

how diverse complications and reactivity effects encountered have served to define in part the rules that govern this new principle of aromatic substitution. By no means has every synthetic opportunity been captured or every troublemaking complication been vanquished. Many problems of mechanism remain unsettled, and some are probably yet unrecognized. The saga is uncompleted. Indeed, perhaps only the first few stanzas have yet been sung.

One still finds in current textbooks statements that unactivated aryl halides are unreactive with nucleophiles except under the strongly basic conditions

conducive to the aryne mechanism. My co-workers and I believe that the books need to be revised.

In this research I have been fortunate to have a group of able co-workers, some of them more the optimist willing to try the long shot, some more the pessimist ever seeking evidence to challenge theoretical hypotheses. Each has made characteristic contributions, and for all I am deeply appreciative. Financial support has been provided by the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, the University of California, the Swiss Stiftung für Stipendien auf dem Gebiete der Chemie, and the Argentine Consejo Nacional de Investigaciones Científicas y Técnicas.

Structure and Stereochemistry in Metalloboron Cage Compounds

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The remarkable ability of boron to form stable, covalently bonded cagelike molecules is by now a familiar fact to most chemists. In its own way, the study of boron cage compounds has emerged as a new kind of organic chemistry in which the main structural patterns (due to the presence of only three valence electrons in the boron atom) feature three-dimensional polyhedral clusters rather than chains and rings. Indeed, the capacity of boron to generate catenated, or self-bonded, molecular networks of considerable complexity is a property exhibited by no other element except carbon. Several decades of research on the boranes and their heteroatom-containing derivatives—carboranes, metalloboranes, metallocarboranes, thia- and phosphaboranes, and others—have produced an enormous proliferation of novel synthetic and structural chemistry, and spawned whole new fields of study. It is striking, therefore, to realize that there are still no discernible limits on the size, elemental composition, or geometry that can be adopted by these molecules. Certainly, the structures and reactions of the boron cage molecules have to a large extent been placed in a rational framework. Boron chemistry is no longer the jungle of disconnected facts it may have seemed at one time, nor is it remote from other areas of research; the recognition of close links between the boron cages and other kinds of clusters is a major development about which more will be said later.

Yet basic questions remain: Is there an upper boundary to polyhedral size? (Cages having 4 to 14 vertices inclusive are presently known.) How many different elements can coexist in a stable polyhedron,

and what extremes of atomic size and electronegativity can be tolerated? (Over 40 elements from main groups 2–6 and many transition metals in a variety of oxidation states have been incorporated into boron frameworks.) What limitations are there on the geometries that can be assumed by polyhedral cages, and on the coordination numbers and valence bond angles that may be adopted by individual atoms in these systems? One thinks here, by way of contrast, of the severe restrictions that govern the stereochemical role of carbon in organic compounds.

Perhaps surprisingly, these fundamental issues now present a more formidable challenge than was apparent several years ago. The fact is that the sophisticated techniques—synthetic, physical, and theoretical—which have been brought to bear on boron cage chemistry have opened up new, previously unsuspected avenues at a far greater rate than they have settled old problems. Though we might have expected the pace of discovery at some point to begin to abate, this has not occurred, and investigators continue to be confronted with reactions that were not supposed to happen and novel molecular structures that no one imagined to exist. These unexpected findings, of course, are of importance in continually reeducating us about the nature of cage and cluster compounds and about bonding and structure generally. Observations that support current theory can be useful, but those that force its extension and reshaping are more likely, in the long run, to advance our basic understanding of nature (which is a prime reason for studying exotic species such as the polyhedral boranes in the first place).

In this Account, following a brief discussion of structure, I will outline in a highly selective fashion some of the more significant twists and turns we and others have recently encountered on the trail of boron cage compounds, concentrating on problems with which my co-workers and I have been directly concerned. An

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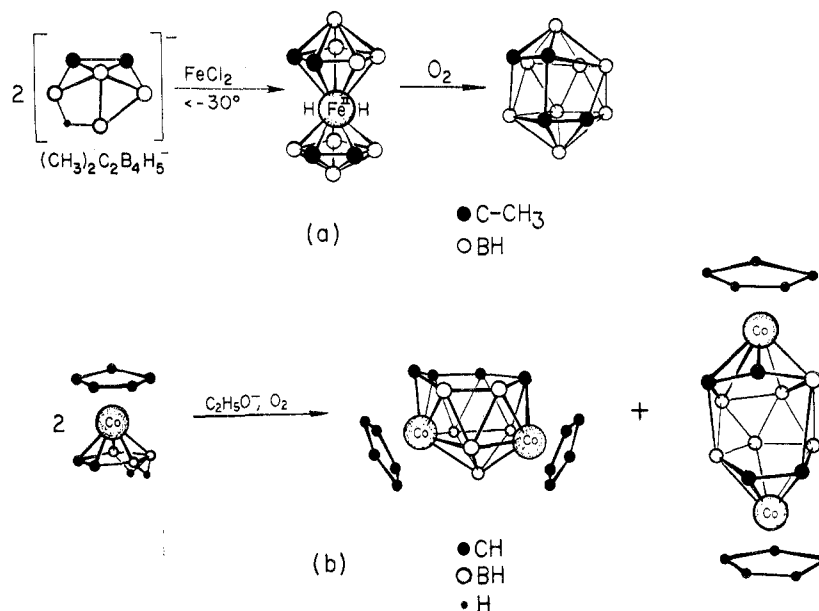


Figure 1. Examples of oxidative fusion. (a) Synthesis of $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5]_2\text{FeH}_2$ and conversion to $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$. (b) Conversion of $1,2,3-(\eta^5\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_3\text{H}_7$ to isomers of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_4\text{B}_6\text{H}_{10}$ (only the two structurally characterized¹⁴ isomers are shown). When reaction b is conducted with the C,C' -dimethyl derivative, $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_5$, a single isomer is obtained which has the structure of the second of the two products shown.

overview of the entire field cannot be given in this space, but a number of recent reviews on carboranes,¹ metallocarboranes,^{1a-c,2} and metalloboranes³ are available.

