

METALLACARBORANES AND METAL-BORON CLUSTERS IN ORGANOMETALLIC SYNTHESIS

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Abstract. This article presents some recent findings in the chemistry of small metallaboranes and metallacarboranes which are direct structural and electronic analogues of metal-arene complexes and of metal clusters, but which exhibit significantly different reactivity. The species to be discussed include complexes of the cyclic $B_4H_8^{2-}$ ligand (isoelectronic with $C_4H_4^{2-}$, cyclobutadienide) and the $B_5H_{10}^-$, $B_5H_9^{2-}$, $C_2B_3H_5^{4-}$, and $C_2B_3H_7^{2-}$ ligands (analogous to $C_5H_5^-$) and their C,C-derivatives. Certain reactions which have potential utility in synthesis, notably oxidative coupling and fusion of ligands via metal μ - and π -complexes, are described, and new observations relevant to the mechanism of the oxidative ligand fusion process are presented. The homogeneous catalysis of hydrogen addition to alkenes and alkynes under mild conditions, via metallaboranes prepared from $B_5H_8^-$ or $B_3H_8^-$ salts in THF, is also discussed.

INTRODUCTION

Studies of metallaboranes and metallacarboranes have been primarily concerned with uncovering their fundamental chemistry and structural principles (1). Not surprisingly, the development of this area has taken many unpredictable turns and serendipity has played a major role. Recently, however, serious attention has also been directed toward exploiting some of the unique characteristics of these compounds in chemical synthesis. In this aspect of the field, interest is centered on the metal atoms in the polyhedral cages as sites of reactivity.

Metal-boron cluster compounds are usually viewed as derivatives of boranes or carboranes in which metal-ligand groups such as $Co(\eta^5-C_5H_5)$ or $Fe(CO)_3$ replace BH units. Not only does this concept have a sound basis in theory (2); it also accurately reflects the experimental facts, since in virtually all cases the synthetic routes to these compounds involve introduction of metals into borane or carborane cages. Moreover, the structures of metallaboranes and metallacarboranes tend to mimic those of the parent or prototype borane system, provided the heteroatom content of the cage framework is not too high (in clusters with a high proportion of metal or carbon atoms in the polyhedron, major structural effects are often seen).

For these reasons, metal-boron cluster chemistry is normally presented from a "borane" viewpoint; the structures and chemistry of these compounds are described primarily in relation to other boranes. Consequently, the organometallic aspects of metal-boron chemistry are often obscured, and important relationships between metallaboranes and metal-hydrocarbon complexes pass with little notice. This article describes some relatively recent work which deals with the role of metals *per se* in several types of metal-boron and metal-boron-carbon systems. While some of this chemistry has its parallels in the metallocene and metal cluster fields, other aspects of it are quite novel and open potentially useful new avenues in synthesis.

This presentation will deal with three main areas: metal complexes of small borane and carborane ligands which are isoelectronic analogues of common

aromatic hydrocarbons; metal-centered linkage and fusion reactions; and the utilization of metallaboranes in organic synthesis, including homogeneous catalysis.

SMALL BORANE AND CARBORANE LIGANDS

All metallaboranes and metallocarboranes contain one or more metal atoms bound into a borane framework and can be described as metal-ligand π -complexes, even when the designated borane "ligand" actually has no existence as a free species. Although analogies are commonly drawn between the metal-ligand binding in metallaboranes and metallocenes, many borane and carborane ligands (e.g., $C_2B_9H_{11}^{2-}$) are structurally quite different from planar hydrocarbon systems such as $C_5H_5^-$ and $C_4H_4^{2-}$, and comparisons are necessarily limited. However, the cyclic planar boron-containing ligands are direct structural and electronic counterparts of the aromatic hydrocarbons (3), and their metal complexes can therefore readily be viewed as straightforward extensions of metallocene chemistry. What makes this particularly interesting is that the cyclic borane and carborane ligands possess features that give them extra versatility: (i) the B-B edges can accept Lewis acids such as H^+ or metals to form B-H-B or B-M-B bridges involving three-center, two-electron bonds; (ii) the non-protonated cyclic planar ligands, such as $C_2B_3H_5^{4-}$, can simultaneously face-bond to two metals above and below the ring plane, forming stable, neutral triple- or multiple-decker π -complexes; (iii) the higher negative charge (usually -2 to -4) on the borane ligands allows the stabilization of high metal oxidation states, extending the range of isolable complexes beyond that of the metal- $C_5H_5^-$ sandwiches; and (iv) the lower electronegativity of boron vs. carbon tends to give metal-borane complexes a more covalent character than metal-hydrocarbon species, often resulting in higher stability for the former. This section deals with boron analogues of two aromatic hydrocarbon systems, $C_4H_4^{2-}$ and $C_5H_5^-$.

Analogues of $C_4H_4^{2-}$

The prototype square planar aromatic borane, $B_4H_4^{6-}$, is unknown but its formal relationship to several real and hypothetical species is illustrated in Fig. 1. As shown, the addition of four protons into B-H-B bridging

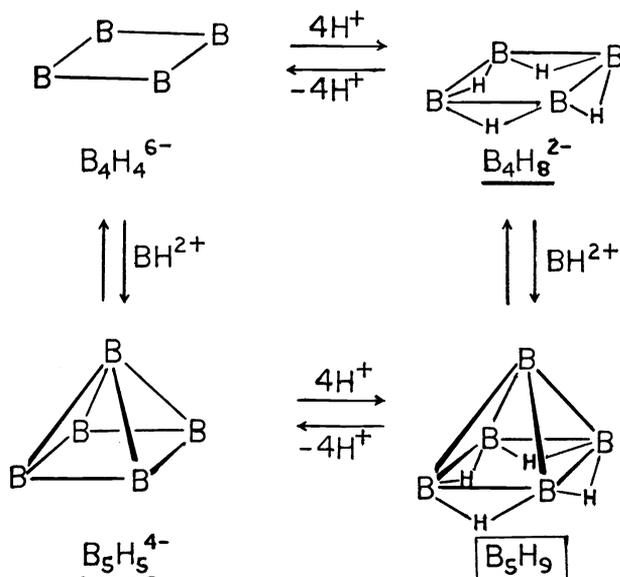


Fig. 1. Cyclic planar and pyramidal borane analogues of the $C_4H_4^{2-}$ ion, with interconversions shown schematically (terminal hydrogens are omitted for clarity). The $B_4H_4^{6-}$ cyclic planar group has not yet been observed, either as free species or in metal-complexed form. Known species. Metal complexes only.

positions yields $B_4H_8^{2-}$, a ligand which has no free existence but is known in the form of three characterized, stable complexes: yellow 1-(η^5 -

$C_5H_5)CoB_4H_8$ (4), yellow $1-[\eta^5-C_5(CH_3)_5]CoB_4H_8$ (5), and orange $1-(CO)_3FeB_4H_8$ (6). The first two compounds were prepared by thermal rearrangement of the 2-isomer (Fig. 2), which in turn was obtained by reaction of the $B_5H_8^-$ ion

