

# The Role of Metals in Borane Clusters

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Metal-boron clusters exhibit a fantastic variety of molecular geometries that stimulate the imagination, lend new insight into the nature of cluster bonding, and open up all manner of possibilities in synthesis. These compounds—the metallaboranes,<sup>1</sup> metallacarboranes,<sup>1a,2</sup> and their relatives—contain one or more metal atoms (transition or main group) bound into a borane cage framework. In some species, it appears that a metal-ligand unit such as  $\text{Co}(\text{C}_5\text{H}_5)$  or  $\text{Fe}(\text{CO})_3$  simply replaces BH so that the gross cage geometry is unchanged (e.g., icosahedral  $\text{CpCoC}_2\text{B}_9\text{H}_{11}$  and  $\text{C}_2\text{B}_{10}\text{H}_{12}$ , or pentagonal-bipyramidal  $\text{CpCoC}_2\text{B}_4\text{H}_8$  and  $\text{C}_2\text{B}_5\text{H}_7$ ); such trends underlie the well-established electron-counting rules developed by Wade<sup>3</sup> and provide a workable theoretical foundation for this area. On the other hand, there are now many examples of stable, well-characterized metallaboron clusters that have no structural counterparts among the boranes and carboranes. In such cases, we are entitled to assume that the metal itself plays a crucial role in stabilizing the observed cage geometry; here the metal is not simply a “surrogate boron” but instead functions in a way that boron (or carbon) cannot. A number of examples appear throughout this Account.

Metal atoms in boron cages can also be important in a different sense, serving as versatile reaction centers on the cage framework and interacting with chemical species external to the cage. If the metal-substrate binding is labile, one has the possibility of creating a catalytic cycle involving the metallaborane, as has been demonstrated in several systems.<sup>4</sup> This kind of metal role is reminiscent of that found in some catalytically active metal clusters,<sup>5</sup> but the metallaboranes offer several advantages. First, so-called “rational” routes to some metallaboranes and metallacarboranes are available, permitting the synthesis of specific designed species;<sup>4a</sup> this is rarely possible with polyhedral metal clusters. Second, in general (with some important exceptions) metallaboranes and metallacarboranes are robust, nondissociating molecules that do not disintegrate under a wide variety of reaction conditions. Finally, there exists the possibility of involving both metal and B-H centers in interactions with attacking substrates (such as unsaturated hydrocarbons or arenes), allowing the development of synthetic schemes unique to metal-boron cluster chemistry; as will be shown, such reactions have been observed in the laboratory.

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Obviously, one could not hope to do justice to this broad subject in a short Account. Moreover, detailed information on the mechanistic role of metals in borane cages is presently so fragmentary that a definitive treatment may be some time away. In this Account I have selected a few examples to illustrate the current state of the art, with the hope of stimulating the flow of ideas between related areas of inorganic and organometallic cluster chemistry.

For an introduction to the general subject of metallaboron cage compounds, the reader is referred to several earlier Accounts<sup>3b,6</sup> and longer reviews.<sup>1,2</sup> Here I shall be concerned with two principal functions of metal atoms in borane frameworks: the “inward-directed” role of cage stabilization and “outward-directed” (i.e., exopolyhedral) interactions with substrate molecules in synthetically useful ways.

## Metals as Stabilizers of Borane Frameworks

After three-quarters of a century of research on the boron hydrides, dating back to Alfred Stock, the basic structural patterns are clear enough.<sup>7</sup> The  $\text{B}_n\text{H}_n^{2-}$  ions have closed polyhedral (closo) geometries and are remarkably stable;  $\text{B}_{10}\text{H}_{10}^{2-}$  and  $\text{B}_{12}\text{H}_{12}^{2-}$  resist degradation even by strong acids. The neutral boranes,  $\text{B}_n\text{H}_{n+m}$ , are mostly open-cage molecules whose structures are polyhedral fragments and exhibit variable stability. Of those having fewer than 10 boron atoms, none can survive more than brief exposure to air or moisture, and many are extremely reactive, e.g.,  $\text{B}_2\text{H}_6$ ,  $\text{B}_5\text{H}_9$ ,  $\text{B}_5\text{H}_{11}$ , and  $\text{B}_3\text{H}_2$ . Other species have been observed only in mass spectra or as transients in reactions; examples are  $\text{B}_4\text{H}_8$  and  $\text{B}_7\text{H}_x$  (no heptaborane has been isolated). Many of these unstable or nonexistent boranes can, however, be obtained as metallaborane analogues in which some of the BH units are replaced by metal-ligand groups that are electronically equivalent in a

(1) (a) Grimes, R. N. In “Comprehensive Organometallic Chemistry”; Wilkinson, G.; Stone, F. G. A.; Abel, E., Eds.; Pergamon Press: Oxford, 1982, Vol. 1. (b) Greenwood, N. N.; Ward, I. M. *Chem. Soc. Rev.* 1974, 3, 231. (c) Greenwood, N. N.; Kennedy, J. D. In “Metal Interactions with Boron Clusters”; Grimes, R. N., Ed.; Plenum: New York, 1982, Chapter 2.

