Inorg. Chem. **2005**, *44*, 466–467

Inorganic Chemistry
Communication

Eight-Vertex Tetrametallic Structures Derived from Cubanes: A Close Relationship between Bisdisphenoidal Metallaborane and Organometallic Clusters

R. Bruce King*

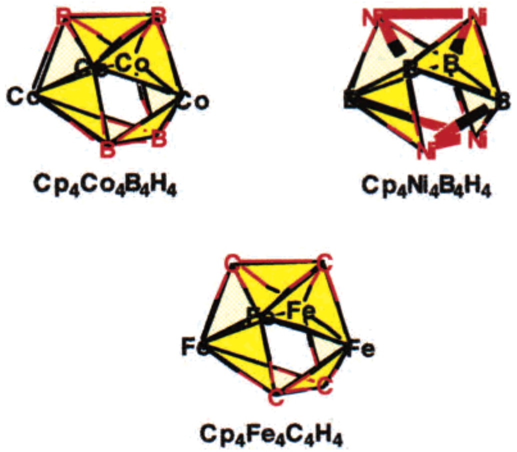
Department of Chemistry, University of Georgia, Athens, Georgia 30602

Received October 19, 2004

The metallaborane $Cp_4Co_4B_4H_4$ and the organometallic cluster $Cp_4Fe_4C_4H_4$ ($Cp = \eta^5$-cyclopentadienyl) not only are isoelectronic but also exhibit completely analogous eight-vertex bisdisphenoidal structures. Such structures, as well as the tetracapped tetrahedral structure of the $Cp_4Fe_4(\mu_3\text{-}CO)_4$ precursor to $Cp_4Fe_4C_4H_4$, can be derived from a cube by insertion of diagonals in each of the six faces. Furthermore, the formation of $Cp_4Fe_4C_4H_4$ from $Cp_4Fe_4(\mu_3\text{-}CO)_4$ can be described as a double diamond–square–diamond process preserving D_{2d} symmetry throughout the process.

The chemistry of boranes and metallaboranes is characterized by the formation of a variety of stable clusters exhibiting structures based on deltahedra or deltahedral fragments. This Communication presents an apparently previously unrecognized direct connection between eight-vertex D_{2d} bisdisphenoidal metallaboranes discovered in the late 1970s and boron-free organometallic clusters discovered much more recently. This direct connection is of interest since it indicates that carbon can completely replace boron in suitably chosen deltahedral organometallic clusters.

The metallaboranes of interest are the bisdisphenoidal metallaboranes $Cp_4M_4B_4H_4$ ($M = Co$[1] and Ni;[2,3] Cp = cyclopentadienyl or methylcyclopentadienyl). In the cobalt derivative, the metal atoms are located at the degree 5 vertices of the bisdisphenoid whereas in the nickel derivative, with four extra apparent skeletal electrons, the metal atoms are located at the degree 4 vertices (Figure 1a). The chemical bonding in these metallaboranes has been extensively discussed in several papers[4−6] and a review.[7] In $Cp_4Co_4B_4H_4$ the 16 skeletal electrons can be accommodated in eight three-center two-electron (3c−2e) bonds in eight of the 12 deltahedral faces (yellow faces in Figure 1a) similar to other n-vertex "isocloso" deltahedral metallaboranes with $2n$ skeletal electrons.[8] Similarly, the 20 skeletal electrons in $Cp_4Ni_4B_4H_4$ can be accommodated by four 3c−2e and six 2c−2e skeletal bonds (yellow faces and bold edges, respectively, in Figure 1a).



$Cp_4Co_4B_4H_4$ $Cp_4Ni_4B_4H_4$

$Cp_4Fe_4C_4H_4$

Figure 1. (a) The bisdisphenoidal metallaboranes $Cp_4M_4B_4H_4$ ($M = Co$ and Ni). (b) The bisdisphenoidal organometallic cluster $Cp_4Fe_4C_4H_4$. The Cp rings on the metal atoms and the H atoms on B and C are omitted for clarity. Faces with 3c−2e bonds are colored yellow, and edges corresponding to 2c−2e bonds are bold. Degree 5 vertices are depicted in black, and degree 4 vertices are depicted in red.

The closely related bisdisphenoidal boron-free organometallic clusters $Cp_4Fe_4C_4H_4$ were first obtained in 1998 by the reduction of the tetrahedral cluster $Cp_4Fe_4(\mu_3\text{-}CO)_4$ with excess $LiAlH_4$ in tetrahydrofuran.[9] The cluster $Cp_4Fe_4C_4H_4$ is exactly isoelectronic with $Cp_4Co_4B_4H_4$ and exhibits an identical bisdisphenoidal structure with the iron atoms at the degree 5 vertices (Figure 1b).