Electron Population and Geometry in Polyhedral Cages

Bonding in boron cage molecules is primarily covalent and electron delocalized.^{4,5} Theory indicates, strongly supported by observation, that an n -vertex closo polyhedron (one in which all faces are triangular) will normally, for $n > 4$, have $n + 1$ bonding molecular orbitals associated with the skeleton;⁶ thus the optimum number of skeletal electrons is $2n + 2$. Removal of one or more vertex units (such as BH or CH) leaves the number of bonding MOs unchanged, so that an n -vertex nido cage (a closo polyhedron with one vertex missing) should have $2n + 4$ skeletal electrons. Similarly, an arachno framework (a closo cage with two missing vertices⁷) is bound together by $2n + 6$ electrons. Other, much rarer, systems are those with $2n + 8$ (hypho) or $2n$ electrons (capped closo). The formal electron count

in a cage framework is the sum of contributions from each vertex unit, excluding electrons involved in bonding to exo-polyhedral ligands and those occupying nonbonding orbitals (as in transition metals). Thus, a BH unit is a 2-electron donor, while CH , $\text{Co}(\eta^5\text{-C}_5\text{H}_5)$, $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)$, and $\text{Fe}(\text{CO})_3$ groups formally supply 3, 2, 3, and 2 electrons to a cage or cluster system. These ideas have been discussed in detail by a number of authors.^{6,8}

A major conceptual breakthrough in recent years, which is only now receiving some of the general recognition it deserves, is the successful application of these electron-counting rules not only to boron species but to a vast array of other cage-like molecules including the metal clusters, organometallic clusters, and hydrocarbon cations such as the pyramidal $\text{C}_6(\text{CH}_3)_6^{2+}$ and $\text{C}_5\text{H}_3(\text{CH}_3)_2^+$ species.^{6,8b,c} As will be seen, this qualitative correlation of structure and framework electron count is not perfect and has many ramifications still to be worked out. It does, however, provide a powerful tool for organizing, predicting, rationalizing, and relating a considerable body of structural information on cage and cluster compounds, and it serves as an extremely useful focal point for discussion of particular molecular species.

Oxidative Cage Fusion: Metal-Assisted Synthesis of Large Cages from Small Ones

An initially routine experiment which opened the way to a rich vista of new synthetic possibilities was the reaction of the $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5^-$ ion (derived from *nido*-2,3- $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_6$ by removal of a bridging proton with NaH) with FeCl_2 in cold tetrahydrofuran (THF) (Figure 1).⁹ Instead of the expected

(1) (a) T. Onak, *Organomet. Chem.*, **5**, 67 (1976); (b) R. Snaith and K. Wade, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. Two*, **1**, 95 (1975); (c) Gmelin's "Handbook of Inorganic Chemistry", Supplementary Works, Vol. 15, 1973; Vol. 27, 1974; Vol. 42, 1976; Vol. 43, 1977; (d) D. S. Matteson, *J. Organometal. Chem.*, **119**, 1 (1976); (e) T. Onak in "Boron Hydride Chemistry", E. L. Muetterties, Ed., Academic Press, New York, N.Y., 1975, Chapter 10; (f) R. N. Grimes, "Carboranes", Academic Press, New York, N.Y., 1970.

(2) (a) G. B. Dunks and M. F. Hawthorne, ref 1e, Chapter 11; (b) R. N. Grimes in "Organometallic Reactions and Syntheses", Vol. 6, E. I. Becker and M. Tsutsui, Ed., Plenum, New York, N.Y., 1977, Chapter 2 (comprehensive review).

(3) (a) N. N. Greenwood and I. M. Ward, *Chem. Soc. Rev.*, **3**, 231 (1974); (b) P. A. Wegner, ref 1e, Chapter 12.

(4) W. N. Lipscomb, ref 1e, Chapter 2, and references therein.

(5) Electrochemical studies on a series of small metallocarboranes containing one to two metal atoms indicate a high degree of electron delocalization: W. E. Geiger, Jr., private communication.

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

(7) (a) R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971); (b) R. E. Williams, *Adv. Inorg. Chem. Radiochem.*, **18**, 67 (1976).

(8) (a) C. J. Jones, W. J. Evans, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 543 (1973); (b) R. N. Grimes, *Ann. N.Y. Acad. Sci.*, **239**, 180 (1974); (c) a topological treatment is given by R. B. King and D. H. Rouvray, *J. Am. Chem. Soc.*, **99**, 7834 (1977).

(9) (a) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.*, **96**, 7116 (1974); (b) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *Inorg. Chem.*, **15**, 1343 (1976).

$[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{Fe}^{II}2^-$ dianion (a still-unknown species), a red crystalline *neutral* compound, $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{Fe}^{II}\text{H}_2$, was isolated in high yield together with a colorless air-stable material, $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$. A similar experiment with CoCl_2^{10} yielded red $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{Co}^{III}\text{H}$ together with the same $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$. Both metal complexes were shown from ^1H and ^{11}B NMR studies to contain metal-hydrogen bonding interactions,^{9b,10} and a recent X-ray study¹¹ of $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2$ revealed that the C_2B_4 ligands are rotated by 87° relative to each other, as shown in Figure 1a. The metal-bound hydrogens have not been precisely located; in solution they evidently undergo rapid tautomeric motion through several locations in the vicinity of the metal atom.^{9b,10}

These metal-hydrogen metallocarboranes are highly reactive compounds and exhibit a multifaceted chemistry.^{9,10,12,13} The most important reaction thus far discovered is the high-yield conversion^{9,10} of both the iron and the cobalt species to the tetracarborane $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ at room temperature in air (Figure 1a). The process clearly involves face-to-face linkage of the two $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4^{2-}$ ligands with loss of four electrons and elimination of the metal and is conveniently labeled oxidative ligand fusion or, more generally, oxidative cage fusion.

The mechanistic details of the fusion process have not yet been established, but recent work indicates that it is a general reaction with considerable potential for the synthesis of novel cage molecules. For example, the oxidative fusion of the *nido*-cobaltaborane $1,2,3-(\eta^5\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_3\text{H}_7$ is brought about simply by treatment with ethanolic KOH between 0 and 25°C followed by exposure to air (Figure 1b).¹⁴ Among other products, the species $(\eta^5\text{-C}_5\text{H}_5)\text{CoC}_4\text{B}_7\text{H}_{11}$ and three isomers of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_4\text{B}_6\text{H}_{10}$ are obtained; two of the latter have been crystallographically characterized¹⁴ as 12-vertex *nido* species which have sharply different geometries, shown in Figure 1b. The analogous treatment of the dimethyl-substituted complex $1-(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_5$ produces only one tetracarborane species, a single isomer of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_6$, in yields of 15–20% (the structure corresponds to the second of the two products in Figure 1b). These cobaltacarborane fusion reactions differ from the $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ preparations mentioned above in that the metal is retained in the cage framework of the products.