(2) (a) Dunks, G. B.; Hawthorne, M. F. In “Boron Hydride Chemistry”; Muettterties, E. L., Ed.; Academic Press: New York, 1975, Chapter 11. (b) Grimes, R. N. *Organomet. React. Synth.* 1977, 6, 63. (c) Onak, T. *Organomet. Chem.* 1976, 5, 67.

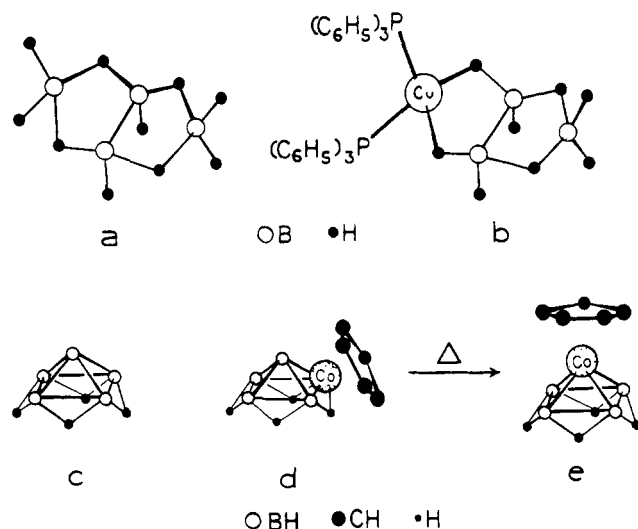
(3) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* 1976, 18, 1. (b) Rudolph, R. W. *Acc. Chem. Res.* 1976, 9, 446. (c) Mingos, D. M. P. *Nature (London), Phys. Sci.* 1972, 236, 99.

(4) (a) Delaney, M. S.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* 1981, 20, 1341 and references therein. (b) Hoel, E. L.; Talebinasab-Savari, M.; Hawthorne, M. F., *J. Am. Chem. Soc.* 1977, 99, 4356 and references therein. (c) Zakharkin, L. I.; Agakhanova, T. B. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1980, 1208 and references therein. (d) Chandrasekaran, E. S.; Thompson, D. A.; Rudolph, R. W. *Inorg. Chem.* 1978, 17, 760.

(5) (a) Robinson, A. L. *Science (Washington, D.C.)* 1976, 194, 1150. (b) Muettterties, E. L. *Ibid.* 1977, 196, 839. (c) Muettterties, E. L. *J. Organomet. Chem.* 1980, 200, 177.

(6) (a) Grimes, R. N. *Acc. Chem. Res.* 1978, 11, 420. (b) Hawthorne, M. F. *Ibid.* 1968, 1, 281.

(7) Lipscomb, W. N. *Science (Washington, D.C.)* 1977, 196, 1047 and references therein.



**Figure 1.** (a) Structure of  $B_4H_{10}$ . (b) Structure of  $[(C_6H_5)_3P]_2CuB_3H_8$ . (c) Structure of  $B_5H_9$ . (d and e) Structures of 2- and 1- $(C_5H_5)CoB_4H_8$  (terminal H atoms are omitted in (c), (d), and (e)).

formal sense. Substitution for even a single boron often works wonders. For example, as analogues of  $B_4H_{10}$  and  $B_5H_9$  (which oxidize violently in air), one has the metal species  $[(C_6H_5)_3P]_2CuB_3H_8$ <sup>8</sup> and 2- $(C_5H_5)CoB_4H_8$ ,<sup>9</sup> both of which are air-stable crystalline solids (Figure 1b,d). The red cobalt complex thermally rearranges<sup>9</sup> to pale yellow 1- $(C_5H_5)CoB_4H_8$  (Figure 1e); both isomers are structural and electronic counterparts of  $B_5H_9$  (Figure 1c). In addition, however, the 1-isomer illustrates metal-borane stabilization in a different sense: it contains the square cyclic  $B_4H_8^{2-}$  ligand, an isoelectronic analogue of the cyclobutadienide ion,  $C_4H_4^{2-}$ . A recent X-ray diffraction investigation<sup>10a</sup> of 1- $(C_5H_5)CoB_4H_8$  disclosed an average Co-B distance of 1.967 (2) Å, statistically identical with the corresponding Co-C bond length in  $(C_5H_5)Co(C_4H_4)$  [1.965 (1) Å]<sup>10b</sup> despite the larger covalent radius of boron vs. carbon; this implies a more covalent metal-ligand interaction in the cobaltaborane complex, a conclusion that is consistent with UV-photoelectron studies of  $B_5H_9$  and analogous metallaboranes.<sup>10c</sup>

How does one achieve "metal substitution" in borane structures? For the larger systems (10 vertices or more) there are reasonably straightforward routes<sup>1,2</sup> involving reactions of metal reagents with open-cage anions such as  $C_2B_9H_{11}^{2-}$  (dicarbollide ion) or  $B_9H_{14}^-$ . Metal insertion into dicarbollide ion completes a 12-vertex closo (icosahedral) cage,<sup>2</sup> while the  $B_9H_{14}^-$  reactions invariably give 6-MB<sub>9</sub> or 6,9-M<sub>2</sub>B<sub>8</sub> frameworks, which are analogues of  $B_{10}H_{14}$  with the metal in the 6- or 6,9-positions at the ends of the basket.<sup>11</sup> Similarly, the pyramidal  $R_2C_2B_4H_5^-$  carborane ions readily form  $\eta^2$ - or  $\eta^5$ -bonded complexes with metals (vide infra) in high yield.<sup>1a,12</sup>

