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Transition-Metal-Promoted Oxidative Fusion with Carborane and Borane Anions. Synthesis of C_4B_n (n = 8–11) Carborane Systems in the Presence of $B_5H_8^-$ and $B_3H_8^-$ Ions

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Simultaneous treatment of $CoCl_2$ or $FeCl_2$ with the 2,3-$(CH_3)_2C_2B_4H_5^-$ and $B_5H_8^-$ ions in THF at room temperature gave mixed-ligand metallacarborane complexes. With $CoCl_2$ the major isolable product was $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_7H_7]$, a yellow air-stable crystalline solid. The reaction with $FeCl_2$ gave several products incuding the known carborane $(CH_3)_4C_4B_8H_8$ and the new species $[(CH_3)_2C_2B_4H_4]FeH_2[(CH_3)_2C_2B_5H_5]$ and $(CH_3)_4C_4B_{11}H_{11}$; the last of these is believed to form by oxidation of an unstable precursor complex, $[(CH_3)_2C_2B_4H_4]FeH_2[(CH_3)_2C_2B_7H_7]$, which was observed mass spectroscopically. The red $[(CH_3)_2C_2B_4H_4]FeH_2[(CH_3)_2C_2B_5H_5]$ complex is moderately air stable but slowly reacted with O_2 to form $(CH_3)_4C_4B_9H_{11}$. From electron-counting arguments the new carboranes $(CH_3)_4C_4B_{11}H_{11}$ and $(CH_3)_4C_4B_9H_{11}$ are proposed to have 15-vertex nido and 13-vertex arachno cage geometries, respectively, but linked-cage structures are not ruled out. In the iron–borane–carborane reaction the order of addition of reagents is important; thus, treatment of $FeCl_2$ initially with $B_5H_8^-$ followed later by $(CH_3)_2C_2B_4H_5^-$ gave species identified mass spectroscopically as $[(CH_3)_2C_2B_5H_5]_2FeH_2$ and $(CH_3)_4C_4B_{10}H_{10}$, neither of which was observed in the previously described "simultaneous" reaction. Surprisingly, the reaction of $FeCl_2$, $(CH_3)_2C_2B_4H_5^-$, and $B_3H_8^-$ gave products and yields almost identical with those obtained in the corresponding $FeCl_2$–$(CH_3)_2C_2B_4H_5^-$–$B_5H_8^-$ reaction. However, the $FeCl_2$–$(CH_3)_2C_2B_4H_5^-$–BH_4^- reaction gave a virtually quantitative yield of the known complex $[(CH_3)_2C_2B_4H_4]_2FeH_2$. The latter complex was found to undergo oxidation to the carborane $(CH_3)_4C_4B_8H_8$ even in the absence of O_2 or other external oxidants, with metallic iron formed as a byproduct. A sequence of events is proposed to account for the observations in the iron–borane–carborane reactions.

Transition-metal-facilitated dimerizations, cyclizations, and polymerizations of hydrocarbons are well-known and constitute a growing area of interest in organic and organometallic synthetic chemistry.[1] One might anticipate that roughly analogous processes should be possible in transition-metal–polyhedral borane systems, and indeed, the "oxidative fusion" reactions[2] that are exhibited by certain types of metal–carborane complexes provide real cases in point. In oxidative fusion, two open-cage (e.g., pyramidal) ligands are face coordinated to a transition-metal atom which is subsequently eliminated, the ligands merging face to face to form a single large polyhedral system (Figure 1). Thus far, the most clearly defined examples involve the stable, isolable bis(carboranyl) complexes[3,4] $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2Co^{III}H$ and $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2Fe^{II}H_2$; each of these undergoes nearly quantitative air oxidation *at room temperature*, forming $(CH_3)_4C_4B_8H_8$, a 12-vertex distorted icosahedron[5] which is formally a $(2n + 4)$-electron nido[6] system. These complexes and the carborane product have been fully characterized by spectroscopic and X-ray methods. Other carborane ligands, e.g., $C_2B_4H_7^-$ and $CH_3C_2B_4H_6^-$, can also be oxidatively fused,[7] and other transition-metal ions such as Ni^{2+} can be employed, but in these cases the metal sandwich intermediates have not been isolated.

Oxidative fusion has also been observed[8] with small metallacarboranes such as $(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$, which undergoes dimerization to several $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$ isomers belonging to different structural classes; thus far, two of these fused complexes have been crystallographically characterized.[8,9] As part of a long-range study of the scope of the oxidative fusion process, we have attempted to prepare mixed-ligand borane–carborane metal complexes, whose ligands might then combine to produce large carboranes, e.g., eq 1.

$$(CH_3)_2C_2B_4H_5^- + B_5H_8^- + FeCl_2 \xrightarrow{?}$$

$$[(CH_3)_2C_2B_4H_4]FeH_2[B_5H_7] + 2Cl^- \xrightarrow[{[O]}]{?} (CH_3)_2C_2B_9H_{11} \quad (1)$$

If successful, reactions of this type could open the way to low-energy designed syntheses of a variety of large cage systems, perhaps including polyhedra larger than any presently known.