Other examples of cage fusion have been encountered. Space limitations preclude mention of all of these, but a type of reaction which may hold a clue to the mechanism of fusion is the insertion^{9b,12,13} of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}$, Ge, or Sn into $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2$ or the $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}^-$ ion (Figure 2). The product of the cobalt insertion has the peculiar structure¹² shown, in which a BH unit occupies a wedging or double-face-capping location between two pentagonal-bipyramidal cages. This geometry can be understood in terms of the framework electron count, which lacks two

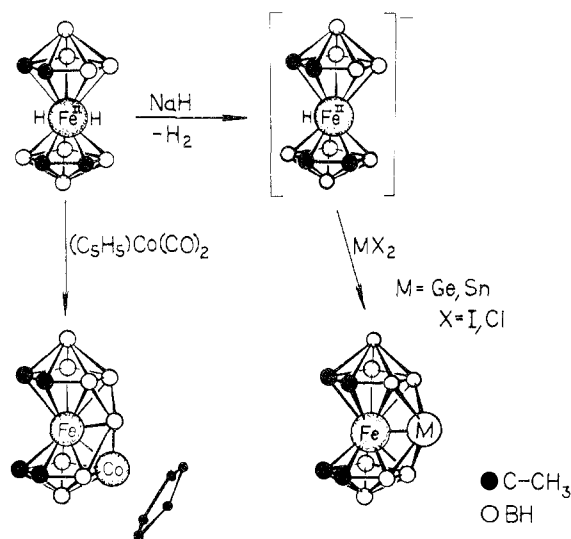


Figure 2. Insertion of Co, Ge, and Sn into $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2$ and the $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}^-$ ion. The structure of the Fe-Co compound is established;¹² those of the Fe-Ge and Fe-Sn species are proposed from NMR data.¹³

electrons of having the full $2n + 2$ complement for each cage, so that the molecule adopts a capped closo structure (further discussion of capped polyhedra appears later in this article). The red to brown germanium and tin species have the formula $\text{MFe}(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ ($\text{M} = \text{Ge}, \text{Sn}$) with the proposed structures based on ^{11}B and ^1H NMR evidence.¹³ These molecules are formally analogous to the Fe-Co complex (since $\text{Co}(\eta^5\text{-C}_5\text{H}_5)$, Sn, and Ge are regarded as two-electron donor units), but NMR data¹³ suggest that the group 4 species have higher symmetry than the Fe-Co complex, with the Ge or Sn atom occupying the “wedging position” between the two 7-vertex polyhedra (Figure 2). The reaction of the $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}^-$ ion with PbCl_2 does not produce insertion of the metal, giving instead $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ in 50% yield; thus Pb^{2+} effectively acts as an oxidant in this case. One can think of the Fe-Sn, Fe-Ge, and Fe-Co species as examples of partial cage fusion (two polyhedra sharing a common edge), which suggests that an intermediate of similar geometry may be involved in the fusion of carborane ligands such as $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4^{2-}$.

Investigation of the cage fusion process is in a very early stage, but it is clear that the metal greatly lowers the activation energy for merger of two separate polyhedra into a single framework (it should be noted that the fusion reactions described here occur at or below room temperature). If the principle of cage fusion facilitated by complexation at metal centers should turn out to be widely applicable, its utility as a synthetic technique could become very broad indeed.¹⁵

Tetracarborane Metallocarboranes and Supraicosahedral Cages

The carborane $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ is a noteworthy compound in its own right. As a 28-electron, 12-vertex ($2n + 4$) cage (with two more framework electrons than icosahedral $\text{C}_2\text{B}_{10}\text{H}_{12}$), it is formally *nido*. However,

(10) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 4818 (1976).

(11) J. R. Pipal and R. N. Grimes, submitted for publication.

(12) W. M. Maxwell, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 3490 (1976).

(13) W. M. Maxwell, K-S. Wong, and R. N. Grimes, *Inorg. Chem.*, **16**, 3094 (1977).

(14) K-S. Wong, J. R. Bowser, J. R. Pipal, and R. N. Grimes, *J. Am. Chem. Soc.*, **100**, 5045 (1978).

(15) Related metal-assisted syntheses include Fehner's¹⁶ addition of two 2-butyne molecules to the square-pyramidal complex $(\text{CO})_5\text{FeB}_4\text{H}_5$ to produce a new carborane, $(\text{CH}_3)_4\text{C}_4\text{B}_4\text{H}_4$, and Pettit's¹⁷ cycloadditions of unsaturated species to cyclobutadiene via complexation to iron.

(16) T. P. Fehner, *J. Am. Chem. Soc.*, **99**, 8355 (1977).

(17) J. S. Ward and R. Pettit, *J. Am. Chem. Soc.*, **93**, 262 (1971).

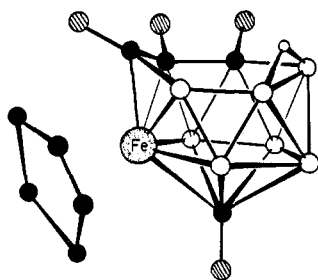


Figure 3. Structure of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_8$.¹⁹

unlike most nido species^{6,7} it has no single large "hole" in the framework; instead, the solid-state structure¹⁸ consists of an icosahedron which has been distorted by stretching two edges to form two four-sided open faces (in solution, an equilibrium exists⁹ between this structure (Figure 1a) and another, structurally undefined isomer, which reverts to the known solid-state geometry on removal of solvent).

The geometry of $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ differs strikingly from all other 12-vertex, 28-electron systems, of which six structurally characterized examples are known: two isomers of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_4\text{B}_6\text{H}_{10}$ ¹⁴ (Figure 1b), $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_8$ ¹⁹ (Figure 3), $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_6\text{-OC}_2\text{H}_5$ (a "split-open" icosahedron),^{13,20} and the $\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{11}^-$ ions ($\text{R} = \text{CH}_3$,²¹ C_6H_5 ²²), which contain a bridging RCH group on the open face of an 11-vertex nido cage. It is surprising, and significant, that a diversity of structures is found among this family of isoelectronic cages. While it is true that these are all open-cage systems as expected, the variation in their gross geometry dramatizes the influence of factors (such as local steric effects) which are beyond the purview of current polyhedral bonding theory. Another notable example of structural dissimilarity, this time among isomers, appears in the 14-vertex diferracarboranes to be described next.

Insertion of transition metals into $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$, both directly and via reduction to the carborane dianion, generated the first metallocarboranes containing four carbon atoms in the same polyhedron.¹⁹ For example, the reaction of the $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8^{2-}$ ion with FeCl_2 gave a 12-vertex nido species, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_8$, and four isomers of a 14-vertex system, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$.^{19,23} The FeC_4B_7 cage was shown via X-ray crystallography¹⁹ to have an unprecedented shape (Figure 3) which resembles a 13-vertex closo polyhedron²⁴ with one vertex removed (a cage geometry that appeared again, more recently, in the $\text{Co}_2\text{C}_4\text{B}_6$ system shown in Figure 1b). In the iron compound, one of the four framework carbon atoms occupies a presumably undesirable⁷ high-coordinate vertex at maximum distance from the other three; this is doubly surprising in that the synthesis from $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$, which has four contiguous cage carbons (Figure 1a), was conducted at room temperature.¹⁹

(18) D. P. Freyberg, R. Weiss, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, **16**, 1847 (1977).

(19) W. M. Maxwell, R. F. Bryan, and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 4008 (1977).