The $Cp_4Fe_4(\mu_3\text{-}CO)_4$ precursor to $Cp_4Fe_4C_4H_4$ can be considered as an Fe_4C_4 tetracapped tetrahedron derived from an Fe_4C_4 cubane by adding diagonals on each of the six faces to generate the six Fe−Fe bonds in the underlying Fe_4 tetrahedron (Figure 2). The carbon atoms of the μ_3-CO

---

* E-mail: rbking@sunchem.chem.uga.edu.

(1) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 257.
(2) Bowser, J. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 4623.
(3) Bowser, J. R.; Bonny, A.; Pipal, J. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1979**, *101*, 6229.
(4) King, R. B. *Polyhedron* **1982**, *5*, 133.
(5) Fehlner, T. P. *J. Organomet. Chem.* **1994**, *478*, 49.
(6) King, R. B. *Inorg. Chem.* **2004**, *43*, 4241.
(7) Kennedy, J. D. *Prog. Inorg. Chem.* **1986**, *34*, 211.
(8) King, R. B. *Inorg. Chem.* **1999**, *38*, 5151.
(9) Okazaki, M.; Ohtani, T.; Inomata, S.; Tagaki, N.; Ogino, H. *J. Am. Chem. Soc.* **1998**, *120*, 9135.

10.1021/ic0485357 CCC: $30.25

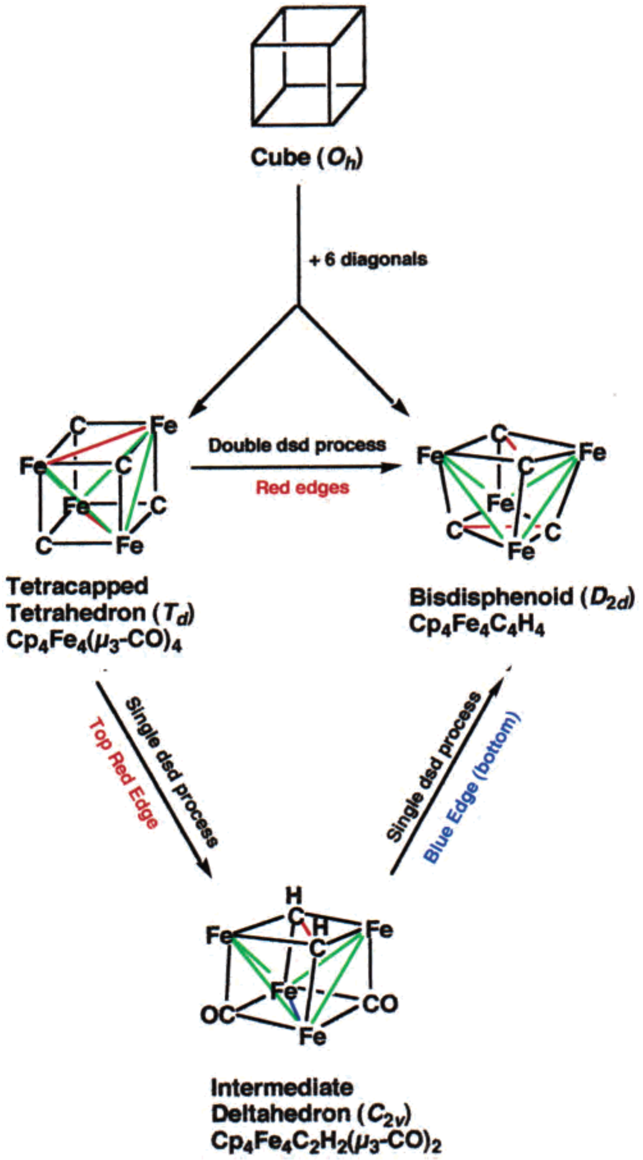


Figure 2. Conversion of a cube to the tetracapped tetrahedron cluster $Cp_4Fe_4(\mu_3\text{-}CO)_4$, the bisdisphenoid cluster $Cp_4Fe_4C_4H_4$, and the intermediate deltahedral cluster $Cp_4Fe_4C_2H_2(\mu_3\text{-}CO)_2$ showing the relevant dsd relationships. The added diagonals generating new edges are indicated in red, green, and blue. The red and blue edges are involved in dsd processes whereas the green edges remain as Fe−Fe bonds and are not involved in any of the dsd processes. External groups (Cp on Fe and H or CO on C) are omitted for clarity except for the CH and CO groups in $Cp_4Fe_4C_2H_2(\mu_3\text{-}CO)_2$.

groups then cap the faces of the Fe_4 tetrahedron, and T_d symmetry is preserved. The bisdisphenoidal structure of the $Cp_4Fe_4C_4H_4$ reduction product of $Cp_4Fe_4(\mu_3\text{-}CO)_4$ can also be derived from a cube by adding four diagonals corresponding to Fe−Fe bonds (green edges in Figure 2) and two diagonals corresponding to the new C−C bonds generated by pairwise coupling of the four μ_3-CO groups in $Cp_4Fe_4(\mu_3\text{-}CO)_4$ (red edges in Figure 2). Thus, in the reduction of $Cp_4Fe_4(\mu_3\text{-}CO)_4$ to $Cp_4Fe_4C_4H_4$ a double diamond−square−diamond (dsd) process is seen to occur involving the diagonals on opposite faces of the underlying cube. In this concerted double dsd process, two Fe−Fe bonds in $Cp_4Fe_4(\mu_3\text{-}CO)_4$ are broken, and the two C−C bonds in $Cp_4Fe_4C_4H_4$ are formed with D_{2d} symmetry being maintained throughout the reaction.