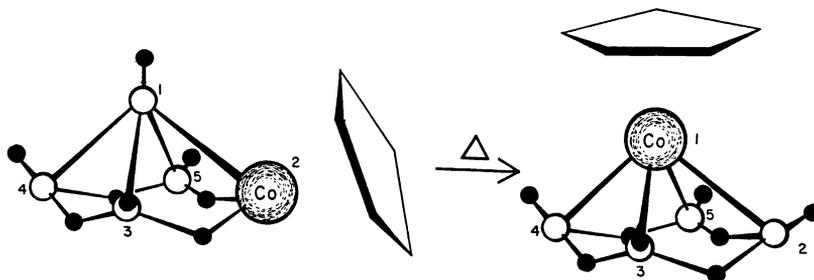


Fig. 2. Thermal rearrangement of red $2-(\eta^5-C_5H_5)CoB_4H_8$ to yellow $1-(\eta^5-C_5H_5)CoB_4H_8$. The $2-[\eta^5-C_5(CH_3)_5]CoB_4H_8$ complex isomerizes similarly.

with $CoCl_2$ and $C_5H_5^-$ (or $C_5(CH_3)_5^-$) in THF solution (4,5); the iron complex was subsequently prepared by direct reactions of B_5H_9 with iron carbonyls (6). Since $B_4H_8^{2-}$ is isoelectronic with cyclobutadienide, $C_4H_4^{2-}$, these transition metal complexes can be directly compared with such known (7) species as $(CO)_3Fe(\eta^4-C_4H_4)$. Photoelectron spectroscopy (8) indicates that the metal-ligand bonding is more ionic in the latter complex than in its borane counterpart $1-(CO)_3FeB_4H_8$, but that there is nonetheless substantial electronic similarity between the two.

Although the original $B_4H_8^{2-}$ complex, $1-(\eta^5-C_5H_5)CoB_4H_8$, was first prepared (4a) in 1973, only recently have we succeeded in confirming its assigned square-pyramidal structure (Fig. 2) by X-ray crystallography (9). (The X-ray structure determination of the red 2-isomer (Fig. 2) has been reported (10)). In the 1-isomer, the observed B-B and B-H_{bridge} distances are close to those in B_5H_9 (11) and the cobalt is equidistant from the four boron atoms. The cobalt-boron distance is 1.980(5) Å, which is not significantly different from the corresponding Co-C (cyclobutadiene) mean value in $(\eta^5-C_5H_5)Co(\eta^4-C_4H_4)$ (12), despite the larger (~ 0.05 Å) covalent radius of boron vs. carbon; thus the $B_4H_8^{2-}$ -cobalt binding is evidently stronger, and probably more covalent, than is the $C_4H_4^{2-}$ -cobalt interaction. The properties of $1-(\eta^5-C_5H_5)CoB_4H_8$ are under further investigation by both experimental and theoretical methods.

Complexes of the planar $B_4H_4^{6-}$ system, the bridge-deprotonated analogue of $B_4H_8^{2-}$, have not yet been reported, but triple-decked sandwiches such as $(\eta^5-C_5H_5)Ni^{IV}(B_4H_4)Ni^{IV}(\eta^5-C_5H_5)$ (an analogue of the known carborane 1,6- $C_2B_4H_6$) should exist. Although triple-decker complexes based on heterocyclic planar ligands such as $C_2B_3H_5^{4-}$ are known (see below), no corresponding homocyclic borane sandwiches have been reported. However, thermal rearrangement of the well-characterized (4,13) violet complex $1,2-(\eta^5-C_5H_5)_2Co_2B_4H_6$ (which has adjacent cobalt atoms in a closo-6-vertex Co_2B_4 cage) is expected to yield the 1,6-isomer, which would be a diprotonated derivative of the triple-decked sandwich $[(\eta^5-C_5H_5)Co^{III}(B_4H_4)Co^{III}(\eta^5-C_5H_5)]^{2-}$. Such a rearrangement would be directly analogous to the known thermal conversion of the closo-carborane 1,2- $C_2B_4H_6$ to its 1,6 isomer (14).

Analogues of $C_5H_5^-$

The simplest borane counterpart of cyclopentadienide, $B_5H_5^{6-}$, is not presently known even in complexed form (unless one regards the pentagonal-bipyramidal $B_7H_7^{2-}$ ion (15) as a "complex" of $B_5H_5^{6-}$ with two apical BH_2^+ units). However, its protonated forms $B_5H_{10}^-$ and $B_5H_9^{2-}$ (Fig. 3) are found in the complexes $1-(\eta^5-C_5H_5)Fe^{II}B_5H_{10}$ (16) and $1-(\eta^5-C_5H_5)Co^{III}B_5H_9$ (17), respectively. In both cases the pentagonal-pyramidal structures were assigned from NMR spectra, but neither crystallographic data nor reaction chemistry have been reported for these species.

In contrast, the corresponding carborane ligands have generated an extensive and varied chemistry. Formal replacement of C with B⁻ gives rise to a series of hypothetical cyclic planar species isoelectronic with $C_5H_5^-$, e.g., $C_4BH_5^{2-}$, $C_3B_2H_5^{3-}$, $C_2B_3H_5^{4-}$, $CB_4H_5^{5-}$, and $B_5H_5^{6-}$; in fact, many transition

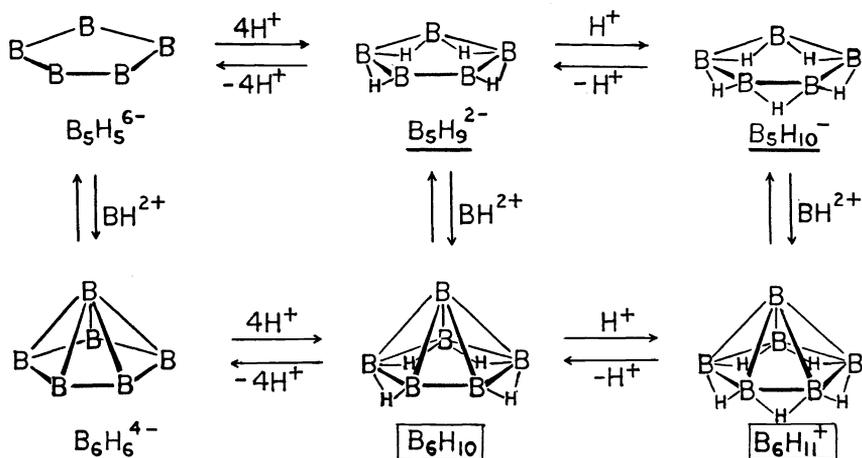


Fig. 3. Cyclic planar and pyramidal borane analogues of C_5H_5^- (for explanation see Fig. 1).

metal complexes based on the C_4B , C_3B_2 , and C_2B_3 cyclic systems are known and structurally established (3,18). In this article, attention will be confined to the 2,3- and 2,4- $\text{C}_2\text{B}_3\text{H}_5^{4-}$ ligands and their pyramidal derivatives, 2,3- and 2,4- $\text{C}_2\text{B}_4\text{H}_6^{2-}$, whose relationship is shown in Fig. 4.

