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Pentalene as a ligand in hypoelectronic diruthenaboranes and diosmaboranes with surface metal–metal double bonding

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ABSTRACT

A previous theoretical study on $Cp_2M_2B_{n-2}H_{n-2}$ ($Cp = \eta^5$-C_5H_5; M = Ru, Os; n = 8–12) derivatives indicated a general energetic preference for structures having M–M distances of 2.7–2.9 Å with corresponding WBIs of 0.3–0.4 suggesting surface metal–metal single bonds. Replacing the two CpM units in these structures with a single PnM_2 unit ($Pn = \eta^5$, η^5-C_8H_6) leads to different types of $PnM_2B_{n-2}H_{n-2}$ (M = Ru, Os; n = 8–12) structures having significantly shorter M═M distances of 2.5–2.7 Å with corresponding higher WBIs of 0.5–0.7 suggesting surface metal–metal double bonds. The lowest energy such structures have central M_2B_{n-2} bisdisphenoids, tricapped trigonal prisms, and edge-bridged tricapped trigonal prisms for the 8-, 9-, and 10-vertex systems, respectively. The lowest energy 11-vertex $PnM_2B_9H_9$ structures are based on the most spherical 11-vertex deltahedron, which can be either a *closo* or *isocloso* polyhedron. The lowest energy 12-vertex $PnM_2B_{10}H_{10}$ structures are based on an "*isoisocloso*" 12-vertex deltahedron with two degree 6 vertices. However, icosahedral $PnM_2B_{10}H_{10}$ structures with surface M═M triple bonds are also energetically accessible.

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1. Introduction

The chemistry of polyhedral metallaboranes dates back to the discovery in the 1960s by Hawthorne and co-workers that BH vertices can be replaced by isolobal transition metal vertices to give very stable compounds [1–3]. Much of this early chemistry involved the replacement of a BH vertex in a polyhedral borane with an isolobal and isoelectronic CpCo vertex ($Cp = \eta^5$-C_5H_5). Shortly after this original discovery the first polyhedral dimetallaboranes were synthesized having two CpCo vertices. The polyhedra in these early metallaboranes were the most spherical deltahedra similar to those found in metal-free boranes and carboranes (Fig. 1) [4,5]. Such deltahedral metallaboranes and dimetallaboranes were found to be very stable species with n-vertex systems having $2n + 2$ Wadean skeletal electrons according to the Wade–Mingos rules [6–9].

Later work led to polyhedral metallaborane and dimetallaborane structures based on deltahedra different from the most spherical deltahedra. Such structures typically but not always were found to contain second and third row transition metals at degree 6 vertices and to exhibit hypoelectronic skeletal electron counts of fewer than $2n + 2$ skeletal electrons for n-vertex systems. The first such n-vertex structures discovered by Kennedy and co-workers [10–13] with only $2n$ Wadean skeletal electrons have the transition metal at a unique degree 6 vertex of an *isocloso* deltahedron, which for the 9- and 10-vertex systems are topologically distinct from the corresponding *closo* deltahedra (Fig. 2). A recent density functional theory (DFT) study on $Cp_2Fe_2B_{n-4}H_{n-2}$ systems of this type suggested the 10-vertex structures of this type to be particularly favorable relative to other alternatives in general agreement with experimental observations [14]. Note that the 11-vertex *isocloso* deltahedron (Fig. 2) is topological identical to the 11-vertex *closo* deltahedron (Fig. 1), which necessarily has a unique degree 6 vertex [15].

The tendency of metal atoms to occupy degree 6 vertices is also reflected in the structures of some even more hypoelectronic dirhenaboranes of the type $Cp^*_2Re_2B_{n-2}H_{n-2}$ ($Cp^* = \eta^5$-Me_5C_5; n = 8–12), discovered by Fehlner, Ghosh, and their co-workers [16–19]. Such dirhenaboranes with n vertices have only $2n-4$ Wadean skeletal electrons by the Wade–Mingos rules [6–9] and have the rhenium atoms at degree 6 or even degree 7 vertices (Fig. 3). The rhenium vertices are located in antipodal positions leaving a belt of lower degree (4 or 5) boron atoms. The disparity between the relatively low curvatures at the degree 6 and 7 antipodal rhenium vertices and the significantly higher curvatures at the degree 4 and 5 equatorial boron vertices leads to highly flattened (oblate) structures, which can conveniently be called *oblatocloso* structures [20]. A recent density functional theory (DFT) study [21] led to the