(20) J. R. Pipal and R. N. Grimes, *J. Am. Chem. Soc.*, **100**, 3083 (1978).

(21) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 2674 (1973).

(22) E. I. Tolpin and W. N. Lipscomb, *Inorg. Chem.*, **12**, 2257 (1973).

(23) W. M. Maxwell, R. Weiss, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 4016 (1977).

(24) (a) D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 1109 (1973); (b) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **13**, 1411 (1974).

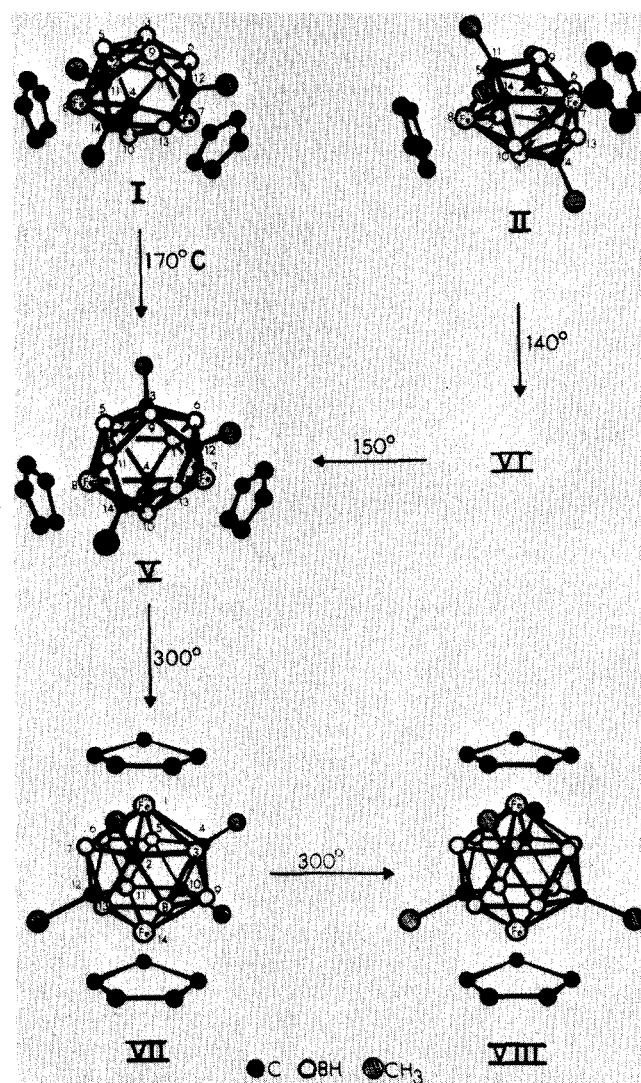


Figure 4. Thermal rearrangement of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ isomers.²³ Structures I, II, V and VIII have been determined crystallographically; that of VII was assigned from NMR data.²³

Stranger still are the geometries of the 14-vertex $\text{Fe}_2\text{C}_4\text{B}_8$ polyhedra.²³ Isomers I and II (Figure 4) each have 30 skeletal electrons, from which closo geometry would be expected (indeed, closo structures had been proposed²⁵ for the isomers of the isoelectronic dicarbon species $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_{10}\text{H}_{12}$). Obviously I and II are not closo, having respectively five- and four-sided open faces; moreover, they are grossly different from each other! At 140–170 °C I and II rearranged to a common isomer, V, whose X-ray determined structure²³ (Figure 4) is essentially that of I with BH and CCH₃ groups interchanged at positions 3 and 11. Thus, the refusal of this system to adopt a closed polyhedral shape persists even at moderately elevated temperature. At 300 °C the closo geometry was finally achieved with the formation of isomers VII and VIII. The structure of VIII, originally proposed from NMR evidence,²³ has been confirmed crystallographically²⁶ and is the thermodynamically favored geometry, a beautifully symmetric bicapped hexagonal antiprism in which all boron atoms are equivalent, as are all of the framework carbon atoms.

(25) W. J. Evans and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, **38** (1974).

(26) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **17**, 6 (1978).

The fact that close geometry was reached in this system only at high temperature illustrates a limitation of the current structural theory of polyhedral cages,^{6,7} namely its inability to deal with isolable intermediates whose structures are strongly influenced by kinetic factors involved in their formation. In large cages such as those discussed here, the activation energy of rearrangement is too high to permit achievement of the preferred geometry except at elevated temperature; consequently molecules such as I, II, and V are locked into unconventional configurations.

Structural predictions based on the electron-counting rules are also violated in other situations which we can only note briefly here. For example, a number of metallocarboranes containing atoms of the third transition series, especially Pd or Pt, exhibit structural anomalies such as stretched polyhedral edges,²⁷ which Mingos²⁸ has attributed to inequalities in the bonding roles of the metal d_{xz} and d_{yz} orbitals.²⁹ A special case of nonconformity in a cobaltaborane complex is discussed below, and other examples are to be expected. The exposure of its limitations does not, of course, detract from the very considerable utility of the skeletal electron-count theory in drawing together an enormous range of cage and cluster structures and in providing a point of departure for more sophisticated and detailed treatments of specific cases.

Turning now to the matter of polyhedral size per se, consider the question we raised earlier: is there an upper limit? The breaking of the "icosahedral barrier" with the synthesis of 13- and 14-vertex dicarbon^{24a,25,31} and tetracarbon^{19,23} metallocarboranes suggests that even larger polyhedra may be accessible. Brown and Lipscomb³² have proposed structures for hypothetical $B_nH_n^{2-}$ anions in which n is 13 to 24 (the largest known member of this family is $B_{12}H_{12}^{2-}$), and they speculate on much larger polyhedra having up to 92 vertices. At present, however, the 14-vertex species are the largest known borane systems.

A 15-vertex cage seems well within reach by the addition of a metal to the open face of isomers I or V of $(\eta^5-C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$ shown in Figure 4. Indeed, in numbering these cages²³ we recognized that each of them can be viewed as a 15-vertex D_{3h} polyhedron (identical with that proposed independently by Lipscomb)³² with one vertex missing. The addition of metal atoms to a 14-vertex metallocarborane might well produce cages even larger than 15 vertices, but this remains to be seen. A different tactic might be the oxidative fusion of two 12-vertex carborane ligands to generate a 24-atom polyhedron, e.g., $[(CH_3)_4C_4B_8H_8]_2FeH_2 \xrightarrow{[O]} (CH_3)_8C_8B_{16}H_{16}$. Other approaches to supracosahedral cages can be postulated,³² and no