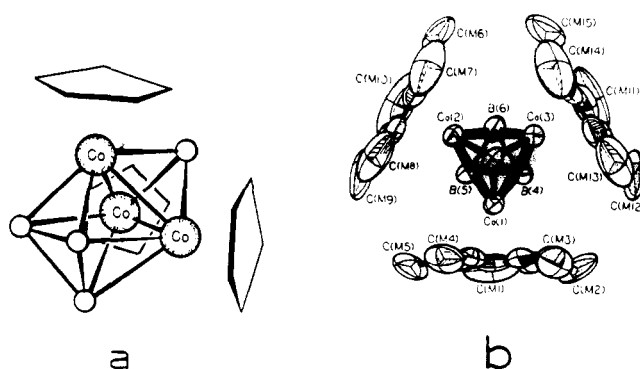
(8) Lippard, S. J.; Ucko, D. A. *Inorg. Chem.* 1968, 7, 1051.

(9) Miller, V. R.; Weiss, R.; Grimes, R. N. *J. Am. Chem. Soc.* 1977, 99, 5646.

(10) (a) Venable, T. L.; Sinn, E.; Grimes, R. N., manuscript in preparation. (b) Riley, P. E.; Davis, R. E. *J. Organomet. Chem.* 1976, 113, 157. (c) Ulman, J. A.; Andersen, E. L.; Fehlner, T. P. *J. Am. Chem. Soc.* 1978, 100, 456.

(11) (a) Lott, J. W.; Gaines, D. F. *Inorg. Chem.* 1974, 13, 2261. (b) Gaines, D. F.; Calabrese, J. C. *Ibid.* 1974, 13, 2419. (c) Venable, T. L.; Sinn, E.; Grimes, R. N. *Ibid.*, 1982, 21, 895.

(12) (a) Grimes, R. N. *Pure Appl. Chem.* 1982, 54, 43. (b) Grimes, R. N. *Coord. Chem. Rev.* 1979, 28, 47 and references therein.



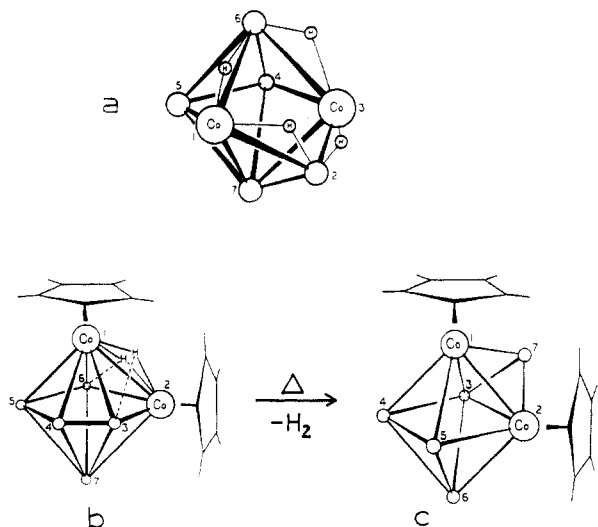
**Figure 2.** (a) Structure of  $(C_5H_5)_3Co_3B_4H_4$ . (b) Structure of  $[C_5(CH_3)_5]_3Co_3B_4H_4$  viewed down the pseudo-3-fold axis.

For the smaller metallaboranes, controlled syntheses of this sort are less common. A readily available borane substrate,  $B_5H_8^-$  (obtained by removal of a B-H-B bridging proton from  $B_5H_9$ ), is extremely reactive toward transition-metal ions and typically generates a multiplicity of products in low individual yields. While this kind of exploratory synthesis is inefficient (as basic science often is), such reactions have been instrumental in uncovering new types of metal-borane clusters and in correcting one's preconceived notions as to what can and cannot exist. In earlier studies<sup>6a,9</sup> we treated  $B_5H_8^-$  with transition-metal halides and  $C_5H_5^-$  ion in cold THF. In the reaction with  $CoCl_2$ ,<sup>9</sup> the reward was a bonanza of new cobaltaboranes having the general formula  $[(C_5H_5)Co]_n(BH)_pH_q$  ( $n = 1-4$ ;  $p = 3-9$ ), which were isolated following workup in air and water. Many of these compounds have been fully characterized by X-ray diffraction analysis,<sup>13</sup> and several of them illustrate the metal-stabilization effect, in that their borane counterparts are unknown; for example,  $(C_5H_5)_2Co_2B_4H_6$ <sup>13c</sup> and  $(C_5H_5)_3Co_3B_3H_5$ ,<sup>13b</sup> each with two bridging hydrogens on a closo 6-vertex cage, are analogues of the hypothetical molecule  $B_6H_8$  (a "deprotonated" version,  $B_6H_6^{2-}$ , does exist).

