, typically generating a degree 6 vertex for the metal atom.

The further development of metallaborane chemistry, particularly in the laboratory of Fehlner and co-workers [12,13], 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 4 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 for metal-free boranes and metallaboranes with a single metal atom, respectively. The most complete set of stable known 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) [14–16].

The following two factors are seen to influence the structures of polyhedral boranes and metallaboranes:

- (1) The Wade–Mingos rules [17–19] generally determine the relationship of the structures of metal-free polyhedral boranes and isoelectronic carboranes to the number of their skeletal electrons. Thus n -vertex *closo* deltahedral boranes having structures based on the “most spherical” deltahedra (Fig. 1) are particularly stable if they contain $2n + 2$ skeletal electrons. In accord with the Wade–Mingos rules the

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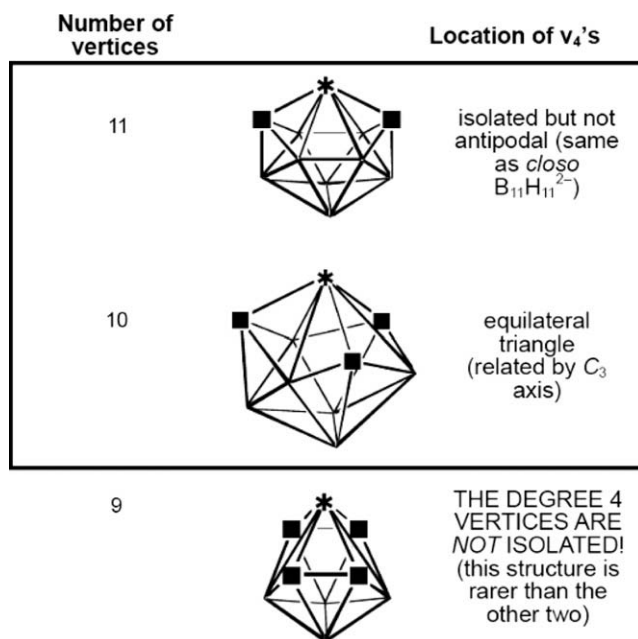


Fig. 1. The *isocloso* deltahedra with 9, 10, and 11 vertices. Degree 4 and 6 vertices are designated by ■ and *, respectively. Degree 5 vertices are unlabeled.

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 $C_2B_{n-2}H_n$ have structures based on the most spherical deltahedra (Fig. 1). This special stability has been ascribed to three-dimensional aromaticity [20–22].

- (2) Different types of vertex atoms have preferred vertex degrees. Thus boron atoms prefer to be located at degree 5 vertices [2,23]. This is why icosahedral borane structures have exceptional stability since in a regular icosahedron, all vertices have degree 5 (Fig. 1). Carbon, in contrast to boron, often prefers degree 4 vertices. On the other hand transition metals often prefer degree 6 vertices. These preferences are manifested in the distribution of the vertex atoms in the lowest energy heteroatomic polyhedral borane structures.

2. Metal-free deltahedral boranes and carboranes

The special significance of $2n+2$ skeletal electrons in the Wade–Mingos rules [17–19] for determining special stability of deltahedral boranes and carboranes can be rationalized by an approach originating from graph theory [21]. 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 towards 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 is a radial orbital pointing to the center

of 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 and $n-1$ 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 [17–19].

In the borane dianions of the type $B_nH_n^{2-}$ as well as isoelectronic carboranes, the delocalization implied by the n -center core bond coupled with the special stability of such boranes suggests a three-dimensional aromatic system [21,22]. The aromaticity of such boranes has been evaluated by the nuclear independent chemical shift (NICS) method [24]. All of the boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$) are found to be strongly diatropic indicating aromaticity [25]. Interestingly enough, the isoelectronic silicon derivatives Si_n^{2-} , which necessarily have lone pairs rather than external hydrogen atoms, are not all diatropic by the NICS method. In particular, the experimentally unknown icosahedral Si_{12}^{2-} is found to be strongly paratropic suggesting an antiaromatic system, which thus is not expected to be stable. This accounts for the fact that icosahedral silicon clusters are unknown despite the high stability of isoelectronic icosahedral boron clusters.

3. Metallaboranes: *isocloso* derivatives

A number of metallaboranes are known with one transition metal vertex and only $2n$ rather than $2n+2$ apparent skeletal electrons. Typical transition metal vertices in such structures are $(\eta^5-C_5H_5)Co$, $(\eta^6-C_6H_6)Fe$, and $Fe(CO)_3$ units serving as donors of two skeletal electrons like BH vertices and $(\eta^5-C_5H_5)Ni$, $(\eta^6-C_6H_6)Co$, and $Co(CO)_3$ units serving as donors of three skeletal electrons like CH vertices. In addition, the H atoms on CH and BH vertices and C_5H_5 and C_6H_6 rings in such structures can be replaced by other monovalent groups (halogen, alkyl, aryl, cyano, etc.). Similarly the CO groups on transition metal vertices can be replaced by other two-electron donor ligands such as R_3P and RNC.

These metallaborane structures often have the metal atom located at a degree 6 vertex. However, the most spherical deltahedra for the nine and ten-vertex systems do not have degree 6 vertices. Therefore the deltahedra found in metallaboranes with nine and ten vertices (Fig. 1), $2n$ skeletal electrons, and a single degree 6 vertex for the metal atom are different from the corresponding most spherical deltahedra. The deltahedra in such metallaboranes can be called *isocloso* deltahedra and are related to the most spherical *closo* deltahedra by one or more diamond–square–diamond rearrangements [26,27].

Several pairs of closely related *closo-isocloso* pairs of structures are of interest. An early example is the pair of ten-vertex $M_2C_2B_6$ structures $(CpM)_2C_2B_6H_8$ ($M = Co, Fe$), which differ only by the two-electron difference between a pair of cobalt and iron atoms (Fig. 2) [28]. The dicobalt species $(CpCo)_2C_2B_6H_8$ has $22 = 2n+2$ skeletal electrons for $n = 10$ corresponding to a *closo* electron count by the Wade–Mingos rules. The $Co_2C_2B_6$ deltahedron in $(CpCo)_2C_2B_6H_8$ is the bicapped square antiprism. The two cobalt atoms are located at degree 5 vertices, which are the highest degree vertices available. The carbon atoms are located at the two available degree 4 vertices, which, when available, are more favorable than degree 5 vertices for carbon atoms.

The diiron species $(CpFe)_2C_2B_6H_8$ differs from the dicobalt species in having only $20 = 2n$ skeletal electrons for $n = 10$ corresponding to the skeletal electron count for an *isocloso* structure. The $Fe_2C_2B_6$ deltahedron is the ten-vertex *isocloso* deltahedron depicted in Fig. 1, which has a single degree 6 vertex, six degree 5 ver-

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