

Opening cobaltadiborane deltahedra by external dimethylamino substituents: Conversion of icosahedra to *isonido* 12-vertex polyhedra

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ABSTRACT

The structures and energetics of the dimethylamino substituted cobaltadiboranes $(\text{Me}_2\text{N})_2\text{C}_2\text{B}_{n-3}\text{H}_{n-3}\text{CoCp}$ ($n = 8-12$) have been investigated by density functional theory. The lowest energy structures are based on the most spherical *closo* deltahedra in accord with the Wade-Mingos rules. Among the nine possible icosahedral 12-vertex $(\text{Me}_2\text{N})_2\text{C}_2\text{B}_9\text{H}_9\text{CoCp}$ structures the four structures with adjacent carbon atoms are the highest energy structures similar to the unsubstituted $\text{CpCoC}_2\text{B}_9\text{H}_{11}$ system. However, the C–C edges in these 12-vertex structures stretch to non-bonding distances of at least $\sim 2.0 \text{ \AA}$ thereby converting the *closo* icosahedron into an *isonido* polyhedron with a tetragonal face with the carbon atoms on the diagonal. The lowest energy structures of the subicosahedral $(\text{Me}_2\text{N})_2\text{C}_2\text{B}_{n-3}\text{H}_{n-3}\text{CoCp}$ ($n = 8-11$) systems are based on the corresponding *closo* deltahedra with a strong energetic preference for degree 4 rather than degree 5 carbon vertices.

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1. Introduction

The seminal work by Hawthorne and coworkers on metallaboranes [1] focused largely on dicarbaborane derivatives in which alkynes provided the source of the two cage carbon atoms in many of the synthetic methods. The preferred structures of most such metalladiboranes were found to be the most spherical *closo* deltahedra (Fig. 1) [2,3]. Such *closo* deltahedra with 6–12 vertices have only degree 4 and 5 vertices except for the 11-vertex *closo* deltahedron which necessarily has a single degree 6 vertex [4]. The Wade-Mingos rules [5–8] relate such n -vertex structures to the presence of $2n + 2$ skeletal electrons where a BH vertex is a donor of two skeletal electrons and a CH vertex is a donor of three skeletal electrons. Considering the 18-electron rule indicates a cyclopentadienylcobalt ($\text{CpCo} = \eta^5\text{-C}_5\text{H}_5$) vertex to be a donor of two skeletal electrons similar to a BH vertex. Thus species of the type $\text{CpCoC}_2\text{B}_{n-3}\text{H}_{n-1}$ as well as species obtained by substitution of external hydrogens on either the $\text{CoC}_2\text{B}_{n-3}$ cluster or the Cp ring were the prototypical very stable metalladiboranes exhibiting *closo* deltahedral structures synthesized in the earliest work in this area.

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Further development of the chemistry of metallaboranes, particularly by Kennedy and coworkers [9–12], led to the identification of less spherical so-called *isocloso* metallaborane deltahedra having a degree 6 vertex for the metal atom as shown in Fig. 2 for the 9- and 10-vertex systems. Metallaborane structures based on n -vertex *isocloso* deltahedra are slightly hypoelectronic since they have $2n$ rather than $2n + 2$ Wadean skeletal electrons. However, removal of one vertex from an *isocloso* deltahedron having $2n$ skeletal electrons gives an *isonido* polyhedron with one non-triangular face. Such n -vertex *isonido* polyhedra retain the $2(n + 1)$ skeletal electrons of the $(n + 1)$ -vertex *isocloso* deltahedra from which they are derived and thus have $2n + 2$ skeletal electrons like n vertex *closo* deltahedra. An *isonido* polyhedron obtained by removal of a degree 4 vertex from an *isocloso* polyhedron has a tetragonal open face. Squeezing a diagonal of this tetragonal open face to a bonding distance leads to a deltahedron which can be a most spherical *closo* deltahedron (Fig. 1). The reverse of such squeezing, namely stretching an edge of a *closo* deltahedron to a non-bonding distance is an alternative way of generating an *isonido* polyhedron. Thus there can be a close relationship between a *closo* deltahedron having all triangular faces and an *isonido* polyhedron with a tetragonal open face.

The original syntheses of dicarbaboranes and their conversion to metalladiboranes used alkynes as the source of the two cage carbon atoms. As a result, kinetically favored but thermodynamically disfavored isomers with adjacent carbon atoms were

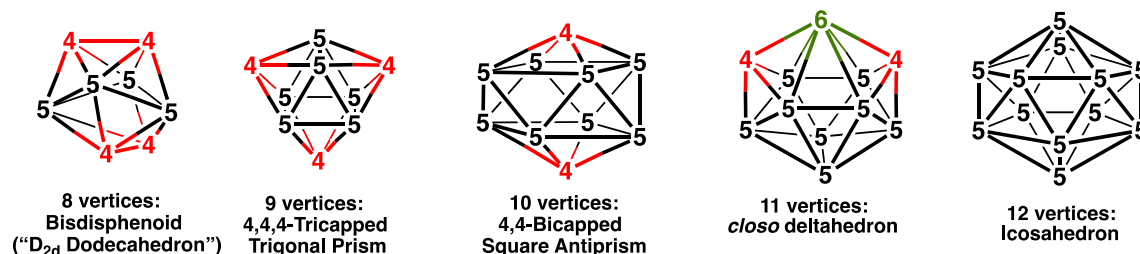


Fig. 1. The most spherical *closo* deltahedra having 8–12 vertices indicating the degree of each vertex. The vertices are also color coded with degree 4, 5, and 6 vertices as red, black, and green, respectively. (Colour online.)