A further example from the same product mixture is the capped-octahedral complex  $(C_5H_5)_3Co_3B_4H_4$  (Figure 2a) in which a BH unit is face-bonded to a triangular  $Co_3$  array.<sup>13b</sup> Again, the corresponding borane,  $B_7H_7$ , is unknown in any geometry; moreover, in the boron cluster family, capped polyhedra are known only in metal-containing systems. The peculiar geometry of this  $Co_3B_4$  cage is nicely explained by the electron-counting rules,<sup>3</sup> which predict that  $n$ -vertex clusters having  $2n$  skeletal valence electrons will adopt capped-closo shapes. In the present case, with 7 vertices and 14 electrons (the sum of individual 2-electron contributions from each BH and  $Co(C_5H_5)$  unit), one expects a capped octahedron, and this is confirmed by <sup>1</sup>H and <sup>11</sup>B NMR as well as X-ray diffraction evidence.<sup>13b</sup> Recently the pentamethylcyclopentadienyl derivative  $[C_5(CH_3)_5]_3Co_3B_4H_4$  (Figure 2b) was obtained from the reaction of  $CoCl_2$ ,  $B_5H_8^-$ , and  $C_5(CH_3)_5^-$  in THF, together with numerous other cobaltaboranes;<sup>14</sup> that it, too, adopts the capped-octahedral geometry analogous to  $(C_5H_5)_3Co_3B_4H_4$  is remarkable, considering the large steric requirements of the  $C_5(CH_3)_5$  ligands. This is nonetheless the case, as proved by an X-ray

(13) (a) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* 1977, 16, 3251. (b) *Ibid.* 1977, 16, 3255. (c) *Ibid.* 1979, 18, 252. (d) *Ibid.* 1979, 18, 257.

(14) Venable, T. L.; Grimes, R. N. *Inorg. Chem.* 1982, 21, 887.



**Figure 3.** Proposed structures of  $[\text{C}_5(\text{CH}_3)_5]_2\text{Co}_2\text{B}_5\text{H}_9$  (a),  $[\text{C}_5(\text{CH}_3)_5]_2\text{Co}_2\text{B}_5\text{H}_7$  (b), and  $[\text{C}_5(\text{CH}_3)_5]_2\text{Co}_2\text{B}_5\text{H}_5$  (c).

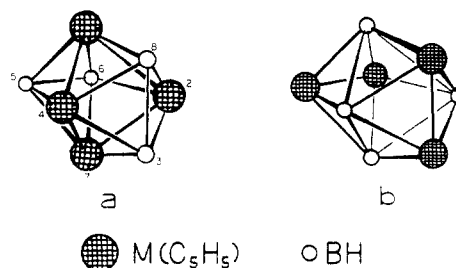
study<sup>15a</sup> that disclosed two effects of intramolecular ligand–ligand crowding: (1) the Co–Co bond lengths are increased to 2.497 (5) Å (mean value) compared to 2.441 (1) Å in  $(\text{C}_5\text{H}_5)_3\text{Co}_3\text{B}_4\text{H}_4$ , and (2) the methyl groups are bent out of the  $\text{C}_5$  ring planes by an average of 0.14 Å; the  $\text{C}_{\text{methyl}}-\text{C}_{\text{methyl}}$  contacts between ligands are as close as 3.33 Å. The interesting lesson one draws from this structure is that the capped-octahedral cluster geometry is so strongly favored in this system that it prevails, despite severe ligand crowding, over other possible arrangements (in fact,  $[\text{C}_5(\text{CH}_3)_5]_3\text{Co}_3\text{B}_4\text{H}_4$  represents the first example of a cluster containing three mutually bonded  $\text{M}[\text{C}_5(\text{CH}_3)_5]$  units<sup>15b</sup>).

In addition to  $[\text{C}_5(\text{CH}_3)_5]_3\text{Co}_3\text{B}_4\text{H}_4$ , the  $\text{CoCl}_2/\text{B}_5\text{H}_8^-/\text{C}_5(\text{CH}_3)_5^-$  reaction also generates two other 7-vertex species,  $[\text{C}_5(\text{CH}_3)_5]_2\text{Co}_2\text{B}_5\text{H}_7$  and  $[\text{C}_5(\text{CH}_3)_5]_2\text{Co}_2\text{B}_5\text{H}_9$ , for which the structures in Figure 3 have been proposed from NMR evidence;<sup>14</sup> here the corresponding boron hydrides, both unknown, are  $\text{B}_7\text{H}_9$  and  $\text{B}_7\text{H}_{11}$ , respectively. Given the fact noted earlier that no isolable heptaboranes exist, the characterization of three metallaborane analogues from a single reaction bears striking testimony to the stabilizing influence of cobalt. Indeed, thermolysis<sup>14</sup> of  $[\text{C}_5(\text{CH}_3)_5]_2\text{Co}_2\text{B}_5\text{H}_7$  produces yet another 7-vertex species,  $[\text{C}_5(\text{CH}_3)_5]_2\text{Co}_2\text{B}_5\text{H}_5$ , which is cage-isoelectronic with  $[\text{C}_5(\text{CH}_3)_5]_3\text{Co}_3\text{B}_4\text{H}_4$  and has been assigned a similar capped-octahedral structure (Figure 3). These  $[\text{C}_5(\text{CH}_3)_5]_2\text{Co}_2\text{B}_5\text{H}_x$  complexes in which  $x = 9, 7,$  and  $5$  contain, formally,  $(2n + 4), (2n + 2),$  and  $2n$  skeletal electrons, which classifies them as nido, closo, and capped closo clusters, respectively; these predictions are completely in accord with their proposed structures in Figure 3.

