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Journal of Organometallic Chemistry 692 (2007) 1773–1782

Journal of Organometallic Chemistry

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Review

# Supraicosahedral polyhedra in carboranes and metallacarboranes: The role of local vertex environments in determining polyhedral topology and the anomaly of 13-vertex *closo* polyhedra ☆

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Received 10 August 2006; received in revised form 7 September 2006; accepted 10 September 2006
Available online 19 September 2006

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## Abstract

Metal-free carboranes having 13 vertices are anomalous since their *closo* polyhedra having the expected 28 skeletal electrons are not the usual deltahedra with exclusively triangular faces but instead polyhedra with one or two trapezoidal faces obtained by removal of one or more edges from the corresponding 13-vertex deltahedron. Removal of such edges converts degree 6 boron vertices in the 13-vertex deltahedron into more favorable degree 5 boron vertices while lowering the degree of nearby carbon vertices. Thus the anomaly of the 13-vertex carborane *closo* polyhedron can be rationalized by the preference of boron for degree 5 vertices. The 12-vertex tetracarbon carborane $(CH_3)_4C_4B_8H_8$ with a *nido* electron count of 28 skeletal electrons but with two quadrilateral faces has a solid state structure derived from a 13-vertex "*closo*" polyhedron with one quadrilateral face by removal of a degree 4 vertex to give the second quadrilateral face. However, the corresponding tetraethyl derivative $(C_2H_5)_4C_4B_8H_8$ has a different solid state structure derived from removal of a degree 6 vertex from an unusual 13-vertex deltahedron with three degree 6 vertices to give an open hexagonal face rather than two quadrilateral faces. In contrast to the 13-vertex *closo* polyhedra, the 14-vertex *closo* polyhedron is a true deltahedron, namely the $D_{6d}$ bicapped hexagonal antiprism, which is found in a carborane derivative as well as in several dimetallacarboranes with the metal atoms always at the degree 6 vertices. However, the 15-vertex *closo* polyhedron, so far found only in the metallaborane 1,2-μ-$(CH_2)_3C_2B_{12}H_{12}$Ru($\eta^6$-*p*-cymene), is a non-deltahedron with one quadrilateral face.

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☆ This paper is dedicated to Prof. G. Pályi in recognition of his many important contributions to inorganic and organometallic chemistry.

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doi:10.1016/j.jorganchem.2006.09.011

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## 1. Introduction

The most stable boron cages, such as $B_{12}H_{12}^{2-}$ and $C_2B_{10}H_{12}$, are based on icosahedral structures [1,2]. In addition, icosahedral cages are found in the stable allotropes of elemental boron and many of the stable metal borides [3,4]. These observations suggest that the favored local vertex environment of a boron atom in a polyhedral cage is a degree 5 vertex, i.e., a vertex where five edges meet similar to all of the vertices of a regular icosahedron [5–8]. Previous papers discuss the role of local vertex environments in determining the most stable and least chemically reactive *closo* [8], *nido* [8], and *arachno* [9] boranes. This method considers boron vertices of degrees differing from the favored degree five to be defective vertices, which must be minimized in number and isolated from each other as much as possible to generate a structure having optimum stability. In addition to accounting for the stability of structures containing boron icosahedra, this approach accounts for the relatively high stability of the neutral binary boranes $B_{10}H_{14}$ and $B_{18}H_{22}$ and the ability of $B_6H_{10}$ to form transition metal complexes [10] such as $(\eta^2\text{-}B_6H_{10})Fe(CO)_4$. All of this work has been concerned with icosahedral or subicosahedral borane structures, i.e., structures based on polyhedra with no more than 12 vertices and the 26 skeletal electrons characteristic of stable icosahedral boron cages consistent with the Wade–Mingos rules [11–14].

One of the challenges in borane chemistry has been the synthesis of supraicosahedral boranes, i.e., boranes with structures based on polyhedra having more than the 12 vertices of the regular icosahedron and the 26 skeletal electrons of stable icosahedral boranes. This has not yet been achieved for homoatomic boranes of the type $B_nH_n^{z-}$ ($n > 12$, $z$ typically 2), even though the existence of such boranes has been the subject of a number of theoretical predictions [15–17]. Isoelectronic supraicosahedral carboranes of the type $C_2B_{n-2}H_n$ ($n > 12$) and their substitution products are more tractable synthetic objectives from a practical point of view. However, even here success was achieved only in 2003 with the discovery of the 13-vertex metal-free carborane 1,2-μ-$C_6H_4(CH_2)_2$–3-$C_6H_5$–1,2-$C_2B_{11}H_{10}$ by Welch and co-workers [18]. Structure determination by X-ray diffraction methods indicates that the $C_2B_{11}$ polyhedron of this carborane is not the 13-vertex deltahedron with the required 22 triangular faces (a docosahedron) expected from the Wade–Mingos rules [11–14]. Instead the polyhedron is a 13-vertex henicosahedron with only 21 faces where 20 of the faces are triangles but the remaining face is a $C_2B_2$ trapezoid. Subsequent very recent work by Deng et al. [19] resulted in the discovery of another 13-vertex metal-free carborane 1,2-μ-$(CH_2)_3$–3-$C_6H_5$–1,2-$C_2B_{11}H_{10}$, where the 13-vertex polyhedron is neither a docosahedron or a henicosahedron but a ditrapezoidal icosahedron with only 20 faces where two of the faces are trapezoids rather than triangles. More recent work [20] has led to the discovery of the 14-vertex metal-free carborane (μ-$CH_2$)$_3C_2B_{12}H_{12}$ in low yield.

This paper surveys the relationships between the polyhedra currently found in supraicosahedral carborane derivatives with the objectives of accounting for the polyhedra already found and suggesting possible structures for larger supraicosahedral carboranes and metallacarboranes.

## 2. Background

### 2.1. The three-dimensional aromaticity in polyhedral boranes and carboranes

Consider a borane or carborane polyhedron 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 (typically to a hydrogen atom or other monovalent atom or group) leaves three internal valence orbitals per vertex atom for a total of $3n$ internal orbitals for the internal skeletal bonding of the polyhedron. These $3n$ internal orbitals are partitioned into two twin internal or tangential orbitals per boron atom and a single unique internal or radial orbital per boron 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 polyhedron and splits these $2n$ orbitals into $n$ bonding and $n$ antibonding orbitals. This bonding is supplemented by an $n$-center core bond formed by the 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 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 [11–14] for a globally delocalized three-dimensional aromatic system [21,22].

For all boranes and carboranes having from six to twelve vertices the globally delocalized borane polyhedron is the most spherical deltahedron (Fig. 1), i.e., a polyhe-