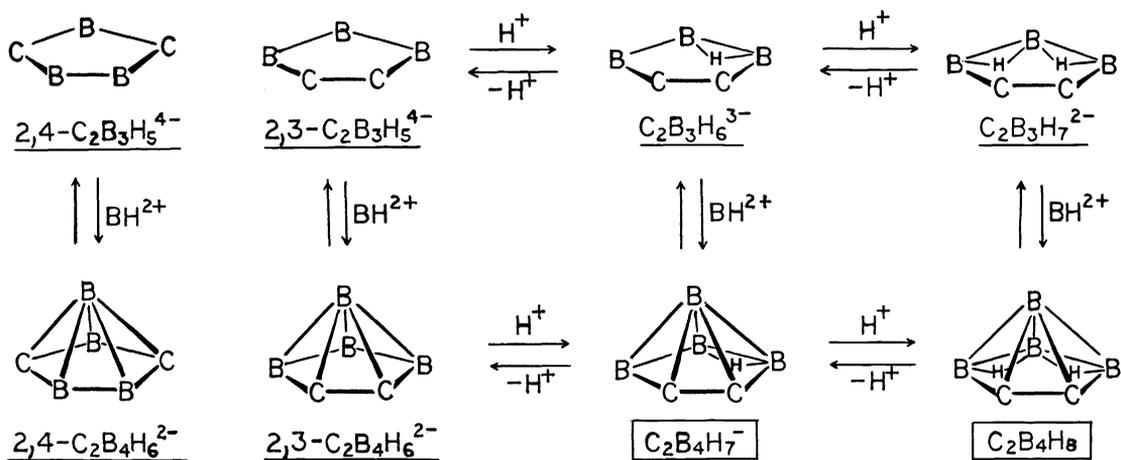
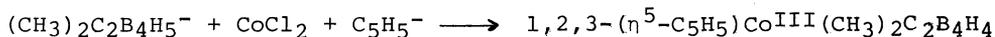


Fig. 4. Cyclic planar and pyramidal carborane analogues of C_5H_5^- (for explanation see Fig. 1).

The nido-carborane 2,3- $\text{C}_2\text{B}_4\text{H}_8$ (Fig. 4, lower right) and its C- and C,C'-substituted derivatives are readily obtained by the reaction of B_5H_9 with alkynes (14,15b). When the acetylene reagent is RCCR where R is CH_3 , C_2H_5 , or C_3H_7 , the corresponding carborane can be prepared on a multigram scale under mild conditions by employing a Lewis base such as triethylamine (19). Even the use of B_5H_9 as a reagent can be bypassed by utilizing B_3H_8^- salts, as recently described (19). Thus, the nido- $\text{R}_2\text{C}_2\text{B}_4\text{H}_6$ system is accessible in practical quantities by standard organometallic techniques and is a starting point for a large sub-field of organometallic chemistry.

Parent 2,3- $\text{C}_2\text{B}_4\text{H}_8$ or more conveniently, its C,C-dialkyl derivatives, can be reversibly bridge-deprotonated by treatment with alkali metal hydrides in THF, generating the nido- $\text{R}_2\text{C}_2\text{B}_4\text{H}_5^-$ anion (20) (Fig. 4). Removal of the second bridging proton to give $\text{R}_2\text{C}_2\text{B}_4\text{H}_4^{2-}$ as shown, does not occur directly, and the dianion has not been observed as a free species; however, reactions

of $R_2C_2B_4H_5^-$ with metal reagents can generate η^5 complexes of $R_2C_2B_4H_4^{2-}$, the second proton being removed in the process (21):



In some cases (e.g., with iron, gallium, and indium reagents), metal complexes of $R_2C_2B_4H_4^{2-}$ have been obtained by direct thermal insertion of the metal into neutral $R_2C_2B_4H_6$ carboranes (22). The monoanion $R_2C_2B_4H_5^-$ has one B-B edge which is receptive to metal (or nonmetal) electrophiles and can form B-M-B bridged complexes (Fig. 5); recent developments involving this type of metal-ligand interaction are discussed below.

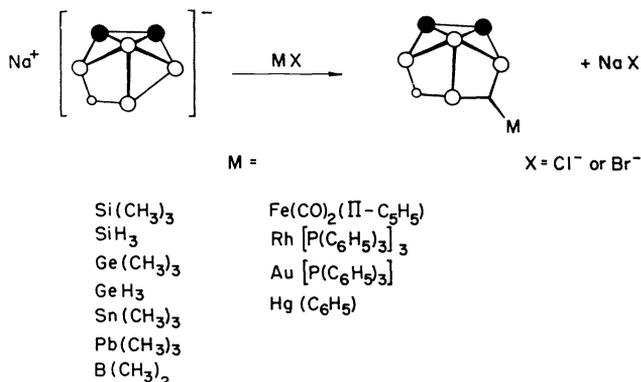


Fig. 5. Formation of μ -ML_n-R₂C₂B₄H₅ complexes.

The planar $C_2B_3H_5^{4-}$ system and its bridge-protonated forms, $C_2B_3H_6^{3-}$ and $C_2B_3H_7^{2-}$, have not been prepared as free ions in solution (nor have their C,C'-dialkyl derivatives), but metal η^5 -complexes incorporating them can be obtained by removal of an apex BH²⁺ group from complexes of the pyramidal $C_2B_4H_6^{2-}$ ligand (21a, 22a) as depicted schematically in Fig. 4. Typical metal complexes of all these ligands are illustrated in Fig. 6. It will be noted that the $C_2B_3H_7^{2-}$ (or $R_2C_2B_3H_5^{2-}$) planar ligand directs its bridging hydrogens away from the metal atom, in a manner analogous to that of 2,3-C₂B₄H₈ (Fig. 4) with the metal replacing the apex BH group; several X-ray structure determinations establish this feature (23-25).

Two isomeric possibilities exist for planar $C_2B_3H_5^{4-}$, and both are found in metal complexes (Fig. 6, a and b) (26-28); similarly, the 2,3- and 2,4-C₂B₄H₆²⁻ pyramidal ligands are both known. The complexes of 2,4-C₂B₃H₅⁴⁻ and 2,4-C₂B₄H₆²⁻, in which the carbon atoms are separated, can be obtained in two ways: insertion of metal groups directly into a carborane cage in which the carbons are already non-vicinal, or thermal rearrangement of the corresponding 2,3-complex (1b, 3a). Thus, at 300°C 1,7,2,3-(η^5 -C₅H₅)₂Co₂C₂B₃H₅ converts quantitatively to the 1,7,2,4 isomer (Fig. 6). In the course of that rearrangement several other isomers in which one cobalt occupies an equatorial (i.e., planar ring) position are formed (28a); one of these, 1,2,4,5-(η^5 -C₅H₅)₂Co₂C₂B₃H₅ has been crystallographically verified (29), as has a mixed-metal analogue, 1,2,4,5-(η^5 -C₅H₅)₂FeHCoC₂B₃H₅ (29) (Fig. 7). In these complexes the pentagonal planar "ligand" is a CoC₂B₃ system which can be described as a metallacycle.

Cage rearrangements of the sort just mentioned are commonplace in boron chemistry, in metal-containing as well as nonmetal systems, but are rare in other types of clusters.

METAL-BRIDGED COMPLEXES AND OXIDATIVE LINKAGE

The principle of metal insertion into a B-B edge of a pyramidal carborane ligand to form a B-M-B bridge as illustrated in Fig. 5, can be extended to bis(carborane) and bis(borane) metal complexes (Fig. 8) (30).