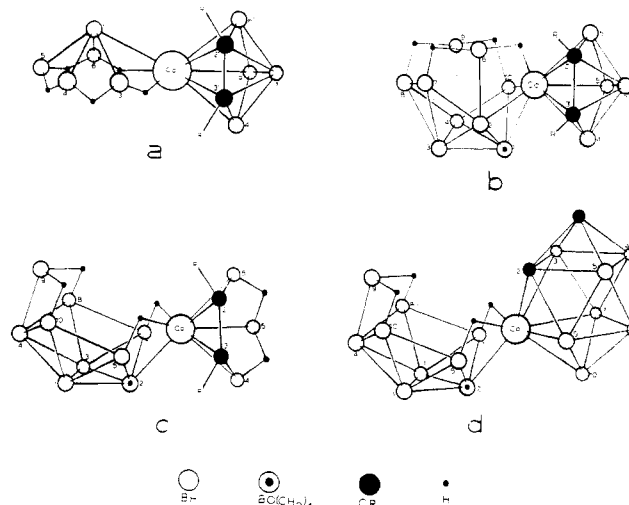
Numerous other examples of metal stabilization of otherwise unknown (or unstable) borane frameworks could be cited, but particularly striking are the tetrametallic “hybrid” metal–boron clusters  $(\text{C}_5\text{H}_5)_4\text{Co}_4\text{B}_4\text{H}_4$ <sup>13d</sup> and  $(\text{C}_5\text{H}_5)_4\text{Ni}_4\text{B}_4\text{H}_4$ <sup>16</sup> that have, respectively,  $2n$  and  $(2n + 4)$  skeletal electrons, yet nonetheless adopt 8-vertex closo geometries in violation of Wade’s rules

(15) (a) Venable, T. L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* 1982, 21, 904. (b) A second example,  $[\text{C}_5(\text{CH}_3)_5]_2\text{Ni}_2(\mu\text{-CO})_2$ , has recently been reported: Maj, J. J.; Rao, D. D.; Dahl, L. F. *J. Am. Chem. Soc.* 1982, 104, 3054.

(16) Bowser, J. R.; Bonny, A.; Pipal, J. R.; Grimes, R. N. *J. Am. Chem. Soc.* 1979, 101, 6229.



**Figure 4.** Structures of  $(\text{C}_5\text{H}_5)_4\text{Co}_4\text{B}_4\text{H}_4$  (a) and  $(\text{C}_5\text{H}_5)_4\text{Ni}_4\text{B}_4\text{H}_4$  (b).



**Figure 5.** Structures of  $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)\text{Co}(\text{B}_5\text{H}_{10})$  (a),  $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)\text{Co}(\text{B}_9\text{H}_{12}\cdot\text{THF})$  (b),  $(\text{R}_2\text{C}_2\text{B}_3\text{H}_5)\text{Co}(\text{B}_9\text{H}_{12}\cdot\text{THF})$  (c), and  $(\text{R}_2\text{C}_2\text{B}_7\text{H}_7)\text{Co}(\text{B}_9\text{H}_{12}\cdot\text{THF})$  (d) ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ ). The structure of (a) is proposed from NMR data; those of (b), (c), and (d) are established from X-ray diffraction studies.

(the “pure” boron counterparts,  $\text{B}_8\text{H}_8$  and  $\text{B}_8\text{H}_8^{4-}$  here again are both unknown). These clusters (Figure 4) have attracted the attention of several theoretical groups<sup>17</sup> in attempts to account for the crystallographically observed structures,<sup>13d,16</sup> which reveal that the metal atoms occupy high-coordinate vertices in the cobalt species but low-coordinate sites in the nickel compound. Both quantitative and qualitative treatments point to a significant degree of local metal–metal bonding interaction in each cluster.

In the metallacarboranes (metal–carbon–boron clusters) both the metal and carbon atoms may serve as stabilizing agents, particularly in the four-carbon clusters that include some truly bizarre cage geometries (here, the framework carbon atoms constitute a major structural influence).<sup>1a,6a,18</sup> However, one large class of metallacarboranes in which the metal plays an indisputably central role (literally and figuratively) is the “commo” complexes wherein a metal occupies vertices in two cages simultaneously (Figure 5). Clearly, this function requires an orbital-rich metal atom and cannot be fulfilled by boron or carbon. In recent work,<sup>19</sup> our group has prepared a new “hybrid” class of commo complexes, in which the metal at once completes both a metallaborane and a metallacarborane cage (Figure

(17) (a) Cox, D. N.; Mingos, D. M. P.; Hoffman, R. *J. Chem. Soc., Dalton Trans.* 1981, 1778. (b) O’Neill, M. E.; Wade, K. *Inorg. Chem.* 1982, 21, 461. (c) King, R. B. *Polyhedron* 1982, 1, 133.