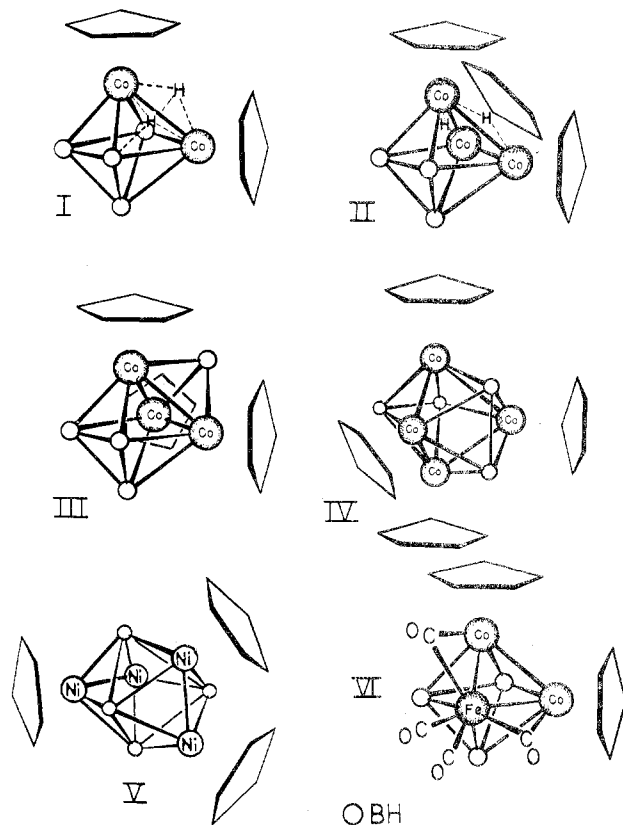


Figure 5. Established structures³⁶ of metallocarborane clusters $(\eta^5-C_5H_5)_2Co_2B_4H_6$ (I), $(\eta^5-C_5H_5)_3Co_3B_3H_5$ (II), $(\eta^5-C_5H_5)_3Co_3B_4H_4$ (III), and $(\eta^5-C_5H_5)_4Co_4B_4H_4$ (IV), $(\eta^5-C_5H_5)_4Ni_4B_4H_4$ (V),^{35b} and proposed structure^{35a} of $(\eta^5-C_5H_5)_2Co_2(CO)FeB_3H_3$ (VI). One C_5H_5 ring in V has been omitted for clarity.

doubt polyhedra much larger than those presently known are attainable; in the extreme, one can envision essentially spherical macromolecules (perhaps stabilized by bridging groups inside the polyhedra) which could form the basis for polymers of novel construction.

Metal-Rich Polyhedra: Borane-Metal Cluster Hybrids

The proposition that boranes and metal clusters are structurally and electronically related^{6,3b,c} is an intriguing idea which, if imaginatively exploited, could have far-reaching consequences both in synthesis and in the development of bonding theory for polyhedral cages. A synthetic goal in which our group has been interested is the preparation of "hybrid" clusters which contain metal and boron atoms in comparable numbers and are expected to exhibit some properties common to both the borane and metal cluster families. Several such compounds have been isolated and structurally characterized, many of them from the reaction of the square-pyramidal $B_5H_8^-$ ion (derived from B_5H_9 by removal of a bridging proton) with $CoCl_2$ and $Na^+C_5H_5^-$ in cold THF followed by air oxidation.³³ The principal metallocarborane product is $2-(\eta^5-C_5H_5)CoB_4H_8$, an air-stable red solid which structurally^{33,34} corresponds to B_5H_9 with one basal BH unit replaced by $Co(C_5H_5)$. In smaller amounts one obtains the metal-rich polyhedra $(\eta^5-C_5H_5)_2Co_2B_4H_6$ (I), $(\eta^5-C_5H_5)_3Co_3B_3H_5$ (II), $(\eta^5-$

(27) (a) A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 2270 (1975), and 962 (1977); (b) W. E. Carroll, M. Green, F. G. A. Stone, and A. J. Welch, *ibid.*, 2263 (1975); (c) G. K. Barker, M. Green, J. L. Spencer, F. G. A. Stone, B. F. Taylor, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 804 (1975).

(28) D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 602 (1977).

(29) Rudolph³⁰ has suggested that, in at least some cases, unexpected open-cage geometry may be due to bridging hydrogen atoms, which are not always detectable in X-ray crystallographic analysis.

(30) D. A. Thompson, T. K. Hilty, and R. W. Rudolph, *J. Am. Chem. Soc.*, **99**, 6774 (1977).

(31) (a) G. B. Dunks, M. M. McKown, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **93**, 2541 (1971); (b) D. F. Dustin and M. F. Hawthorne, *ibid.*, **96**, 3462 (1974); (c) D. F. Dustin, W. J. Evans, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 805 (1973).

(32) L. D. Brown and W. N. Lipscomb, *Inorg. Chem.*, **16**, 2989 (1977).

(33) (a) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 5078 (1973); (b) V. R. Miller and R. N. Grimes, *ibid.*, **98**, 1600 (1976); (c) V. R. Miller, R. Weiss, and R. N. Grimes, *ibid.*, **99**, 5646 (1977).

(34) L. G. Sneddon and D. Voet, *J. Chem. Soc., Chem. Commun.*, 118 (1976).

$C_5H_5)_3Co_3B_4H_4$ (III), and $(\eta^5-C_5H_5)_4Co_4B_4H_4$ (IV); other isolated species include $(\eta^5-C_5H_5)CoB_9H_{13}$ (an analogue of $B_{10}H_{14}$), and the C, C' -propenylene-bridged triple-decked sandwich complex $\mu-C_3H_4-(\eta^5-C_5H_5)_2Co_2C_2B_3H_3$.^{33c} Compounds I-IV have recently been obtained in higher yield^{35a} from the treatment of $2-(\eta^5-C_5H_5)CoB_4H_7^-$ with $CoCl_2$ and $Na^+C_5H_5^-$.

The structures of the colored crystalline, air-stable cobaltaboranes I-IV (Figure 5) have been established crystallographically³⁶ and are in agreement with ^{11}B and 1H NMR data.³³ The octahedral-cage complexes I and II are 14-electron ($2n + 2$) closo systems, electronically analogous to $B_6H_6^{2-}$, $C_2B_4H_6$, $(CO)_3FeC_2B_3H_5$, and $(\eta^5-C_5H_5)CoC_2B_3H_5$, and to octahedral metal clusters such as $Co_6(CO)_{14}^{4-}$ and $(C_2H_5)_2C_2Co_4(CO)_{10}$. Complexes I and II, however, each contain two nonterminal hydrogen atoms, which in the case of I have been precisely located by X-ray studies^{36b} and found to reside approximately over the centers of the Co_2B triangular faces. NMR observations on II (particularly the characteristic high-field Co-H signals in the 1H spectra) indicate tautomeric movement of these hydrogens on the polyhedral surface in the vicinity of the cobalt atoms.^{33c}

The capped octahedral species III^{33,36a} is the only known boron compound with that geometry and is one of a very small group of capped polyhedral clusters, all of which have fewer than $2n + 2$ skeletal bonding electrons and have been called electron-hyperdeficient.³⁷ Theory^{38,39,40b} suggests that capping a face of a closo polyhedron produces no change in the number of framework bonding MOs, so that a $2n$ -electron system can achieve a closed-shell electronic structure by adopting the geometry of a monocapped ($n - 1$)-vertex polyhedron; thus, a 7-vertex 14-electron cage such as III is a capped octahedron. Other structurally characterized examples include $Os_7(CO)_{21}$ ⁴⁰ and $Rh_7(CO)_{16}$ ^{3-,41} both capped octahedra; $Os_6(CO)_{18}$ ^{40b}, a capped trigonal bipyramid; $(\eta^5-C_5H_5)_2Fe_2C_2B_6H_8$,⁴² a capped tricapped trigonal prism; and $(\eta^5-C_5H_5)CoFe(CH_3)_4C_4B_8H_8$ ¹² (Figure 2).