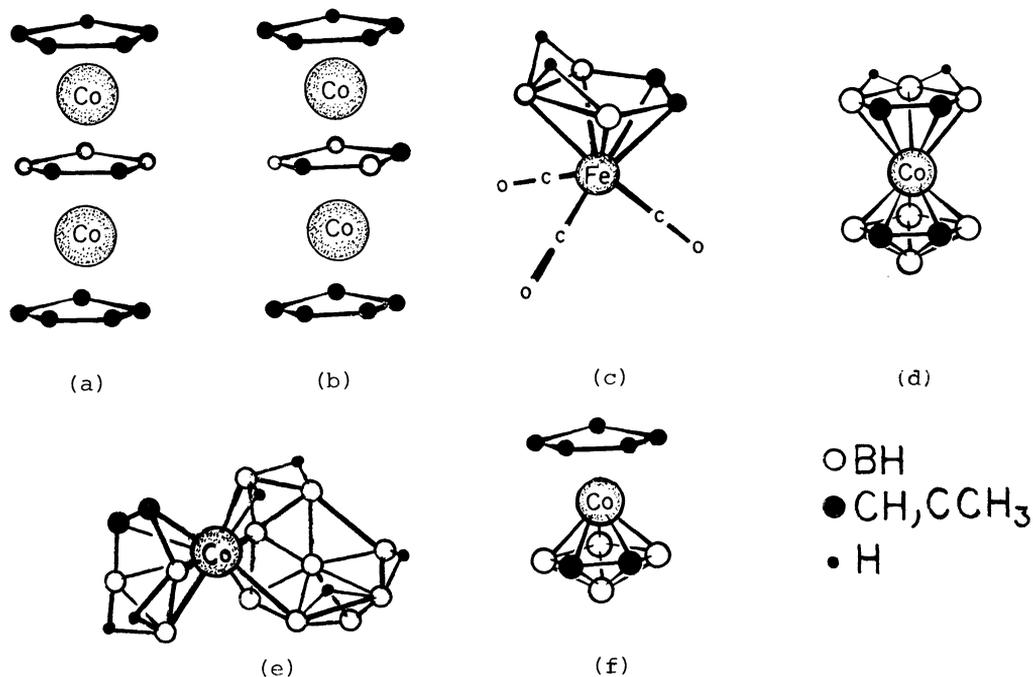


Fig. 6. Complexes of the cyclic planar and pyramidal ligands $R_2C_2B_3H_3^{4-}$ (a and b), $R_2C_2B_3H_5^{2-}$ (c, d, and e), and $R_2C_2B_4H_4^{2-}$ (d and f). (a) 1,7,2,3-(C_5H_5) $_2Co_2C_2B_3H_5$; (b) 1,7,2,4-(C_5H_5) $_2Co_2C_2B_3H_5$; (c) $(CO)_3FeC_2B_3H_7$; (d) $[(CH_3)_2C_2B_3H_5]Co-[(CH_3)_2C_2B_4H_4]^-$; (e) $[(CH_3)_2C_2B_3H_5]Co[B_9H_{12} \cdot THF]$; (f) $[(CH_3)_2C_2B_4H_6]Co(C_5H_5)$. All species shown have been characterized by X-ray diffraction.

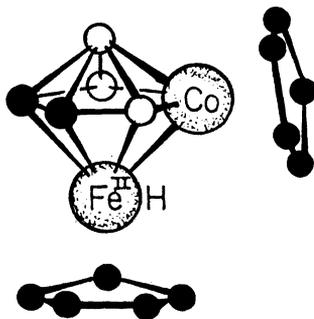


Fig. 7. Structure of 1,2,4,5-($\eta^5-C_5H_5$) $_2Fe^{II}(H)Co^{III}C_2B_3H_5$ and 1,2,4,5-($\eta^5-C_5H_5$) $_2Co_2C_2B_3H_5$.

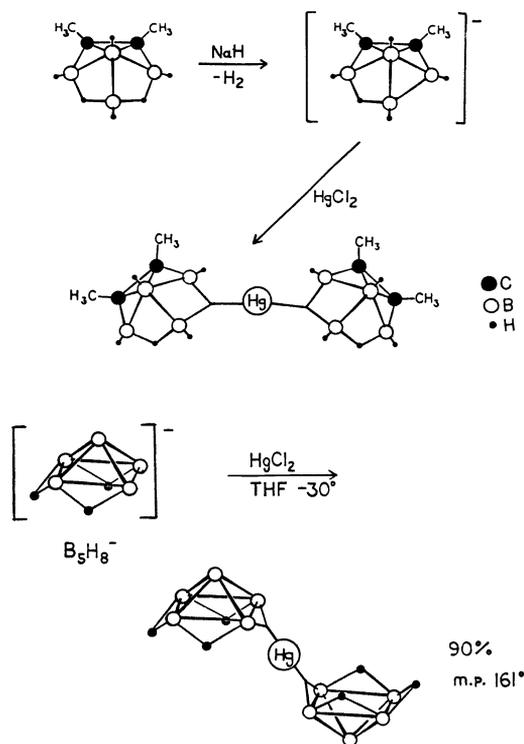


Fig. 8. Formation of $\mu, \mu' - [(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5]_2\text{Hg}$ (top) and $\mu, \mu' - (\text{B}_5\text{H}_8)_2\text{Hg}$ (bottom).

The bridged structures shown were deduced from ^{11}B and ^1H NMR spectra; analogous mercury-bridged cobaltacarboranes have also been prepared (Fig. 9) and the structures of $\mu\text{-HgCl} - [(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Co}(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_4]$ and $\mu, \mu' - [(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_4]_2\text{Hg}$ have been established by X-ray diffraction studies as shown in Fig. 10 (31). These compounds can be formally described as complexes of cyclic planar $(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_3^{4-}$ (see above) which is η^2 -coordinated to mercury via a B-B edge; the remaining B-B site is protonated, forming a B-H-B bridge.

The white, air-stable complex $\mu, \mu' - [(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5]_2\text{Hg}$ on heating in benzene at 180° liberates mercury metal and forms in high yield the linked carborane $5,5' - [(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5]_2$ as shown in Figure 11. This process (30) can be described as oxidative coupling since the two ligands, which carry a formal negative charge, generate a neutral biscarborane as $\text{Hg}(\text{II})$ is reduced to the free metal. Reactions of SnCl_2 with the $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5^-$ and B_5H_8^- ions (32) give more complex products whose proposed structures involve both direct inter cage linkage as well as metal bridging (Fig. 12). A possible sequence for the formation of such compounds involves initial generation of a bis(carboranyl)tin or bis(boranyl)tin intermediate which rapidly converts to the biscarborane or bisborane, respectively; complexation of one such unit plus a reagent (monomer) anion to tin would produce the observed species.

These results suggest that metal-promoted coupling of boron substrates may be a general and synthetically useful reaction. It clearly differs from the oxidative coupling of polyhedral boranes or carboranes by chemical and electrochemical processes [e.g., the conversion of $\text{B}_{10}\text{H}_{10}^{2-}$ to $(\text{B}_{10}\text{H}_9)_2^{2-}$ (33), of $\text{CB}_9\text{H}_{10}^-$ to $(\text{CB}_9\text{H}_9)_2^{2-}$ (34), and of $\text{C}_2\text{B}_9\text{H}_{12}^-$ to $(\text{C}_2\text{B}_9\text{H}_{11})_2$ (35)], which do not involve metal complexation.