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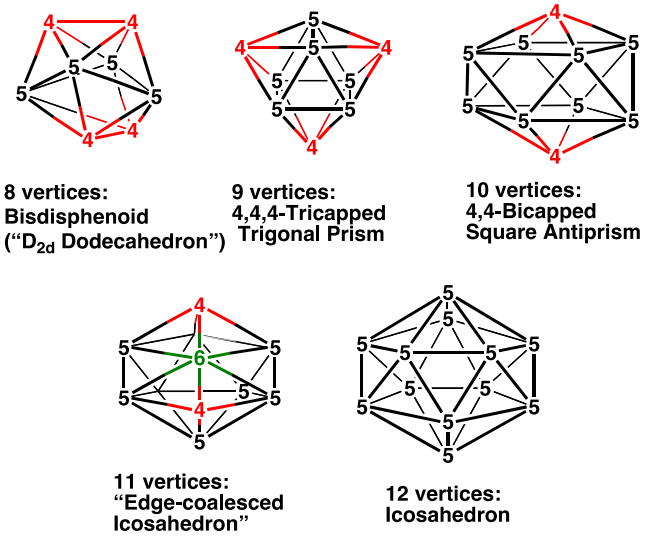

Fig. 1. The most spherical deltahedra having from 8 to 12 vertices found in *n*-vertex metallaboranes having $2n + 2$ Wadean skeletal electrons. In Figs. 1–3 the numbers indicate the vertex degrees. In Figs. 1 and 2 vertices are color coded with degree 4, 5, and 6 vertices being red, black, and green, respectively. (Color Online.)

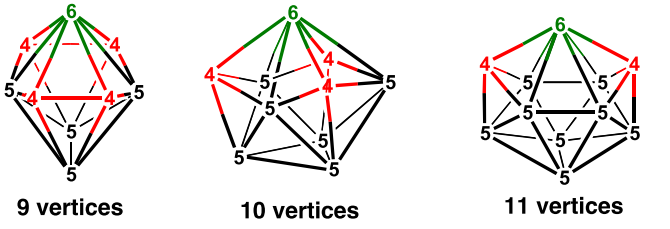

Fig. 2. The *isocloso* deltahedra found in metallaboranes found in *n*-vertex systems having $2n$ Wadean skeletal electrons. A metal atom rather than a boron atom is located at the unique degree 6 vertex.

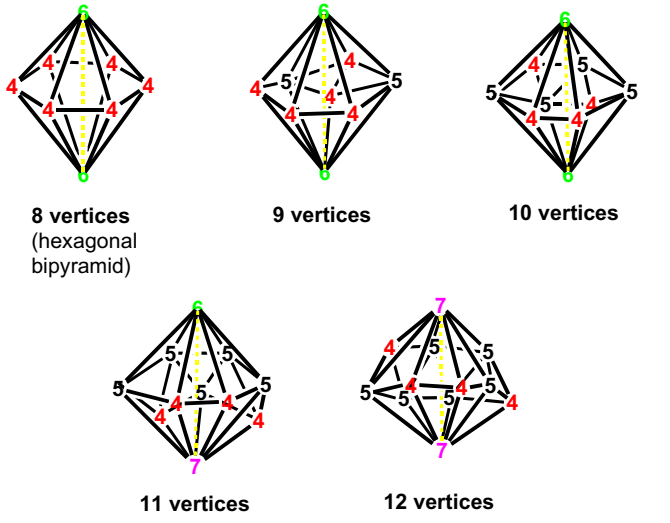

Fig. 3. The *oblatocloso* deltahedra found in the experimental structures of the $Cp^*_2Re_2B_{n-2}H_{n-2}$ dirhenaboranes (n = 8, 9, 10, 11, 12).