The unique BH group capping a Co_3 face in III is reminiscent of the tricobalt carbon clusters, $(CO)_9Co_3CR$,⁴³ and there is both structural^{36a} and NMR^{33c} support for this analogy although no chemical studies on III have been conducted as yet.

Compound IV is a $2n$ -electron system with $n = 8$, but the established structure^{36b} (Figure 5) is obviously not a capped polyhedron but rather a regular 8-vertex dodecahedron with idealized D_{2d} symmetry, structurally

analogous to $C_2B_6H_8$ and the $B_8H_8^{2-}$ anion despite the fact that IV has two fewer skeletal electrons than these latter species. This molecule represents one of the more flagrant violations of the electron-counting rules and one of the very few in which neither large cage size nor heavy metal atoms (vide supra) are involved. It may be that the highly symmetric D_{2d} structure is stabilized by trans-cage Co-Co interactions which compensate for the shortage of two electrons. Moreover, the D_{2d} polyhedron is, in geometric terms, easily accessible from several capped structures (e.g., the tetra-B-capped Co_4 tetrahedron and the mono-B-capped Co_4B_3 pentagonal bipyramid)^{33c} by fairly small atomic movements.

Very recently, two tetranickel clusters, green $(\eta^5-C_5H_5)_4Ni_4B_4H_4$ (V in Figure 5) and brown $(\eta^5-C_5H_5)_4Ni_4B_5H_5$, were isolated in substantial yield from the reaction of $(\eta^5-C_5H_5)_2Ni$, sodium amalgam, and $B_5H_8^-$ ion in cold THF.^{35b} The structure of V, determined from X-ray data, is remarkable in that it is a closo dodecahedral cage despite its 20 skeletal valence electrons (four more than the Co_4B_4 species, IV) and has the metal atoms in *low*-coordinate vertices! Structural phenomena of this kind are likely to keep theoreticians occupied for some time to come.

Other metal-rich metalloboron clusters have appeared: we have obtained^{35a} $(\eta^5-C_5H_5)_2Co_2(CO)_4FeB_3H_3$ (VI in Figure 5), a species proposed to contain a $FeCo_2B_3$ cage, by reaction of $2-(\eta^5-C_5H_5)CoB_4H_8$ with $Fe(CO)_5$, and Sneddon⁴⁴ has prepared $(\eta^5-C_5H_5)_3Co_3B_5H_5$, whose structure is not yet known but may be analogous to $(\eta^5-C_5H_5)_4Co_4B_4H_4$ (IV). Closo metalloboranes with lower metal-boron ratios [e.g., $(\eta^5-C_5H_5)_2Ni_2B_{10}H_{10}$] have also been reported.⁴⁵ In addition, the hundreds of known metallocarboranes include a few having as many as three metal atoms in 9- to 12-vertex polyhedra.²

The nature of the metal-metal interactions in the metal-rich clusters is of interest, particularly when one attempts a comparison with the "pure" metal clusters. At present the available data are mostly structural,³⁶ the average bonded Co-Co distances in I, II, III, and IV are respectively 2.531 (1), 2.483 (1), 2.441 (1), and 2.477 (1) Å, which are comparable to values normally observed in cobaltacarboranes and in cobalt cluster compounds (for example, the mean Co-Co distance in $RCCo_3(CO)_9$ clusters is 2.47 Å).⁴⁶ In the Ni_4B_4 cluster V, the Ni-Ni distance is unusually short at 2.354 (1) Å. From all indications there are substantial bonding interactions between the metal centers in these metalloboranes, but a more precise evaluation will have to await chemical and electrochemical studies which are currently in progress in several laboratories.

Cycloborane-Transition-Metal Sandwich Complexes

Another class of metalloboron cage structures having a close relationship to an important organometallic area consists of sandwich complexes containing a borane or heteroborane ligand which is *cyclic planar* (disregarding bridge hydrogens); such compounds are direct structural counterparts of the metallocenes. The earliest

(35) (a) R. Weiss, J. R. Bowser, and R. N. Grimes, *Inorg. Chem.*, **17**, 1522 (1978); (b) J. R. Bowser and R. N. Grimes, *J. Am. Chem. Soc.*, **100**, 4623 (1978).

(36) (a) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **16**, 3255 (1977); (b) J. R. Pipal and R. N. Grimes, submitted for publication.

(37) This term¹² recognizes the fact that all borane-type polyhedra are electron-deficient in the classical (Lewis) sense.

(38) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962).

(39) D. M. P. Mingos and M. I. Forsyth, *J. Chem. Soc., Dalton Trans.*, **610** (1977).

(40) (a) C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, **37**, C39 (1972); (b) R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Am. Chem. Soc.*, **95**, 3802 (1973); (c) C. R. Eady, B. F. G. Johnson, J. Lewis, R. Mason, P. B. Hitchcock, and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 385 (1977).

(41) V. G. Albano, P. L. Bellon, and G. F. Ciani, *Chem. Commun.*, 1024 (1969).

(42) K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 296 (1975).

(43) D. Seyferth, *Adv. Organomet. Chem.*, **14**, 97 (1976).

(44) L. W. Hall, G. J. Zimmerman, and L. G. Sneddon, *J. Chem. Soc., Chem. Commun.*, 45 (1977).

(45) B. P. Sullivan, R. N. Leyden, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 455 (1975).

(46) B. R. Penfold and B. H. Robinson, *Acc. Chem. Res.*, **6**, 73 (1973).