METAL-PROMOTED OXIDATIVE LIGAND FUSION

The concept of joining two cyclic or pyramidal moieties face-to-face in an efficient, low-energy process (Fig. 13) was unknown prior to its discovery in 1974 (36).

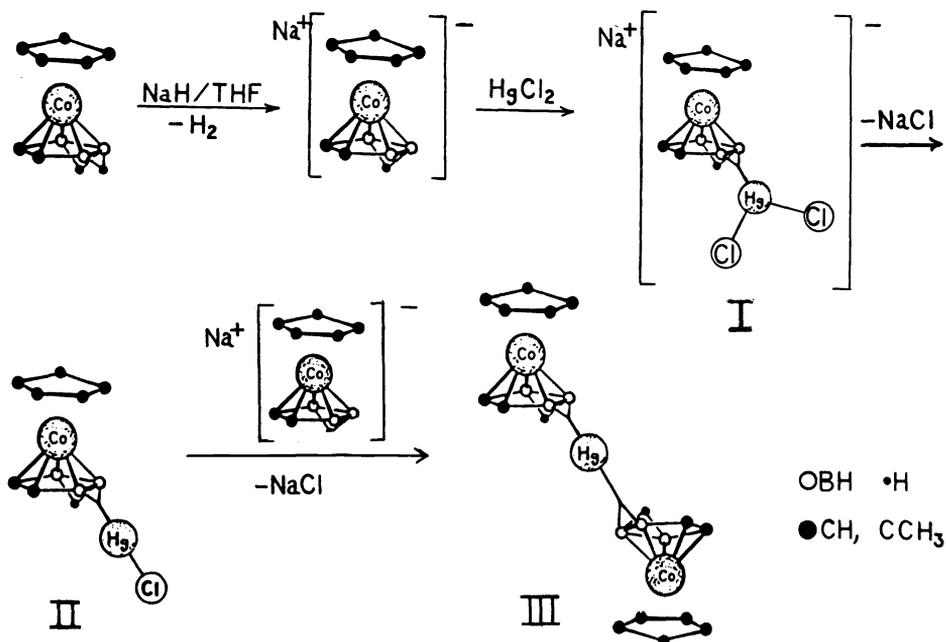


Fig. 9. Formation of mercury-bridged cobaltacarborane complexes. Structures of II and III are established; that of I is proposed from spectroscopic data.

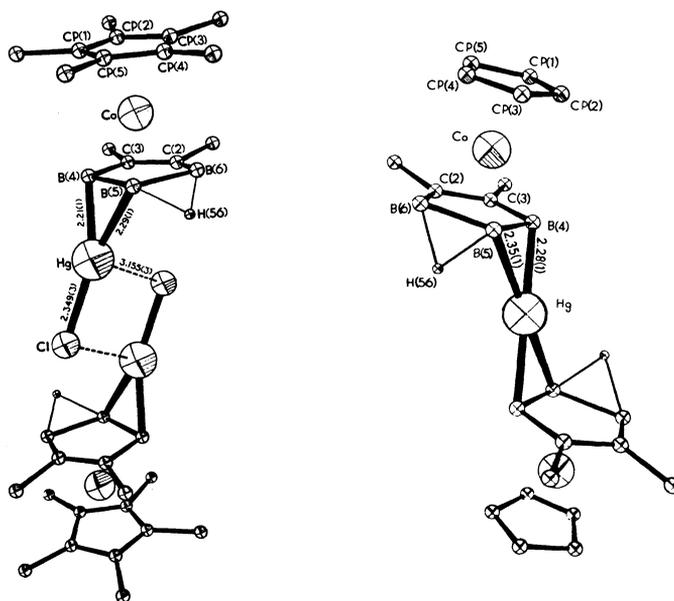


Fig. 10. Structures of $\mu\text{-HgCl}-[(\eta^5\text{-C}_5(\text{CH}_3)_5\text{Co}(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_4)]$ (left) and $\mu, \mu'\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_4]_2\text{Hg}$ (right).

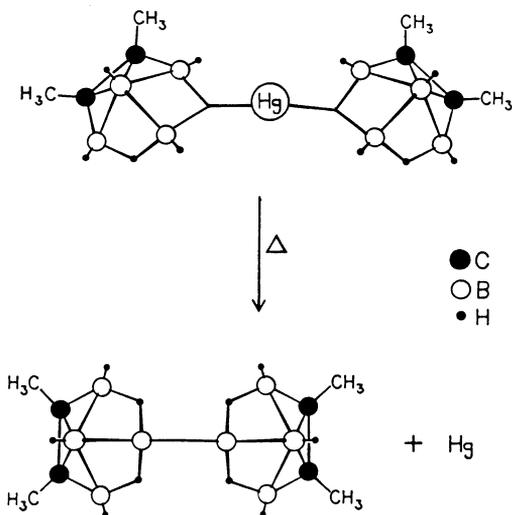


Fig. 11. Synthesis of 5,5'-[(CH₃)₂C₂B₄H₅]₂ from the mercury-linked bis-carborane complex by oxidative coupling.

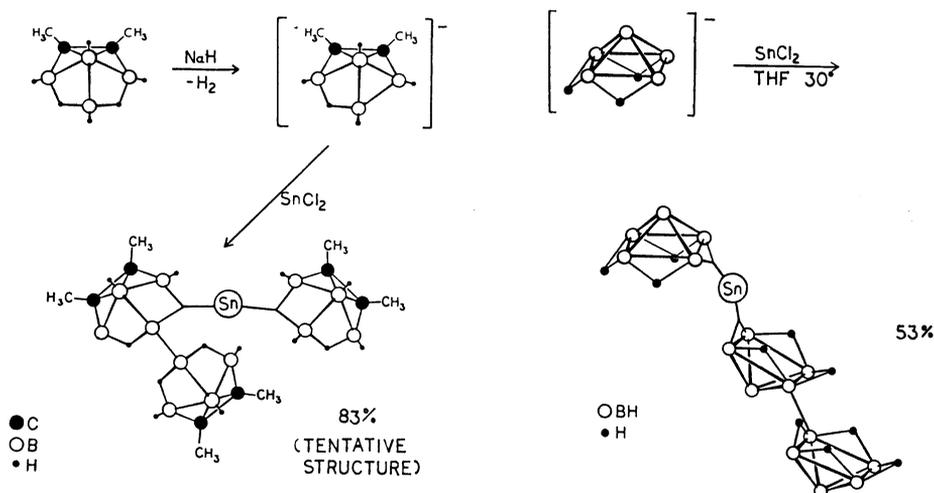


Fig. 12. Synthesis of linked carborane- and borane-tin complexes.

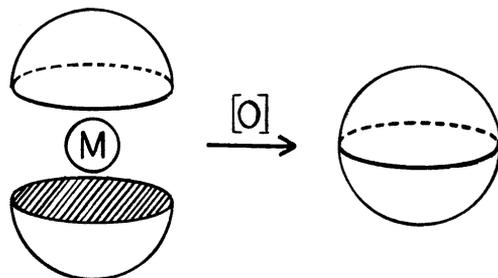


Fig. 13. Schematic representation of the oxidative fusion process, where the hemispheres represent carborane or borane ligands.