(18) Grimes, R. N. *Adv. Inorg. Chem. Radiochem.*, in press.

(19) (a) Borodinsky, L.; Grimes, R. N. *Inorg. Chem.* 1982, 21, 1921. (b) Borodinsky, L.; Sinn, E.; Grimes, R. N. *Ibid.* 1982, 21, 1928.

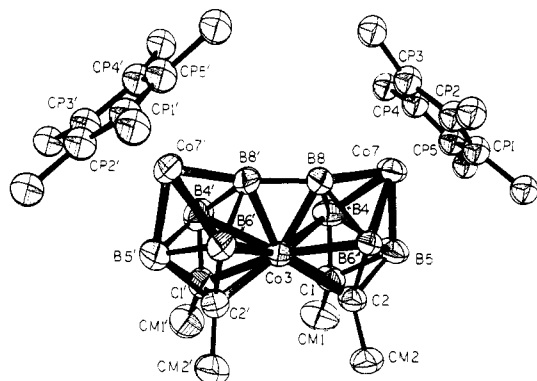


Figure 6. Structure of  $(C_5(CH_3)_5)_2Co_3(CH_3)_4C_4B_8H_7$  (hydrogen atoms omitted).

5). Here, the extraordinary synthetic versatility afforded by combining three different components—borane, carborane, and metal—is clearly apparent.

A thus-far unique kind of *commo*-metallacarborane is the species  $[C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$ , whose solid-state structure (Figure 6)<sup>20</sup> consists of two 8-vertex  $Co_2C_2B_4$  cages joined at a common cobalt atom and also features a direct boron–boron bond [1.758 (5) Å] between the two polyhedra. In THF solution, NMR data reveal that this B–B link is broken, and the “extra” proton (which in the solid evidently occupies a niche near the central cobalt) tautomerizes between the two formerly linked boron atoms, B-8 and B-8'.<sup>20</sup> The role of the central cobalt atom as the linchpin holding this system together is quite clear; less obvious is the question of electronic influence by the metal centers, transmitted through the skeletal framework.

### Metals as Agents in Synthesis

Metal–boron clusters in which the metal is coordinatively unsaturated can function as effective catalysts (or catalyst precursors) for the homogeneous hydrogenation of hydrocarbons, as has been reported extensively.<sup>4</sup> Other synthetic roles for metals in boron chemistry are emerging. Three of these will be touched on here: metal-promoted coupling, metal-promoted fusion, and metal-promoted intramolecular hydrogen transfer.

**Metal-Linked Complexes and Oxidative Coupling.** *nido*-Boranes and -carboranes such as  $B_5H_9^-$  and  $R_2C_2B_4H_5^-$  ( $R = H$ , alkyl) readily combine with  $HgCl_2$  or  $SnCl_2$  to give bis(borane) or bis(carborane)  $\mu, \mu'$  complexes nearly quantitatively.<sup>12a,21</sup> On heating in benzene,  $\mu, \mu'-(R_2C_2B_4H_5)_2Hg$  ejects the metal (as elemental mercury) and forms the symmetrical bis(carborane), 5,5'- $(R_2C_2B_4H_5)_2$  (Figure 7), again in high yield; the net process involves 1-electron oxidation of two  $R_2C_2B_4H_5^-$  anions by  $Hg^{2+}$ . The bis(carborane), an air-sensitive liquid, is cleaved by oxygen in benzene solvent to give a *B*-phenylmonocarborane, 4- $C_6H_5-(CH_3)_2C_2B_4H_5$ .<sup>21</sup>

Since analogous mercury-linked complexes can be prepared from *nido*-cobaltacarboranes (Figure 8),<sup>22</sup> metal-promoted oxidative coupling may ultimately prove useful as a general synthetic procedure for boron clusters. Indeed, similar (but more complex) coupling