Reaction of $Cp_4Fe_4(\mu_3\text{-}CO)_4$ with a more limited amount of $LiAlH_4$ for a shorter period of time leads to the cationic derivatives[10] $[Cp_4Fe_4(\mu\text{-}CO)_3(\mu_3\text{-}CH)]^+$ and $[Cp_4Fe_4(\mu_3\text{-}CO)_2(\mu_3\text{-}CH)_2]^{2+}$. These exhibit tetracapped tetrahedral structures closely related to that of $Cp_4Fe_4(\mu_3\text{-}CO)_4$ but with one or two $\mu_3\text{-}CH^+$ groups replacing μ_3-CO groups. Note that $\mu_3\text{-}CH^+$ and μ_3-CO groups are both donors of two skeletal electrons in metal cluster structures.

An eight-vertex deltahedron intermediate between the T_d tetracapped tetrahedron of $Cp_4Fe_4(\mu_3\text{-}CO)_4$ and the D_{2d} bisdisphenoid of $Cp_4Fe_4C_4H_4$ is found in $Cp_4Fe_4C_2H_2(\mu_3\text{-}CO)_2$, which has been obtained by reduction of the dication $[Cp_4Fe_4(\mu_3\text{-}CO)_2(\mu_3\text{-}CH)_2]^{2+}$ with Cp_2Co in acetonitrile.[11] In the structure of $Cp_4Fe_4C_2H_2(\mu_3\text{-}CO)_2$ five of the six Fe−Fe distances are bonding distances in the range 2.48−2.58 Å, whereas the sixth Fe···Fe distance is clearly a nonbonding distance of 3.44 Å. The Fe_4C_4 polyhedron in $Cp_4Fe_4C_2H_2(\mu_3\text{-}CO)_2$ has C_{2v} symmetry and can be derived from the tetracapped tetrahedron of $Cp_4Fe_4(\mu_3\text{-}CO)_4$ by a single dsd rearrangement (Figure 2). In order to count skeletal electrons, the $Cp_4Fe_4C_2H_2(\mu_3\text{-}CO)_2$ cluster can be dissected into a $Cp_4Fe_4C_2H_2$ octahedron and two μ_3-CO groups. The cluster then has the 14 skeletal electrons required by the Wade−Mingos rules[12−14] for a globally delocalized octahedron by receiving four electrons from the four CpFe vertices, six electrons from the two CH vertices, and four electrons from the two μ_3-CO groups. A second dsd rearrangement of $Cp_4Fe_4C_2H_2(\mu_3\text{-}CO)_2$ using the blue Fe−Fe edge in Figure 2 gives the bisdisphenoid of $Cp_4Fe_4C_4H_4$.

In summary, the exact analogy between the metallaborane $Cp_4Co_4B_4H_4$ and the organometallic cluster $Cp_4Fe_4C_4H_4$ shows how deltahedral borane-type structures and chemistry can be observed in boron-free molecules. Since the $Cp_4Fe_4(\mu_3\text{-}CO)_4$ precursor to $Cp_4Fe_4C_4H_4$ and related compounds can be obtained by the simple pyrolysis[15,16] of the readily available $[CpFe(CO)_2]_2$, these organoiron clusters are potentially available in even larger quantities than their metallaborane analogues. This is particularly true since the only reported preparation[1] of $Cp_4Co_4B_4H_4$, namely from NaCp + NaB_5H_8 + $CoCl_2$, gives the product in very low yield.

Acknowledgment. I am indebted to the National Science Foundation for partial support of this work under Grant CHE-0209857.

IC0485357

---

(10) Okazaki, M.; Ohtani, T.; Takano, M.; Ogino, H. *Organometallics* **2004**, *23*, 4055.
(11) Okazaki, M.; Ohtani, T.; Ogino, H. *J. Am. Chem. Soc.* **2004**, *126*, 4105.
(12) Wade, K. *Chem. Commun.* **1971**, 792.
(13) Mingos, D. M. P. *Nat. Phys. Sci.* **1972**, *99*, 236.
(14) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.
(15) King, R. B. *Inorg. Chem.* **1966**, *5*, 2227.
(16) Westmeyer, M. D.; Mason, M. A.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1998**, *120*, 114.