It was found that the reaction of the 2,3-(CH₃)₂C₂B₄H₅⁻ ion (Fig. 4) with FeCl₂ or CoCl₂ in THF produced the red, air-sensitive commo-metallacarboranes [(CH₃)₂C₂B₄H₄]₂Fe^{II}H₂ and [(CH₃)₂C₂B₄H₄]₂Co^{III}H in which one or two of the bridging protons on the carborane ligands are retained and are associated

with the metal, probably bridging FeB_2 or CoB_2 faces (37). On exposure to air or other oxidants, THF solutions of these complexes are converted to a colorless, air-stable tetracarborane, $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ (Fig. 14); the process occurs below room temperature in yields approaching 100%. Both com-

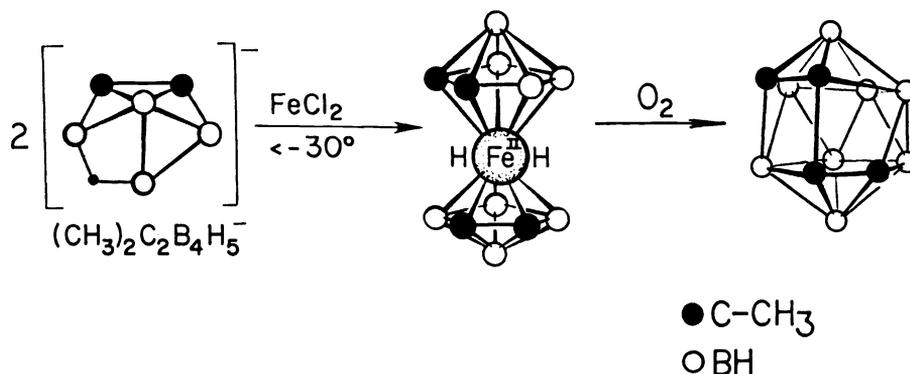


Fig. 14. Formation of $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ via $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2$.

plexes are diamagnetic and the carborane ligands each carry a formal -2 charge, so that the fusion involves a net four-electron oxidation. The structures of both the iron compound (38) and the carborane product (39) have been established by X-ray crystallography, and in both species the two pyramidal $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$ units are mutually rotated by about 90° (Fig. 14). The $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ product has a distorted-icosahedral cage structure in which two C---C edges are nonbonding, creating two four-sided open faces; in the skeletal-electron count formalism (2), the system is a 28-electron, 12-vertex polyhedron of the nido class. With two more skeletal electrons than the well-known icosahedral $\text{C}_2\text{B}_{10}\text{H}_{12}$ system, $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ reflects one form of polyhedral distortion induced by the addition of two electrons to a 26-electron, 12-vertex (closo) system. Such distortion is highly sensitive to the nature and location of the skeletal heteroatoms, and in fact at least seven structurally distinct classes of 28-electron, 12-vertex cages have thus far been characterized (40).

Extensive studies have established that oxidative fusion occurs with some frequency in carborane chemistry, occurring, for example, with metallocarboranes as well (Fig. 15) (18,41). However, in contrast to the conversion of the $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{MH}_x$ species to $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$, many of these fusion reactions are quite complex and generate a variety of products; that in Fig. 15, for example, produces three isomers of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_4\text{B}_6\text{H}_{10}$, all of different structural classes. Fusion can evidently occur with two different ligands, as shown by the conversion of $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2[(\text{CH}_3)_2\text{C}_2\text{B}_7\text{H}_7]$ to $(\text{CH}_3)_4\text{C}_4\text{B}_{11}\text{H}_{11}$, which is believed to be a 15-vertex carborane (42).

In an effort to understand the fusion process in greater detail, we have focused attention on the $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2 \xrightarrow{\text{O}_2} (\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ reaction and have established a number of facts including, very recently, a most surprising discovery. These findings are described elsewhere (43), but the essential points are summarized below.

1. The corresponding $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{FeH}_2$ complexes, in which R is C_2H_5 or C_3H_7 , undergo fusion similar to that of the methyl derivative to form, respectively, $(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8$ and $(\text{C}_3\text{H}_7)_4\text{C}_4\text{B}_8\text{H}_8$. When $\text{R} = \text{H}$, the iron complex is unstable and the results inconclusive (32). The oxidation of $[(\text{C}_6\text{H}_5)\text{HC}_2\text{B}_4\text{H}_4]\text{FeH}_2$ produces, as expected, a mixture of $(\text{C}_6\text{H}_5)_2\text{C}_4\text{B}_8\text{H}_{10}$ isomers.

2. As the structures of $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2$ and $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ imply, the fusion process is intramolecular and does not involve ligand dissociation. Thus, solutions containing equimolar mixtures of $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{FeH}_2$ and $(\text{R}'_2\text{C}_2\text{B}_4\text{H}_4)_2\text{FeH}_2$ where $\text{R} \neq \text{R}'$ (for example, $\text{R} = \text{CH}_3$ and $\text{R}' = \text{C}_2\text{H}_5$) on oxidation give only $\text{R}_4\text{C}_4\text{B}_8\text{H}_8$ and $\text{R}'_4\text{C}_4\text{B}_8\text{H}_8$; no mixed-ligand products $(\text{R}_2\text{R}'_2\text{C}_4\text{B}_8\text{H}_8)$ are detected. Moreover, $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{FeH}_2$ complexes do not undergo ligand exchange with free $\text{R}'_2\text{C}_2\text{B}_4\text{H}_5^-$ ion in solution.

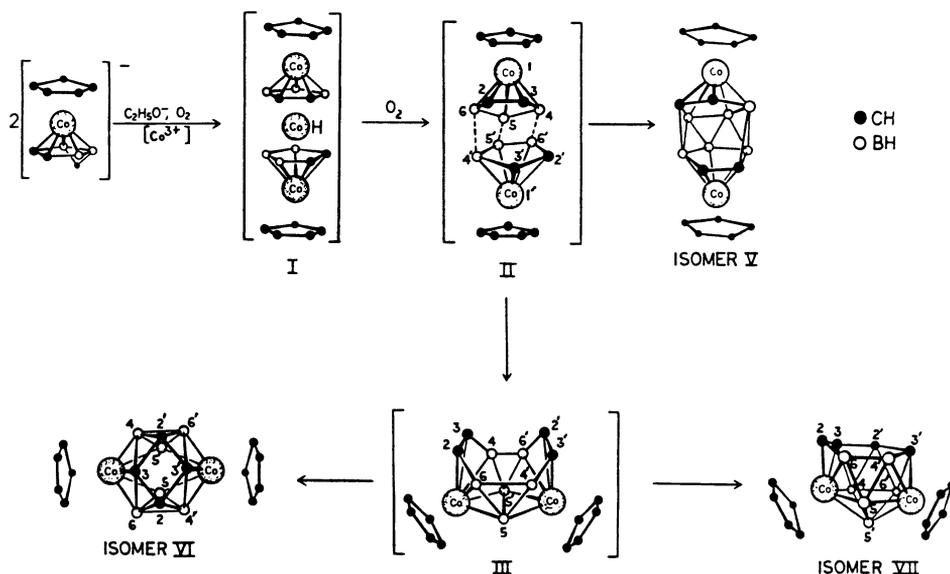


Fig. 15. Oxidative fusion of $(\eta^5\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_3\text{H}_6^-$ ion to form three isomers of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_4\text{B}_6\text{H}_{10}$. The structures of V and VII are crystallographically established.