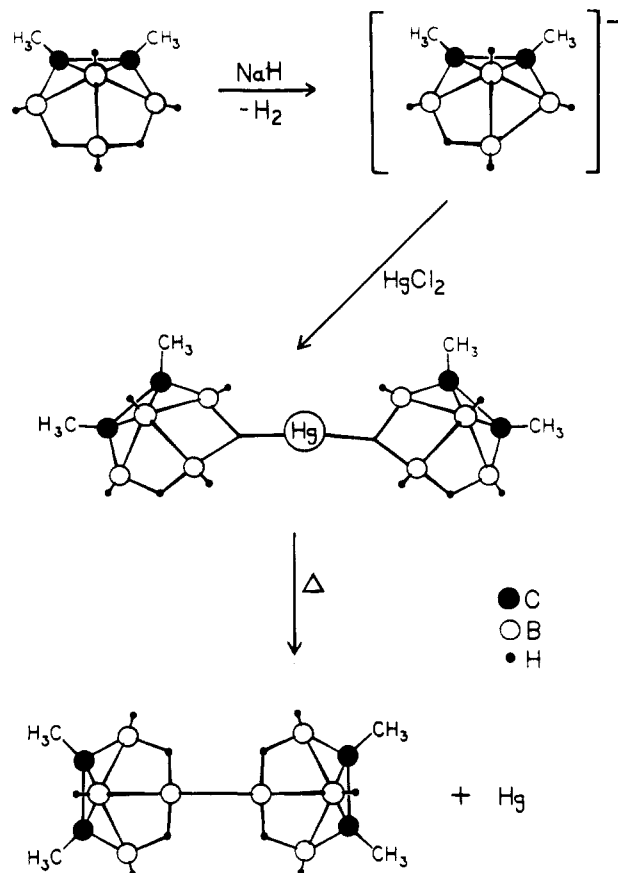


Figure 7. Synthesis of 5,5'- $[(CH_3)_2C_2B_4H_5]_2$  via  $\mu, \mu'-(CH_3)_2C_2B_4H_5)_2Hg$ .

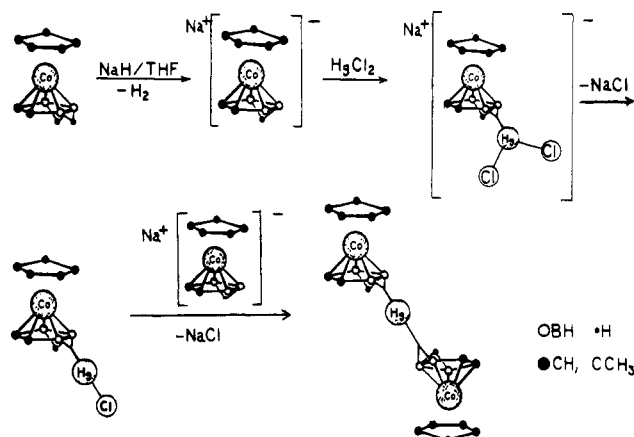


Figure 8. Synthesis of  $[\mu-HgCl](C_5R_5)Co(CH_3)_2C_2B_4H_5$  and  $\mu, \mu'-(C_5R_5)Co(CH_3)_2B_4H_5)_2Hg$  ( $R = H$  or  $CH_3$ ). Structures of these complexes are established from X-ray data; the bracketed  $\mu$  complex is a proposed intermediate.<sup>22</sup>

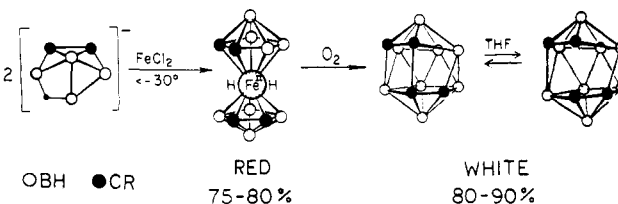


Figure 9. Synthesis of  $R_4C_4B_8H_8$  ( $R = CH_3, C_2H_5$ , or  $n-C_3H_7$ ) via oxidative fusion of carborane ligands in  $(R_2C_2B_4H_4)_2FeH_2$ . The  $R_4C_4B_8H_8$  species are fluxional in THF solution, as shown.

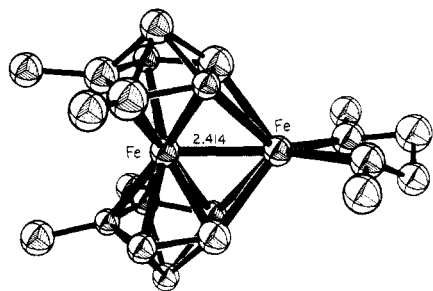
reactions have been observed with tin-bridged carboranes.<sup>12a</sup>

**Oxidative Fusion.** The face-to-face joining of two open-cage polyhedral fragments<sup>6a,12</sup> would appear a

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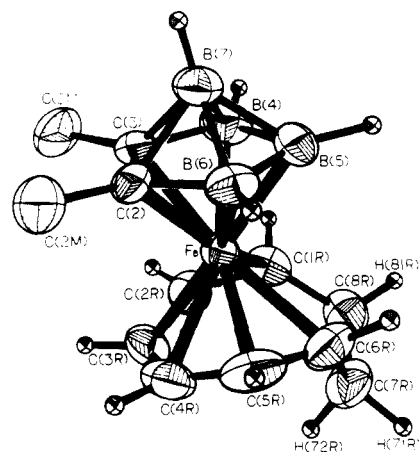
**Figure 10.** Structure of  $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{Fe}_2(\text{OCH}_3)_2\text{C}_2\text{H}_4$ , an intermediate in the formation of  $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$  from  $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2$ .