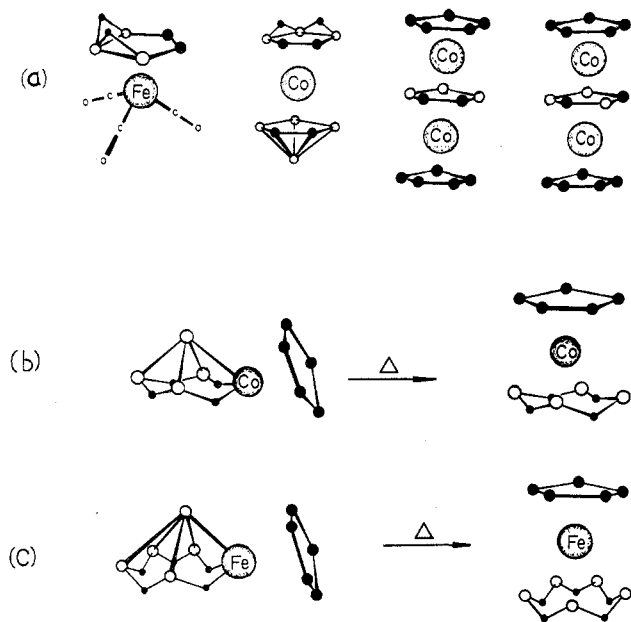


Figure 6. Complexes of cyclic planar borane and carborane ligands. (a) Left to right:⁴⁷ $(C_2B_3H_7)Fe(CO)_3$, $(C_2B_3H_7)Co(CO)(C_2B_4H_6)$, $1,7,2,3-(\eta^5-C_5H_5)_2Co_2(C_2B_3H_5)$, and $1,7,2,4-(\eta^5-C_5H_5)_2Co_2(C_2B_3H_5)$; (b) rearrangement of $2-(\eta^5-C_5H_5)CoB_4H_8$ to $1-(\eta^5-C_5H_5)CoB_4H_8$ ^{33a,c}; (c) rearrangement of $2-(\eta^5-C_5H_5)FeB_5H_{10}$ to $1-(\eta^5-C_5H_5)FeB_5H_{10}$.⁵⁶ ●, CH or C(CH₃); ○, BH; •, bridging H.

examples^{47a-c} were complexes of the carborane ligands $C_2B_3H_7^{2-}$ and $C_2B_3H_5^{4-}$, both isoelectronic with $C_5H_5^-$ (Figure 6a). The structures of $1,2,3-(CO)_3FeC_2B_3H_7$,^{47a,b} $[2,3-(CH_3)_2C_2B_3H_5]CoH[2,3-(CH_3)_2C_2B_4H_4]$,¹⁰ and the triple-decked sandwiches $1,7,2,3-$ and $1,7,2,4-(\eta^5-C_5H_5)_2Co_2C_2B_3H_5$,^{47c,e,f} all originally deduced from NMR data, have been confirmed by X-ray crystallographic analysis.^{47c,d,g,48} In addition, a unique triple-decker whose structure was *not* known until the X-ray study was conducted^{47h} contains a planar bicyclic $C_5B_3H_7^{4-}$ central ring and was evidently formed by partial insertion of a cyclopentadiene ring into a cobaltaborane cage.^{33c} Other groups, notably those of Herberich and of Siebert, have reported double- and triple-decked transition-metal complexes containing derivatives of the planar ligands $C_4BH_5^{2-}$,⁴⁹ $C_2B_2SH_4^{2-}$,⁵⁰ $C_2BN_2H_5^0$,⁵¹ and $C_3B_2H_5^{3-}$,⁵² all of which are electronic analogues of $C_5H_5^-$.

Metalloboranes containing the cyclic ligands $B_4H_8^{2-}$ and $B_5H_{10}^-$ (isoelectronic with $C_4H_4^{2-}$ and $C_5H_5^-$, respectively) are also known. Thus, rearrangement^{33a,c} of the previously mentioned $2-(\eta^5-C_5H_5)CoB_4H_8$ at 200 °C

produced the 1-isomer (Figure 6b) which is both a B_5H_9 analogue [with $Co(C_5H_5)$ replacing an apex BH group] and, at the same time, a cyclobutadiene sandwich analogue. A second example of a complex of planar $B_4H_8^{2-}$, $1-(CO)_3FeB_4H_8$, has been prepared in several laboratories⁵³ and its UV photoelectron spectrum has been measured,⁵⁴ as has that of $1,2,3-(CO)_3FeC_2B_3H_7$. From these data it has been concluded⁵⁴ that the metal participates extensively in framework bonding and that the $Fe(CO)_3$ group is indeed electronically similar to the BH unit it replaces, as is assumed in the skeletal-electron bonding theory. Moreover, comparison with the UV photoelectron spectra⁵⁴ of closely related species such as B_5H_9 and $(CO)_3FeC_4H_4$ lends support to the concept that metalloboron sandwich complexes are, as suggested,^{33,53,55} intermediate in character between the boranes and the metallocenes.

Very recently a complex of cyclic planar $B_5H_{10}^-$, $1-(\eta^5-C_5H_5)FeB_5H_{10}$ ("pentaboraferrrocene"), was obtained⁵⁶ by thermolysis of the 2-isomer at 175 °C (Figure 6c) following preparation of the latter from $Na^+B_5H_8^-$, $FeCl_2$, and $Na^+C_5H_5^-$. From ¹¹B and ¹H NMR data both isomers are proposed to have pentagonal-pyramidal geometry analogous to B_5H_{10} , with a $(C_5H_5)FeH$ unit formally replacing BH; the 1-isomer is isoelectronic and *isostructural* with ferrocene. A cobalt analogue of this complex, $1-(\eta^5-C_5H_5)CoB_5H_9$, has also been prepared⁵⁷ and shown to exhibit B_5H_{10} -like tautomerism of the four bridging hydrogens.

The almost unlimited potential of metalloboron chemistry is well illustrated by these sandwich species, which in some respects exhibit an even broader chemistry than that of the metallocenes themselves. For example, while $(\eta^5-C_5H_5)CoB_4H_8$ and $(\eta^5-C_5H_5)FeB_5H_{10}$ exist as isomers, there are apparently no cases of similar isomerism among the metallocene sandwiches (perhaps the possibility should be reexamined). Moreover, the numerous triple-decked heteroborane complexes stand in contrast to the lone example⁵⁸ of an isolable triple-decker system containing $C_5H_5^-$ as the central ligand, viz., the $(C_5H_5)_3Ni_2^+$ ion and its derivatives. The cycloborane ligands, like their carborane counterparts,² thus derive special significance from their ability to coordinate transition-metal ions in many cases more effectively than do the arenes, thereby extending the realm of metallocene sandwich complexes into structurally novel areas.