In the study reported herein, our attempts at mixed-ligand complex formation and fusion led not to the expected products but to new four-carbon carboranes which we believe to be the first examples of supraicosahedral carboranes without metal atoms.

Results and Discussion

Reaction of $B_5H_8^-$, $(CH_3)_2C_2B_4H_5^-$, and $CoCl_2$. Previous work in our laboratory had established the following reactions (2)–(4).[4,10,11] In the present investigation, we attempted to

$$(CH_3)_2C_2B_4H_5^- + Co^{2+} \xrightarrow{THF} \underset{\substack{\text{red, air sensitive}\\ [\text{oxidizes to } (CH_3)_4C_4B_8H_8]}}{[(CH_3)_2C_2B_4H_4]_2Co^{III}H} \quad (2)$$

$$(CH_3)_2C_2B_4H_5^- + Co^{2+} + C_5H_5^- \xrightarrow{THF} \underset{\text{red, air stable}}{1,2,3\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4} \quad (3)$$

$$B_5H_8^- + Co^{2+} + C_5H_5^- \xrightarrow{THF} \xrightarrow{O_2} \underset{\text{red, air stable}}{2\text{-}(\eta^5\text{-}C_5H_5)Co^{III}B_4H_8} \text{ (main product)} + \text{many other cobaltaboranes} \quad (4)$$

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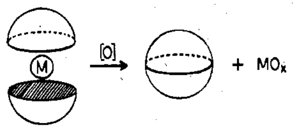

Figure 1. Schematic diagram of the oxidative fusion process, where hemispheres represent anionic carborane ligands and M is a transition-metal cation.

Table I. ^{11}B FT NMR Data (32.1 MHz)[a]

compd	δ[b] (J, Hz)	rel areas
$[(CH_3)_2C_2B_4H_4]CoH$-$[(CH_3)_2C_2B_7H_7]$ (I)	12.2 (141), 0.0 (142), −7.7 (150),[c] −19.3 (161), −26.4 (171)	3:3:1:2:2
$[(CH_3)_2C_2B_4H_4]FeH_2$-$[(CH_3)_2C_2B_5H_5]$ (II)	26.3 (176), 2.9 (~170),[c] −2.7 (157), −14.5 (156)[d]	1:1:4:3
$(CH_3)_4C_4B_{11}H_{11}$ (III)[e,f] (C_6D_6)	16.9, 10.8, 2.9, −2.6, −8.7, −20.9, −23.6, −26.6, −30.0	1:3:3:5:3 1:1:1:1[g]
$(CH_3)_4C_4B_{11}H_{11}$ (IIIA) (rearranged isomer, in C_6D_6)	8.0 (170), 1.65 (160), −3.6 (174), −32.2 (155)[h]	1:1:8:1
$(CH_3)_4C_4B_9H_{11}$ (V)[i]	1.3, −3.6, −5.4, −15.2	2:3:3:1

[a] All spectra were obtained in $CDCl_3$ solution except where otherwise indicated. In each case, both undecoupled and ^1H-decoupled spectra were obtained; in the decoupled spectra all H–B doublets collapse to singlets. [b] Chemical shifts are relative to $BF_3{\cdot}O(C_2H_5)_2$ with a positive sign indicating deshielding. [c] Estimated from overlapped peaks. [d] Asymmetric peak with shoulder on upfield side. [e] Chemical shifts are given for the proton-decoupled spectrum. [f] Probable mixture of isomers. [g] Approximate areas. [h] Small peaks at δ +36.6, −9.0, and −13.6, also observed, were assigned to minor side products of the isomerization. [i] Proton-decoupled spectrum. Resonances in the undecoupled spectrum were heavily overlapped and couplings were not measurable.

coordinate $(CH_3)_2C_2B_4H_4^{2-}$ and a borane anion ligand to a common cobalt ion and thereby form a mixed-ligand borane–carborane complex, via the reaction of $CoCl_2$ with $Na^+B_5H_8^-$ and $Na^+(CH_3)_2C_2B_4H_5^-$ simultaneously. However, the major isolable product was a mixed-ligand bis(*carboranyl*) species, $[2,3\text{-}(CH_3)_2C_2B_4H_4]CoH[2,3\text{-}(CH_3)_2C_2B_7H_7]$, I, obtained in 21% yield as a yellow air-stable solid (mp 79°) and purified by sublimation at 30 °C onto a cold finger. The mass spectrum of this complex exhibits a cutoff at m/e 300 corresponding to the parent ion, and the profile of intensities in the parent region is consistent with the formula given above; a high-resolution mass measurement (see the Experimental Section) confirmed the elemental composition.

