Inorg. Chem. **1999,** *38,* 5151−5153

Topological Aspects of the Skeletal Bonding in "*Isocloso*" Metallaboranes Containing "Anomalous" Numbers of Skeletal Electrons

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Received May 25, 1999

Removal of the transition metal vertex from an "*isocloso*" metallaborane having 9, 10, or 11 vertices and 2ν skeletal electrons leads to a $B_nH_n^{2-}$ ligand or isoelectronic derivative thereof having one open hexagonal face for hexahapto bonding to the transition metal and $2\nu - 7$ triangular faces. The numbers of available skeletal electrons and orbitals in such *isocloso* metallaboranes correspond to ν 2-electron 3-center bonds in ν of the $2\nu - 4$ faces of the original metallaborane deltahedron. This contrasts with the 2-electron ν-center core bond and the ν surface bonds in the *closo* metal-free $B_nH_n^{2-}$ and $C_2B_{n-2}H_n$ deltahedra with $2\nu + 2$ skeletal electrons. A diamond−square process removing an M−B edge from an *isocloso* metallaborane to give an "*isonido*" metallaborane converts a set of six skeletal orbitals from two 2-electron 3-center bonds into three 2-electron 2-center bonds.

The structures of the most stable cage boranes are based on deltahedra with the maximum numbers of degree 4 and degree 5 vertices, where a deltahedron is defined as a polyhedron in which all faces are triangles. Such *closo* deltahedral boranes were recognized in the early 1970s[1] to contain $2\nu + 2$ skeletal electrons, where ν is the number of vertices of the deltahedron. Electron-rich polyhedral boranes containing more than $2\nu + 2$ skeletal electrons were considered to be derived from larger *closo* deltahedral boranes by removal of either one vertex to give so-called *nido* structures with $2\nu + 4$ apparent skeletal electrons or two vertices to give so-called *arachno* structures with $2\nu + 6$ apparent skeletal electrons.[2] These skeletal electron counting rules apply to almost all polyhedral borane structures in which the vertices are boron or other nonmetal atoms such as carbon or sulfur.

Shortly after the discovery of deltahedral boranes, it was found that very stable polyhedral metallaboranes could be obtained by the replacement of one or more boron vertices in the polyhedral structure with an isolobal and isoelectronic transition metal vertex. The first such compounds were the so-called "dicarbollides" of Hawthorne and co-workers,[3] which have icosahedral MC_2B_9 structures with the same 26 skeletal electrons ($26 = 2\nu + 2$ for $\nu = 12$) as the simple icosahedral $C_2B_{10}H_{12}$ or $B_{12}H_{12}^{2-}$ and with the transition metal at one of the degree 5 vertices of the icosahedron. However, as metallaborane chemistry was developed further, particularly by Kennedy and co-workers,[4−7] a variety of deltahedral metallaborane structures were discovered based on deltahedra topologically distinct from the deltahedra found in simple boranes and carboranes. Of particular interest are the 9- and 10-vertex structures based on a deltahedron with the transition metal at a degree 6 vertex whereas the corresponding metal-free deltahedron has only degree 4 and 5 vertices (Figures 1 and 2). What is even more interesting is the fact that such "anomalous" metallaborane deltahedra are also "disobedient" in not having the expected $2\nu + 2$ skeletal electrons but only 2ν skeletal electrons.[4] Such disobedient deltahedral metallaborane skeletons with the anomalous 2ν skeletal electrons have been called "*isocloso*" metallaboranes. These *isocloso* deltahedral structures are derived from the corresponding *closo* deltahedron by diamond−square−diamond (dsd) rearrangements.[8,9] In such dsd rearrangements the intermediate polyhedron with a single quadrilateral face looks like a *nido* polyhedron (Figures 1 and 2), but one obtained by removal of a vertex of degree 4 rather than a larger degree from a deltahedron having $\nu + 1$ vertices. However, such apparent *nido* polyhedra do not have the expected[2] $2\nu + 4$ skeletal electrons but instead only $2\nu + 2$ skeletal electrons and accordingly have been called "*isonido*" polyhedra.[5,6] The 11-vertex *closo*/*isocloso* pair (Figure 2) is different from the 9- and 10-vertex *closo*/*isocloso* pairs (Figures 1 and 2) in that the 11-vertex *closo* and *isocloso* polyhedra are topologically equivalent with a single degree 6 vertex even though they are related by a diamond−square−diamond rearrangement like the 9- and 10-vertex *closo*/*isocloso* deltahedral pairs (Figure 2). This relates to the topological impossibility of an 11-vertex deltahedron having only degree 4 and 5 vertices.[10]

The reason for the anomalous electron counts in the *isocloso* structures (i.e., two electrons less than the $2\nu + 2$ skeletal electrons expected from "Wade's rules" [1]) has been the cause for some speculation. Ideas to rationalize this anomaly include postulation of Jahn−Teller distortions removing orbital degeneracies in the HOMO/LUMO region,[11−14] and postulating four-

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(1) Wade, K. *Chem. Commun.* **1971**, 792.