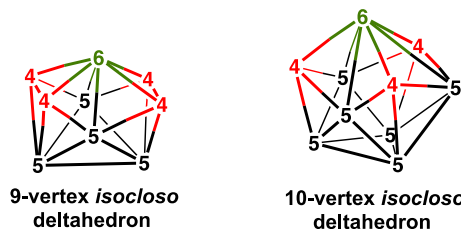


Fig. 2. Experimentally realized *isocloso* deltahedra showing a degree 6 vertex for a metal atom in a metallaborane structure.

initially produced. In many cases, including the unsubstituted icosahedral dicarbaboranes $C_2B_{10}H_{12}$, pyrolysis of the initially produced structures with adjacent carbon atoms leads to migration of the carbon atoms away from each other. This produces lower energy isomers having non-adjacent carbon atoms.

A largely unexplored issue is whether external substituents can be found for metalladiboraboranes which lead to significant deviations from the most spherical *closo* deltahedral structures for n -vertex systems having $2n + 2$ Wadean skeletal electrons. In this connection dialkylamino substituents are of interest since zwitterionic resonance structures with positive charges on the nitrogen atoms and negative charges on the carbon vertices to which they are bonded can effectively provide additional skeletal electrons for the central MC_2B_{n-3} cage (Fig. 3). A full donation of an otherwise lone pair on the nitrogen atom into the skeletal bonding in an n -vertex metalladiboraborane would convert a $2n + 2$ *closo* skeletal electron count into a $2n + 4$ *nido* skeletal electron count. The Wade-Mingos rules [5–8] would therefore suggest stretching one or more deltahedral edges to non-bonding distances thereby converting the original *closo* deltahedron into a *nido* polyhedron with one “open” non-triangular face. This open face can be a quadrilateral, pentagon, or hexagon depending on how many original deltahedral edges are stretched.

Possible synthetic routes to dialkylamino-substituted icosahedral carboranes, $(R_2N)_2C_2B_{10}H_{10}$, could involve either reactions of

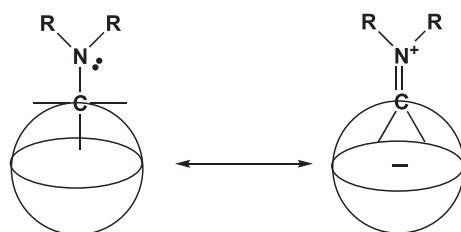


Fig. 3. Schematic representation of the electron transfer from the nitrogen lone pair of the external dialkylamino group to the carbaborane cage. The carbaborane cage is represented generically by a sphere.

bis(dialkylamino)alkynes, $R_2NC\equiv CNR_2$, with decaborane derivatives or treatment of the lithiated derivative $B_{10}H_{10}C_2Li_2$ with hydroxylamine derivatives. Dialkylamino dicarbollides of the type $[(R_2N)_2C_2B_9H_{11}]^-$ obtained by base degradation of $(R_2N)_2C_2B_{10}H_{10}$ analogous to the original syntheses of $CpCoC_2B_9H_{11}$ and related derivatives by Hawthorne and coworkers [1] could then provide a means of introducing transition metals into dialkylamino-substituted dicarbaborane structures.

Other aspects of the chemistry of bis(dialkylamino)acetylenes suggest the fragility of their $C\equiv C$ triple bonds towards even complete cleavage in suitable organometallic systems. Thus di-*tert*-butylacetylene, $Me_3CC\equiv CMe_3$, retains the central carbon–carbon bond upon reaction with iron carbonyls under suitable conditions to give the a tetrahedrane derivative $(Me_3C)_2C_2Fe_2(CO)_6$ [13]. Reaction of the dialkylaminoacetylene $Et_2NC\equiv CNEt_2$ with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ gives a product of analogous stoichiometry $(Et_2N)_2C_2Fe_2(CO)_6$ [14]. However, its structure is totally different with two separate bridging diethylaminocarbyne ligands having their carbyne carbon atoms not within bonding distance of each other [15]. Thus the $C\equiv C$ triple bond in $Et_2NC\equiv CNEt_2$ undergoes complete cleavage upon such reactions with iron carbonyls (see Fig. 4).

We now report comprehensive theoretical studies on the dimethylamino-substituted $(Me_2N)_2C_2B_{n-3}H_{n-3}CoCp$ ($n = 8–12$) cobaltadiboraboranes for comparison with earlier work [16,17] on the corresponding unsubstituted $CpCoC_2B_{n-3}H_{n-1}$ systems. As is the case for the unsubstituted derivatives, we still find the lowest energy $(Me_2N)_2C_2B_{n-3}H_{n-3}CoCp$ structures to be based on the corresponding most spherical *closo* deltahedra (Fig. 1) in accord with the Wade-Mingos rules [5–8]. However, we find that the dimethylamino substituents lead to some stretching of edges involving the carbon atoms to which they are attached. This effect is especially significant for the $(Me_2N)_2C_2B_9H_9CoCp$ structures based on icosahedra with adjacent carbon atoms in which C–C edges of the icosahedra are stretched to clearly non-bonding lengths. The resulting central 12-vertex C_2B_9Co polyhedra can be considered to be *isonido* polyhedra with an open tetragonal face. This is consistent with the $2n + 2$ Wadean skeletal electrons of these systems.

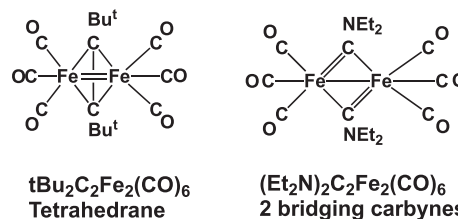


Fig. 4. Comparison of the tetrahedrane structure of $(Me_3C)_2C_2Fe_2(CO)_6$ having a C–C bond with the bridging diethylaminocarbyne structure of $(Et_2N)_2C_2Fe_2(CO)_6$ without a direct C–C bond.

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