3. The fusion of $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{FeH}_2$ in the absence of air is solvent-dependent, occurring in moderately strongly basic ethers such as THF, but only slowly, if at all, in weak bases such as $(\text{C}_2\text{H}_5)_2\text{O}$.

4. In THF in the absence of air, red diamagnetic $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2$ gradually (hours) converts to a purple paramagnetic species, which on exposure to air rapidly becomes green and finally forms colorless $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$. (The cobalt(III) counterpart, in contrast, exhibits no such sequence of color changes, instead converting directly to $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ when exposed to air).

5. The extremely air-sensitive purple species, which is an intermediate in at least one fusion pathway, turns out unexpectedly to have two iron atoms, and is formulated as $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{Fe}^{\text{III}}_2\text{H}_2 \cdot \text{L}_2$, where L_2 is $2(\text{CH}_2)_4\text{O}$ or $(\text{CH}_3\text{O})_2\text{C}_2\text{H}_4$ depending on the solvent employed. The structure revealed by an X-ray diffraction study (Fig. 16) contains one iron atom in a central (commo) location similar to that in the original $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2$ complex, while the other iron is attached via two normal Fe-B bonds, two long Fe-B links, and an Fe-Fe interaction (2.42 Å). In addition, the "outer" iron is coordinated to solvent, as shown.

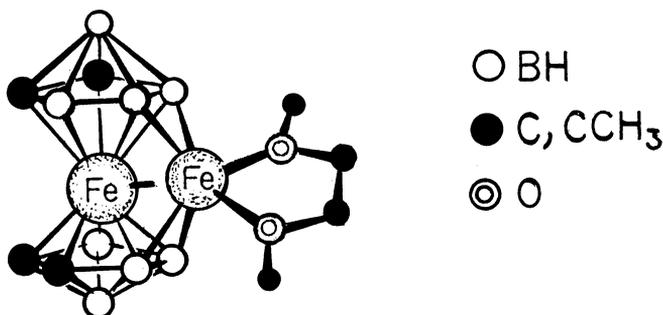


Fig. 16. Heavy-atom structure of $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{Fe}_2^{\text{III}}\text{H}_2 \cdot \text{L}_2$ ($\text{L} = (\text{CH}_3\text{O})_2\text{C}_2\text{H}_4$) established from X-ray data.

Mössbauer spectra indicate that both iron atoms are Fe(III), consistent with the observed paramagnetism. At this writing, the origin of the second iron atom has not been established but there are indications that the $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2$ samples contain traces of solvated Fe^{3+} , which initiate and

catalyze the fusion process via release of additional Fe^{3+} ions. Accordingly, catalytic quantities of FeCl_3 in THF rapidly convert $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{Fe}^{\text{I}}\text{H}_2$ to purple $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{Fe}_2^{\text{III}}\text{H}_2$ but the reaction ceases at this stage; however, addition of stoichiometric amounts of FeCl_3 , or of O_2 , cause virtually instantaneous conversion to colorless $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$.

The observed structure of the diiron complex (Fig. 16) bears some similarity to that of $(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2$ (Fig. 17a) which was obtained by insertion of a $\text{Co}(\text{C}_5\text{H}_5)$ unit into $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2$ (44); in this case, however, the "wedging" site is occupied by a BH unit which has been displaced by cobalt. The proposed structure of $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeSn}$ and its germanium analogue (45) (Fig. 17b) are also of this class.

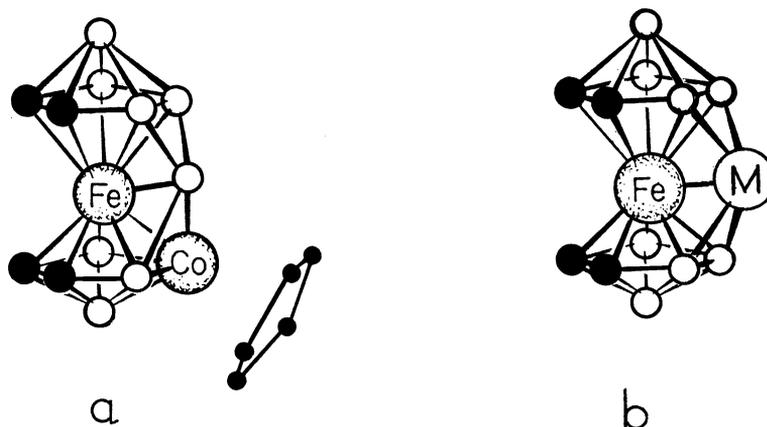


Fig. 17. Established structure of $(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ (a) and proposed structure of $\text{M}_{\text{IV}}\text{Fe}(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ ($\text{M}_{\text{IV}} = \text{Ge}$ or Sn) (b).

6. Another recent clue to the fusion mechanism (or to a fusion mechanism, as there may be more than one) is given by the X-ray-determined structure (46) of $[\eta^5\text{-C}_5(\text{CH}_3)_5]_2\text{Co}_3(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_7$ (Fig. 18), in which the two CoC_2B_4 ligands, coordinated to a common cobalt atom, are also joined by a direct B-B link. While this particular species is air-stable and does not undergo further fusion, this previously unknown type of interligand B-B coupling may represent an early stage in the fusion process; in this particular molecule it is possible that the bulky $\text{C}_5(\text{CH}_3)_5$ ligands prevent further steps from taking place.

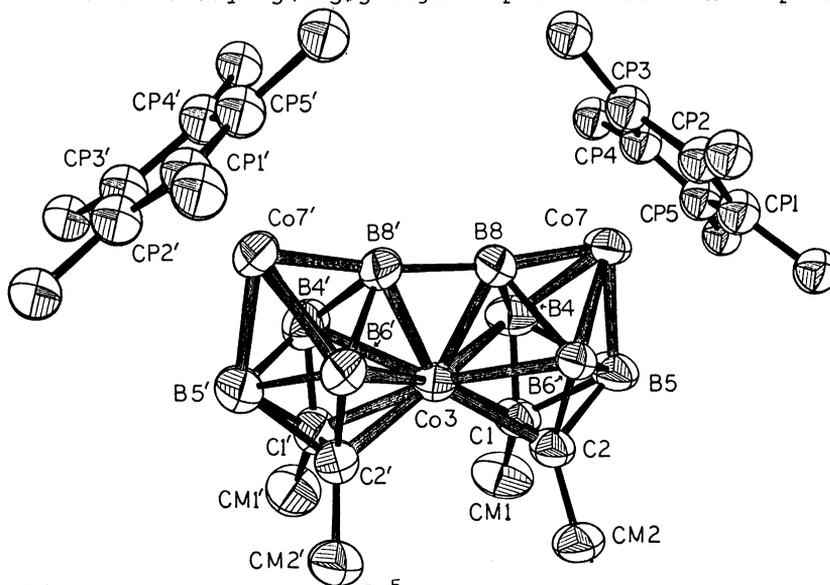


Fig. 18. Structure of $[\eta^5\text{-C}_5(\text{CH}_3)_5]_2\text{Co}_3(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_7$. All boron atoms except B(8) and B(8') have terminal hydrogen atoms; another hydrogen is believed to be located near the central cobalt but was not found in the X-ray study.