gratifying conclusion that the experimentally observed *oblatocloso* structures are the lowest energy structures for the corresponding unsubstituted cyclopentadienyl derivatives $Cp_2Re_2B_{n-2}H_{n-2}$ (n = 8–12). In addition, some interesting higher energy $Cp_2Re_2B_{n-2}H_{n-2}$ structures were found in this theoretical study, including *closo* and *isocloso* deltahedral structures having adjacent rhenium atoms with short Re-Re distances and relatively high Wiberg bond indices (WBIs) suggesting formal triple or quadruple rhenium-rhenium bonds on the deltahedral surface. A subsequent theoretical study [22] showed that if the two CpRe units are replaced by a single $PnRe_2$ unit (Fig. 4: Pn = η^5, η^5-C_8H_6 where C_8H_6 = pentalene), these structures containing surface rhenium–rhenium multiple bonds become the lowest energy structures. The effect of the pentalene ligand is to force the two rhenium atoms to remain in adjacent positions in the polyhedral structure thereby geometrically excluding the possibility of *oblatocloso* structures having the rhenium atoms in antipodal positions. Also note that the bis(pentahapto) pentalene ligand is effectively a 10-electron donor to the pair of rhenium atoms since each of the two carbon atoms shared by both rings of the pentalene unit can effectively donate their π electron simultaneously to both rhenium atoms.

These three fundamental types of dimetallaborane structures indicate increasing deviation from sphericity as the number of Wadean skeletal electrons is decreased from the $2n + 2$ skeletal electrons for the most spherical *n*-vertex *closo* structures (Fig. 1) through the $2n$ skeletal electrons for the *n*-vertex *isocloso* structures (Fig. 2) to the $2n-4$ skeletal electrons for the flattened *oblatocloso* structures (Fig. 3). However, systems with the intermediate $2n-2$ Wadean skeletal electrons remain unknown experimentally. In order to gain some insight regarding possible structures for such dimetallaboranes, the $Cp_2M_2B_{n-4}H_{n-2}$ systems (M = Ru, Os; n = 8–12) were investigated by DFT as examples of $2n-2$ Wadean skeletal electron systems [23]. Reasonable experimental routes are potentially available for the synthesis of at least the diruthenaboranes of this type. Thus the 8-vertex species [24] $Cp^*_2Ru_2B_6H_{12}$, the 10-vertex species [24–26] $Cp^*_2Ru_2B_8H_{12}$ and $Cp^*_2Ru_2B_8H_{14}$, and the 12-vertex species [27] $Cp^*_2Ru_2B_{10}H_{16}$ have been synthesized as possible precursors for syntheses of the corresponding $Cp^*_2Ru_2B_{n-2}H_{n-2}$ derivatives by dehydrogenation reactions ($Cp^* = \eta^5$-Me_5C_5).

Theoretical studies on these $Cp_2M_2B_{n-2}H_{n-2}$ systems (M = Ru, Os; n = 8–12) with $2n-2$ Wadean skeletal electrons predict the lowest energy such structures to have central deltahedra with $n-1$ or $n-2$ vertices. Triangular faces containing one or two metal vertices in this central deltahedron are capped by the remaining BH vertices [23]. This generates larger deltahedra having one or two degree 3 vertices leading to tetrahedral cavities. In all of the lowest energy such structures the metal atoms are located at the highest degree vertices, most frequently degree 6 vertices in accord with expectation. These metal vertices share a deltahedral edge with M–M distances ranging from 2.7 to 2.9 Å and Wiberg bond indices of ~0.3 to ~0.4. These M–M deltahedral edges can be considered to be formal single bonds. The structural pattern is found to change drastically for the 12-vertex systems $Cp_2M_2B_{10}H_{10}$ (M = Ru, Os) where the lowest energy structures are "*isoisocloso*" deltahedra having two degree 6 vertices for the metal atoms as well as eight degree 5 and two degree 4 vertices. Such systems have no degree

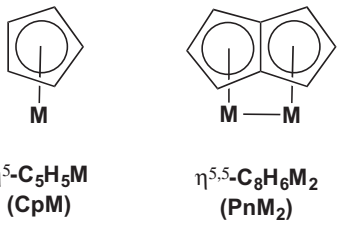

Fig. 4. The CpM and PnM_2 units in dimetallaborane structures.

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