(2) Rudolph, R. W.; Pretzer, W. P. *Inorg. Chem.* **1972**, *11*, 1974.

(3) Callahan, K. P.; Hawthorne, M. F. *Adv. Organomet. Chem.* **1976**, *14*, 145.

(4) Bould, J.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1992**, 563.

(5) Kennedy, J. D.; Štíbr, B. In *Current Topics in the Chemistry of Boron*; Kabalka, G. W., Ed.; Royal Society of Chemistry: Cambridge, 1994; pp 285−292.

(6) Kennedy, J. D. In *The Borane-Carborane-Carbocation Continuum*; Casanova, J., Ed.; Wiley: New York, 1998; Chapter 3, pp 85−116.

(7) Štíbr, B.; Kennedy, J. D.; Drdáková, E.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1994**, 229.

(8) Lipscomb, W. N. *Science* **1966**, *153*, 373.

(9) King, R. B. *Inorg. Chim. Acta* **1981**, *49*, 237.

(10) King, R. B.; Duijvestijn, A. J. W. *Inorg. Chim. Acta* **1990**, *178*, 55.

(11) Baker, R. T. *Inorg. Chem.* **1986**, *25*, 109.

(12) Johnston, R. L.; Mingos, D. M. P. *Inorg. Chem.* **1986**, *25*, 3321.

(13) Johnston, R. L.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1987**, 647.

(14) Johnston, R. L.; Mingos, D. M. P. *Polyhedron* **1986**, *5*, 2059.

10.1021/ic990601v CCC: $18.00

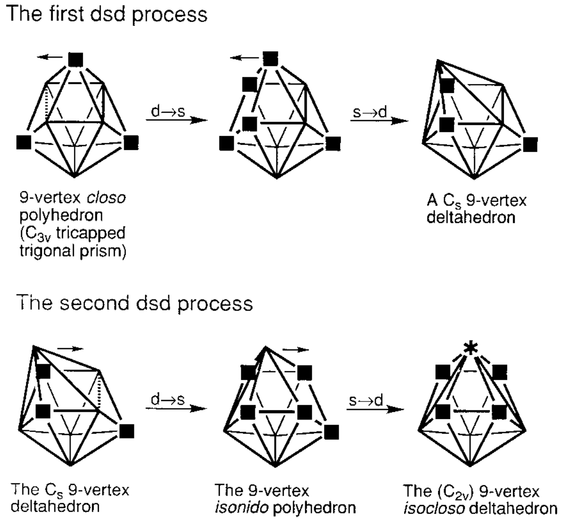

Figure 1. Sequence of two diamond−square−diamond (dsd) processes leading from the *closo* 9-vertex deltahedron (i.e., the C_{3v} tricapped trigonal prism) to the 9-vertex *isocloso* deltahedron. For clarity in Figures 1 and 2, the degree 4 and 6 vertices are indicated by squares and asterisks, respectively, and the edges broken in the d → s stage of the dsd process are indicated by hashed lines.

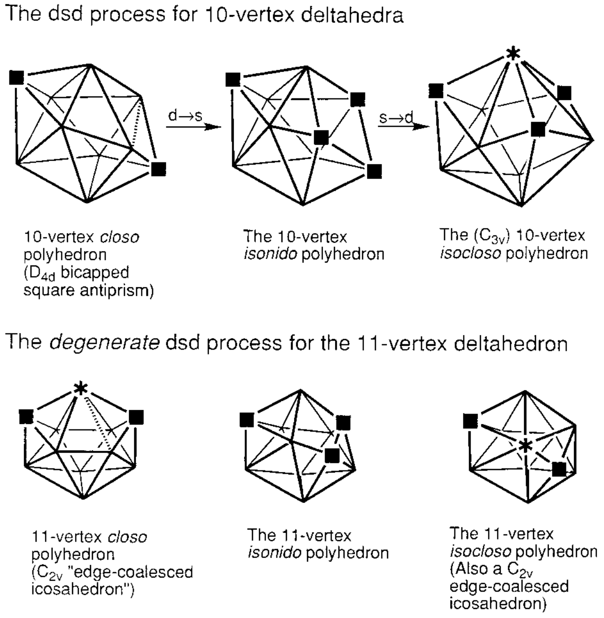

Figure 2. dsd processes for 10- and 11-vertex deltahedra. Note that the *isocloso* deltahedron for the 11-vertex structure is topologically equivalent to the 11-vertex *closo* polyhedron so that this dsd process is a *degenerate* dsd process in contrast to the dsd processes in the 9- and 10-vertex polyhedral systems.