ORGANIC REACTIONS ON METAL-BORON CLUSTERS

The fact that transition metals can promote facile, low-energy fusion of two carborane cages suggests that perhaps carborane and hydrocarbon systems can be fused or linked via metal sandwich intermediates. More generally, the concept of employing metal sites in metallaboranes and metallacarboranes as loci for low-energy transformations of organic substrates has many intriguing possibilities. Indeed, Hawthorne and others (47) have reported effective metallacarborane catalysts for the hydrogenation, hydrosilylation, and isomerization of alkenes, and Sneddon (48) has described metal-catalyzed additions of alkynes to boranes, which no doubt proceed via complexes of some type. In our laboratory, we have begun to explore the chemistry of metallacarborane-arene sandwich compounds and also to examine the catalytic properties of metallaboranes derived from small borane anions. A brief summary of some recent observations concludes this paper.

Reaction of $R_2C_2B_4H_5^-$ ions with $FeCl_2$ and $C_8H_8^{2-}$ ion.

Addition of a THF solution of $Na^+(CH_3)_2C_2B_4H_5^-$ or its C,C'-diethyl analogue to $Na_2C_8H_8$ and $FeCl_2$ in THF forms, in good yield, orange, air-stable, diamagnetic $(R_2C_2B_4H_4)Fe(\eta^6-C_8H_{10})$ where $R = CH_3$ or C_2H_5 (49). Formulation of these products as complexes of C_8H_{10} rather than $C_8H_8^{2-}$ indicates that two protons are acquired from the carborane anion reagent (the only plausible source) and suggests that the hydrocarbon ligand must be η^6 -cyclooctatriene. This has been confirmed by an X-ray structure determination on the dimethyl complex (Fig. 19) and by the Mössbauer spectrum (50), which is consistent with the presence of Fe(II). The mechanism of formation of this species and the chemical properties of the cyclooctatrienyl ligand are under study, as are related reactions involving other metals and other cyclic hydrocarbon systems.

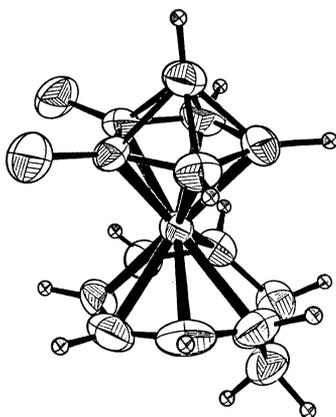


Fig. 19. Structure of $[(CH_3)_2C_2B_4H_4]Fe(\eta^6-C_8H_{10})$

Hydrogenation of alkenes and alkynes catalyzed by metal-borane complexes derived from $B_5H_8^-$ and $B_3H_8^-$ ions.

Reactions of the extremely reactive $B_5H_8^-$ ion with transition metal halides in ethereal solvents in the presence of $C_5H_5^-$ or $C_5(CH_3)_5^-$ ions have produced a variety of cobalt, iron, and nickel metallaboranes having 1 to 4 metal atoms per cage, a number of which are structurally novel (4, 5, 18, 51). Since the hydrocarbon ligands in these complexes are firmly bound to the metals and sterically block incoming substrate molecules, they are not per se good prospects as active catalysts; however, the cages themselves in many cases have several attractive features: high metal content, metals in adjacent positions in the framework, and reactive metal-hydrogen-boron bridging groups. Hence we have examined reactions of metal ions with $B_5H_8^-$ and with $B_3H_8^-$ in the absence of "capping" ligands such as $C_5H_5^-$, in the hope of forming metallaborane complexes bearing coordinatively unsaturated metal atoms which would be catalytically active (52). We found that these borane substrates interact with metal salts including $CoCl_2$, $NiBr_2$, $RuCl_3$, and $RhCl_3$ to form deeply colored solutions which, in varying degrees, catalyze

the homogeneous hydrogenation of alkenes and alkynes under mild conditions (23°C and 1-3 atm of H₂). Table I summarizes some typical data (52). Not surprisingly, the extreme reactivity of these complexes creates major problems in isolating and characterizing individual species, which are mostly ionic, nonvolatile, and tend not to survive column chromatography even under oxygen-free conditions.

TABLE I. CATALYST SYSTEMS DERIVED FROM Na⁺B₅H₈⁻ AND METAL HALIDES

Metal : Na ⁺ B ₅ H ₈ ⁻ : Substrate = 1:2:20 in THF at 23°C; P _{H₂} = 2.5 atm				
Metal Halide	Substrate	Duration of Experiment	% Conversion of Substrate	Products
CoCl ₂	MeC≡CMe	6 days	100	$\begin{matrix} \text{Me} & & \text{Me} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{matrix}$, MeCH ₂ CH ₂ Me (1:1.3)
"	MeC≡CMe (dry)	8 days	76	$\begin{matrix} \text{Me} & & \text{Me} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{matrix}$
NiBr ₂	MeC≡CMe	7 days	100	$\begin{matrix} \text{Me} & & \text{Me} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{matrix}$, MeCH ₂ CH ₂ Me (1:1)
"	"	41 hr	{ 25 (THF) 45 (dry) }	" "
"	 C≡CH	21.5 hr	100	 CH=CH ₂
"	H ₂ C=CH-CH ₃	12 days	100	CH ₃ CH ₂ CH ₃
RuCl ₃	MeC≡CMe	21.5 hr	100	MeCH ₂ CH ₂ Me
"	EtC≡CEt	91.5 hr	60	EtCH=CHEt
"	 (dry)	96 hr	29	
RhCl ₃	MeC≡CMe	{ 10 min 5 min }	80 64	$\begin{matrix} \text{Me} & & \text{Me} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{matrix}$, MeCH ₂ CH ₂ Me (2.3/3.3 : 1)
"	" (dry)	40 hr	98	MeCH ₂ CH ₂ Me

If the catalytic species in these metallaborane systems can be identified, they are likely to be different in function, and certainly in structure, from the known metallacarborane hydride catalysts of ruthenium and rhodium (47) in which the role of the carborane framework may be essentially passive. A particularly intriguing possibility is that the borane frameworks in the small metallaborane complexes may be directly involved in the catalytic mechanism, thereby constituting a new class of catalysts. Quite possibly such systems will be capable of simultaneously promoting two or more reactions at different sites on a given organic substrate (or on different substrates). Metal-boron "hybrid" cluster catalysts modeled after such known species as (η⁵-C₅R₅)₂Co₂B₄H₆, (η⁵-C₅R₅)₃Co₃B₄H₄ (R = H, CH₃), (η⁵-C₅H₅)₃Co₃B₃H₅, (η⁵-C₅H₅)₄Co₄B₄H₄, and (η⁵-C₅H₅)₄Ni₄B₄H₄ (4, 5, 18, 51), but with coordinatively unsaturated metal and/or boron centers, are prime candidates for this role. Indeed, clusters of this type may be involved in the catalytic systems summarized in Table I.

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