priori to be a high-energy process, yet it occurs with extraordinary facility in certain bis(carborane)-metal complexes (Figure 9). Recent work<sup>23</sup> has established that, at least in the iron and cobalt systems, ligand fusion is truly intramolecular and there is no exchange of carborane units. In polar, basic solvents such as THF or dimethoxyethane (DME), the conversion of  $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{FeH}_2$  to  $\text{R}_4\text{C}_4\text{B}_8\text{H}_8$  proceeds via a purple, paramagnetic, extremely air-sensitive intermediate that has two iron atoms in a wedge-type structure,<sup>24</sup> as disclosed by X-ray diffraction (Figure 10).<sup>25</sup> In this species, Mössbauer, ESR, and magnetic susceptibility studies reveal that both metals are present as Fe(II), but the outer iron is high spin with four unpaired electrons while the central iron is low spin. The diiron species is produced rapidly from  $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{FeH}_2$  on addition of catalytic amounts of  $\text{FeCl}_3$  in THF but also forms slowly merely on standing in THF or DME. Excess  $\text{FeCl}_3$  reacts with the diiron complex to form the carborane  $\text{R}_4\text{C}_4\text{B}_8\text{H}_8$  quantitatively in seconds.<sup>23</sup>

Ligand fusion reactions have been observed in other metal-carborane complexes as well<sup>12</sup> [e.g., the conversion<sup>26</sup> of  $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)\text{CoH}(\text{R}_2\text{C}_2\text{B}_7\text{H}_7)$  to a possible supraicosahedral product,  $\text{R}_4\text{C}_4\text{B}_{11}\text{H}_{11}$  (where  $\text{R} = \text{CH}_3$ ), and we are attempting to delineate the conditions required for fusion to occur. Discovery of the  $\text{FeCl}_3$ -catalyzed process and the diiron intermediate mentioned above suggests a number of new directions to be explored.

**Metal-Promoted Hydrogen Transfer.** The bridging proton in pyramidal  $\text{R}_2\text{C}_2\text{B}_4\text{H}_5^-$  anions is capable of playing a facile, versatile role in synthesis. On complexation with  $\text{Fe}^{2+}$  to form  $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{FeH}_2$  (Figure 9), the "extra" protons become partially associated with the metal (as revealed by NMR), probably tautomerizing over several  $\text{FeB}_2$  triangular faces.<sup>27,28</sup> It is possible, as has been speculated elsewhere,<sup>28</sup> that these hydrogens are involved somehow in the oxidative fusion process.

Studies of carborane-metal-aromatic hydrocarbon complexes utilizing the  $\text{R}_2\text{C}_2\text{B}_4\text{H}_5^-$  substrate have recently given some interesting results.<sup>12a,29</sup> In the re-



**Figure 11.** Structure of  $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]\text{Fe}(\eta^6\text{-C}_8\text{H}_{10})$ .

action of  $\text{R}_2\text{C}_2\text{B}_4\text{H}_5^-$  ( $\text{R} = \text{CH}_3$  or  $\text{C}_2\text{H}_5$ ),  $\text{FeCl}_2$ , and  $\text{C}_8\text{H}_8^{2-}$  (cyclooctatetraenide ion), the major product ( $\sim 30\%$ ) is orange, air-stable  $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)\text{Fe}^{\text{II}}(\eta^6\text{-C}_8\text{H}_{10})$ , whose structure is shown in Figure 11. Here the arene has been converted to a *triene* by addition of two hydrogens; since the  $\text{R}_2\text{C}_2\text{B}_4\text{H}_5^-$  ligand can supply only one proton, the other evidently is acquired via a different route which has not yet been established. Similar reactions with  $\text{R}_2\text{C}_2\text{B}_4\text{H}_5^-$ ,  $\text{CoCl}_2$ , and  $\text{C}_8\text{H}_8^{2-}$  give several isomers of  $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)\text{Co}^{\text{III}}(\text{C}_8\text{H}_9)$  that contain the unusual  $\text{C}_8\text{H}_9^-$  ligand in several different structural manifestations.<sup>29</sup> In this case only one hydrogen is transferred between ligands, presumably via an intramolecular mechanism.

The  $\text{C}_8\text{H}_{10}$  ligand in the iron complex is readily displaced by benzene or other arenes over  $\text{AlCl}_3$ , and several  $(\eta^6\text{-C}_6\text{R}_3\text{R}'_3)\text{Fe}[(\text{C}_2\text{H}_5)_2\text{C}_2\text{B}_4\text{H}_4]$  products ( $\text{R} = \text{R}' = \text{H}$ ;  $\text{R} = \text{CH}_3$ ,  $\text{R}' = \text{H}$ ;  $\text{R}' = \text{CH}_3$ ) have been characterized by X-ray crystallography.<sup>30</sup> These ligands are anticipated to be relatively labile and may render the metal site catalytically active.

## Summary

If one thinks of metallaboranes and metalla-carboranes as hybrid species that reflect the properties of both metal clusters and boron hydrides, the enormous structural variety and chemical versatility inherent in this class of compounds are not surprising. Relatively few polyhedral clusters whose skeletal framework is composed entirely of metal atoms or entirely of boron atoms exhibit anything approaching the thermal, hydrolytic, and oxidative stability of the metallaboron cages. In general, the metal-plus-boron combination utilizes the covalent, electron-delocalized character intrinsic to boron networks, together with the orbital richness and  $\pi$ -bonding capability of transition-metal centers. Obviously this area presents many possibilities for exploitation in synthesis, whose systematic study will require the combined experience and insights of transition-metal, borane, and organometallic chemists.

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