orbital rather than the usual three-orbital involvement of the transition metal vertex to provide the "extra" electron pair.[4] In this paper I show how consideration of the *isocloso* metallaboranes as metal complexes of open borane ligands can provide the observed skeletal electron count simply by a network of 2-electron 3-center skeletal bonds in some of the triangular faces of the *isocloso* deltahedron. This bonding topology contrasts with the well-established bonding topology of the deltahedral boranes and carboranes such as $B_nH_n^{2-}$ and $C_2B_{n-2}H_n$ with a ν-center core bond in addition to surface bonding considered as a "resonance hybrid" of the Hamiltonian circuits of the deltahedron.[15,16]

Simple examples of such *isocloso* compounds are the 11-vertex ruthenium complexes of the type (arene)$RuB_{10}H_{10}$ (arene = *p*-cymene, hexamethylbenzene, etc.).[17] The Ru atom in such compounds can be considered to have a typical +2 formal oxidation state and the B_{10} ligand to be the dianion $B_{10}H_{10}^{2-}$. The compound can be seen to have 22 skeletal electrons (=2ν for ν = 11), with each neutral vertex [(arene)Ru or BH] contributing 2 skeletal electrons. However, the $B_{10}H_{10}^{2-}$ unit in this structure is not the closed bicapped square antiprismatic structure found in the isolated dianion $B_{10}H_{10}^{2-}$ with 16 triangular faces but instead has an open structure with 1 hexagonal face and 12 triangular faces (Figure 3). Similarly, *isocloso* metallaboranes with 9 and 10 vertices can be considered to be transition metal derivatives of open $B_8H_8^{2-}$ and $B_9H_9^{2-}$ anions with 1 hexagonal face and $2\nu - 10$ triangular faces. However, in many cases one or more of the external hydrogen atoms in the open $B_{\nu-1}H_{\nu-1}^{2-}$ ligand are replaced by either Lewis base ligands (e.g., phosphines or isocyanides) or other monovalent groups [e.g., Cl in $(Me_3P)_2HIrB_8H_7Cl$ (ref 18)], and/or a boron atom is replaced by a carbon atom with the necessary adjustments in electron count. In all cases the open $B_{\nu-1}H_{\nu-1}^{2-}$ ligand can be regarded as a hexahapto ligand toward the transition metal vertex.

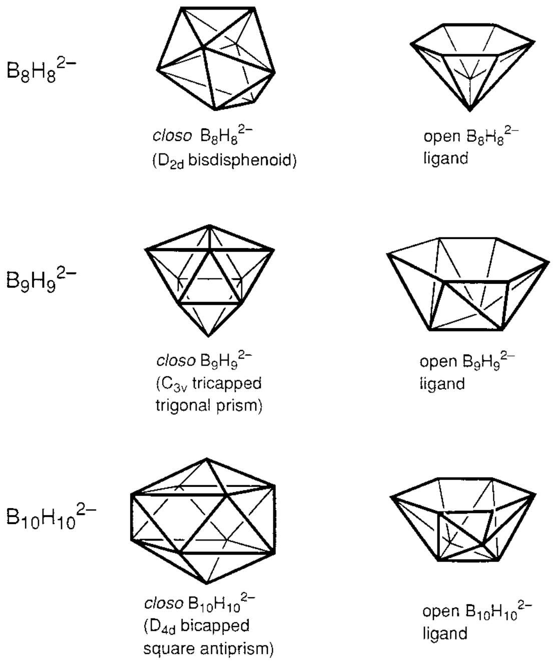

Figure 3. A comparison of the $B_nH_n^{2-}$ *closo* deltahedra and the open $B_nH_n^{2-}$ ligand polyhedra in *isocloso* complexes for n = 8, 9, and 10.

Consider the bonding topology in a deltahedron with ν vertices, which can be shown by Euler's theorem to have $2\nu - 4$ faces and $3\nu - 6$ edges.[19] If each vertex (e.g., a neutral BH vertex or isoelectronic/isolobal equivalent) contributes three skeletal (internal) orbitals and two skeletal electrons (i.e., a 2ν skeletal electron system), then the numbers of skeletal orbitals and electrons are correct for 2-electron 3-center bonds in ν of the $2\nu - 4$ faces, leaving $\nu - 4$ faces without 2-electron 3-center bonds. These ν 2-electron 3-center bonds can be partitioned into $\nu - 3$ B−B−B bonds in the open $B_{\nu-1}H_{\nu-1}^{2-}$ ligand and three

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(15) King, R. B.; Rouvray, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 7834.