Summary

The kinds of metalloboron cage systems dealt with in this Account represent only a small sampling of recent developments in what is now recognizably a field of enormous scope. It is a curious fact that the cage boranes, once seemingly set apart from the more familiar areas of chemistry, have assumed a central role in linking conceptually, for the first time, many disparate classes of molecular species—the metal clusters, the organometallic cluster complexes, the metallocenes,

(47) (a) R. N. Grimes, *J. Am. Chem. Soc.*, **93**, 261 (1971); (b) L. G. Sneddon, D. C. Beer, and R. N. Grimes, *ibid.*, **95**, 6623 (1973); (c) D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, and G. J. Palenik, *ibid.*, **95**, 3046 (1973); (d) J. P. Brennan, R. N. Grimes, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **12**, 2266 (1973); (e) R. N. Grimes, D. C. Beer, L. G. Sneddon, V. R. Miller, and R. Weiss, *ibid.*, **13**, 1138 (1974); (f) R. Weiss and R. N. Grimes, *J. Organometal. Chem.*, **113**, 29 (1976); (g) W. T. Robinson and R. N. Grimes, *Inorg. Chem.*, **14**, 3056 (1975); (h) J. R. Pipal and R. N. Grimes, *ibid.*, **17**, 10 (1978).

(48) J. R. Pipal, W. M. Maxwell, and R. N. Grimes, *Inorg. Chem.*, **17**, 1447 (1978).

(49) (a) G. E. Herberich, J. Hengesbach, U. Kölle, and W. Oschmann, *Angew. Chem., Int. Ed. Engl.*, **16**, 42 (1977); (b) G. E. Herberich, J. Hengesbach, U. Kölle, G. Huttner, and A. Frank, *ibid.*, **15**, 433 (1976).

(50) (a) W. Siebert and K. Kinberger, *Angew. Chem., Int. Ed. Engl.*, **15**, 434 (1976); (b) W. Siebert, T. Renk, K. Kinberger, M. Bochmann, and C. Krüger, *ibid.*, **15**, 779 (1976); (c) W. Siebert and W. Rothermel, *ibid.*, **16**, 333 (1977).

(51) G. Schmid and J. Schulze, *Angew. Chem.*, **89**, 258 (1977).

(52) W. Siebert and M. Bochmann, *Angew. Chem.*, **89**, 483 (1977).

(53) N. N. Greenwood, C. G. Savory, R. N. Grimes, L. G. Sneddon, A. Davison, and S. S. Wreford, *J. Chem. Soc., Chem. Commun.*, 718 (1974).

(54) J. A. Ulman, E. L. Anderson, and T. P. Fehlner, *J. Am. Chem. Soc.*, **100**, 456 (1978).

(55) R. N. Grimes, *Pure Appl. Chem.*, **39**, 455 (1974).

(56) R. Weiss and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 8087 (1977).

(57) L. G. Sneddon, private communication.

(58) (a) H. Werner and A. Salzer, *Synth. Inorg. Met.-Org. Chem.*, **2**, 239 (1972); (b) A. Salzer and H. Werner, *Angew. Chem., Int. Ed. Engl.*, **11**, 930 (1972).

the carbonium cluster ions, and the boranes. At the same time, the versatility inherent in boron cage chemistry is continually creating new opportunities to explore structural features and phenomena that are difficult to approach otherwise; for example, the construction and study of very large polyhedra, the thermal mobility of metal atoms on polyhedral surfaces, and the low-energy fusion of cage frameworks. The unfolding of these and many other facets of polyhedral metal-

loborane chemistry, along with the developing ties to other areas, will be fascinating to watch.

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Liquid-Liquid Critical Phenomena

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Over the last decade or so, theoreticians and experimentalists have developed a framework for understanding the behavior of matter near critical points which promises to encompass an amazing medley of phenomena.¹ The mixing and unmixing of two liquids as temperature and composition are varied is one of these phenomena—one which is of particular interest to chemists.

In thinking of liquid-liquid critical phenomena, it is useful to keep in mind the analogous liquid-gas critical phenomena. Figure 1a shows the phase diagram of a system of one component. By Gibb's phase rule for one component, there is a pressure-volume-temperature surface (shown shaded) where one phase exists and a coexistence curve (shown dashed) along which two phases (a "gas" and a "liquid") exist. As the temperature increases, the coexistence region narrows and the coexisting phases become more and more alike until, at the critical point, the two phases are indistinguishable. Figure 1b shows the projection of the coexistence curve onto the TV plane; it is this projection which we will find convenient for our analogy with liquid-liquid critical phenomena.

When another component is added, the phase rule tells us that an additional degree of freedom is gained. Thus, for a binary mixture a coexistence curve becomes a coexistence surface and a critical point becomes a line of critical points. Figure 2a shows a temperature-composition-pressure diagram for a binary liquid mixture with liquid-liquid immiscibility. We will be concerned here with constant pressure sections of this diagram, such as that shown in Figure 2b, which is analogous to Figure 1b. Below the critical point, the system consists of two coexisting liquid phases of different composition. As the temperature is raised, the two phases become more and more alike until, at the

critical point, the two liquid phases are indistinguishable.

The liquid-liquid critical solution point shown in Figure 2b has an *upper* critical solution temperature (UCST)—the mixture mixes at higher temperatures and unmixes at lower temperatures. When the opposite happens—mixing at lower temperatures and unmixing at higher temperatures—the associated critical point has a *lower* critical solution temperature (LCST). Both kinds of critical points can occur in the same system, forming a closed miscibility gap. As examples, the mixture aniline + cyclohexane has an UCST at 29.5 °C, triethylamine + water has a LCST at 18.5 °C, and 2,6-lutidine + water shows both an UCST at 231 °C and a LCST at 34 °C.²

Let us think about what is happening at a liquid-liquid phase transition. Consider a liquid mixture at the critical composition and above its UCST: a homogeneous mixture of one liquid phase (see Figure 2b). Suppose now that the temperature is lowered toward critical. Near the critical point, the two phases are very nearly identical, so it takes little energy for small regions of one phase or the other to form in the "homogeneous" liquid. The nearer the system is to the critical point, the larger these "fluctuations" become. Within millidegrees of the critical point, the size of these fluctuation regions, termed the "correlation length" and denoted by ξ , becomes thousands of angstroms. In fact, the correlation length diverges toward infinity very close to the critical point.

This divergence of the correlation length causes the intense light scattering near critical points known as "critical opalescence". It has been found that many thermodynamic properties—compressibility, heat ca-

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(1) Reviews of critical phenomena in general can be found in: M. E. Fisher, *Rep. Prog. Phys.*, **30**, 615 (1967); P. Heller, *ibid.*, **30**, 731 (1967); L. P. Kadanoff, W. Gotze, D. Hamblen, R. Hecht, E. A. S. Lewis, V. V. Palciauskas, M. Rayl, and J. Swift, *Rev. Mod. Phys.*, **39**, 395 (1967); H. E. Stanley, "Introduction to Phase Transitions and Critical Phenomena", Oxford University Press, New York, N.Y., 1971.

(2) Liquid-liquid miscibility gaps have been catalogued by A. W. Francis in "Liquid-Liquid Equilibrium", Interscience, New York, N.Y., 1963, and in "Critical Solution Temperatures", American Chemical Society, Washington, D.C., 1961.