(16) Stone, A. J.; Alderton, M. J. *Inorg. Chem.* **1982**, *21*, 2297.

(17) Bown, M.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3039.

(18) Bould, J.; Crook, J. E.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *Chem. Commun.* **1982**, 346.

(19) King, R. B. *Applications of Graph Theory and Topology in Inorganic Cluster and Coordination Chemistry*; CRC Press: Boca Raton, FL, 1993.

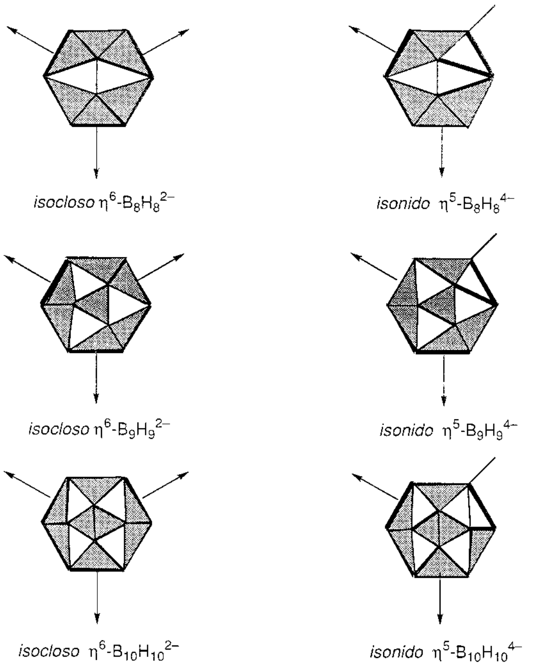

Figure 4. Locations of the B−B−B 3-center bonds (shaded faces) in the B_nH_n *isocloso* and *isonido* ligands. The points of connection of the peripheral hexagon to the metal vertex are indicated by arrows (for 2-electron 3-center M−B−B bonds) or lines (for 2-electron 2-center M−B bonds in the *isonido* complexes). Bold edges correspond to 2-electron 2-center B−B bonds in the *isonido* $B_nH_n^{4-}$ ligands.

M−B−B bonds to connect the open hexagonal face of the $B_{\nu-1}H_{\nu-1}^{2-}$ ligand to the transition metal vertex. Thus, three of the “vacant” faces (i.e., faces without 3-center bonds) are in the connection of the open hexagonal face of the $B_{\nu-1}H_{\nu-1}^{2-}$ ligand to the transition metal vertex, and the remaining $\nu - 7$ vacant faces are found within the $B_{\nu-1}H_{\nu-1}^{2-}$ ligand. The arrangements of the B−B−B bonds in the $B_{\nu-1}H_{\nu-1}^{2-}$ ligands for the interesting cases $\nu - 1 = 8$, 9, and 10 are given in Figure 4, with the faces containing B−B−B 2-electron 3-center bonds being shaded and the vacant B−B−B faces being unshaded.

Now consider the breaking of one M−B edge in an *isocloso* deltahedron by a diamond−square process to form the corresponding *isonido* deltahedron (Figures 1 and 2). The $B_{\nu-1}$ ligand now becomes a pentahapto $B_{\nu-1}H_{\nu-1}^{4-}$ ligand, and the extra skeletal electron pair converts the 6 skeletal orbitals of adjacent M−B−B and B−B−B 2-electron 3-center bonds into one M−B and two B−B 2-electron 2-center bonds (Figure 4). An example of such an *isonido* complex is the 9-vertex complex $(Ph_3P)_2Ir(CO)CB_7H_8$ (ref 7) containing a $(Ph_3P)_2IrCO$ vertex donating three skeletal electrons and the η^5-$CB_7H_8^{3-}$ ligand isoelectronic with η^5-$B_8H_8^{4-}$. The Ir thus has the typical +3 formal oxidation state and coordination number 6 if the open face of the $CB_7H_8^{3-}$ ligand is considered to be tridentate like cyclopentadienyl.

This paper shows that the analysis of the bonding topology in *isocloso* cage metallaboranes having 2ν skeletal electrons is as simple as that of the *closo* cage boranes having $2\nu + 2$ skeletal electrons and that each vertex atom in both structure types, including the transition metal vertices, can be considered to provide three skeletal orbitals. In the case of the *isocloso* metallaboranes, the skeletal bonding consists of 2-electron 3-center bonds in ν of the $2\nu - 4$ faces of the deltahedron. However, in the case of the *closo* boranes, the skeletal bonding consists of one ν-center core bond at the center of the deltahedron and ν 2-electron 2-center bonds in the surface of the deltahedron.

Acknowledgment. I am indebted to the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

IC990601V