The 32.1-MHz ^{11}B FT NMR spectrum of I (Table I) is not particularly informative, but the range of chemical shifts is compatible with the ^{11}B spectra of the related cobaltacarborane complexes $(6,9\text{-}C_2B_7H_9)_2Co^-$ (formerly numbered 6,7)[12] and $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2CoH$.[4] The 100-MHz ^1H FT NMR spectrum (Table II) contains two methyl peaks of equal area, indicating that each of the carborane ligands, viewed separately, has equivalent C–CH_3 groups and hence a local mirror plane bisecting the framework C–C bond. From the mild conditions of synthesis it can be assumed that the cage carbon atoms in each ligand remain adjacent and are in the metal-bonded face as shown in Figure 2. Figure 2 as drawn suggests the presence of an *overall* molecular mirror plane, but this cannot be confirmed from the NMR data since magnetic interaction between the carborane ligands may be so weak that different rotamers cannot be distinguished.[13] The "extra" proton bound to cobalt exhibits a broad peak at δ −12.3 [relative to $(CH_3)_4Si$] in the region typical of metal–hydrogen resonances.

Table II. ^1H FT NMR Data (100 MHz)

compd	δ[a] (rel area)	assignt
I ($CDCl_3$)	2.35 (3), 2.23 (3)	CH_3
	−12.3[b] ($w_{1/2}$ = 45 Hz)	Co–H
II ($CDCl_3$)	2.43 (3), 2.26 (3)	CH_3
	−12.4[b] ($w_{1/2}$ = 75 Hz)	Fe–H
III (C_6D_6)[c]	1.60 (8), 1.43 (5), 1.17 (1), −0.05 (1)	CH_3
IIIA (rearranged isomer in C_6D_6)	2.14 (1), 1.73 (1), 1.38 (1), 1.27 (1)	CH_3
V ($CDCl_3$)	2.30 (1), 1.97 (1)	CH_3

[a] Chemical shifts relative to $(CH_3)_4Si$ with positive sign indicating deshielding. [b] Broad peak, area not measurable. [c] Probable mixture of isomers; areas given are approximate.

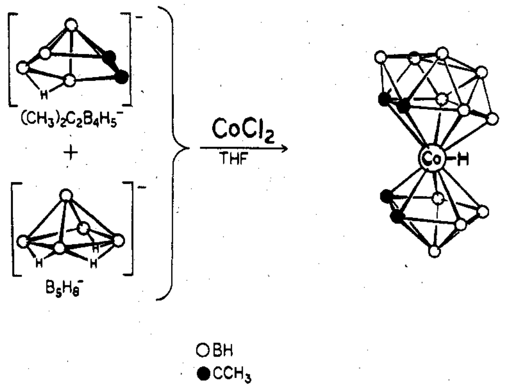

Figure 2. Formation of $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_7H_7]$ (I) with proposed structure of I indicated.

The proposed $6,9\text{-}(CH_3)_2C_2B_7H_7^{2-}$ ligand in I is a *C,C′*-dimethyl derivative of the $6,9\text{-}C_2B_7H_9^{2-}$ ("dicarbazapide") ligand found in several previously reported metallacarboranes,[12] and the $2,3\text{-}(CH_3)_2C_2B_4H_4^{2-}$ moiety in I occurs in numerous complexes also.[3,4,10,14] However, mixed-ligand complexes involving small carborane ligands have not previously been reported. Since I appeared unreactive toward oxygen and failed to undergo oxidative fusion (in contrast to $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2CoH$),[4] we turned our attention to the $B_5H_8^-$–$(CH_3)_2C_2B_4H_5^-$–$FeCl_2$ reaction system.

Reaction of $B_5H_8^-$, $(CH_3)_2C_2B_4H_5^-$, and $FeCl_2$ (Simultaneous). This system was found to be highly sensitive to experimental details, particularly the order of addition of reagents.[26] Treatment of an equimolar THF solution of the $B_5H_8^-$ and $(CH_3)_2C_2B_4H_5^-$ ions with $FeCl_2$ at room temperature generated H_2, B_2H_6, and the volatile complex $BH_3{\cdot}THF$, the solution turning dark purple. Removal of the solvent and workup of the residue in carbon tetrachloride (primarily to liberate monomeric species from the resinlike matrix) gave several products which were sublimed together onto a cold finger and subsequently separated by high-pressure liquid chromatography (HPLC). In addition to the known[3] carborane $(CH_3)_4C_4B_8H_8$ (64% yield on the basis of starting carborane), the major isolated products were red $[(CH_3)_2C_2B_4H_4]FeH_2[(CH_3)_2C_2B_5H_5]$ (II) (mp 71 °C, 11% yield) and colorless $(CH_3)_4C_4B_{11}H_{11}$ (III) (mp 68 °C, obtained in 2.3% yield). In addition, mass spectra of the sublimed product mixture re-

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

(12) George, T. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1969**, *91*, 5475.

(13) This is evidently the case in the closely related species $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$ in which the ligands are mutually rotated[25] by 90°, yet the four methyl groups are equivalent in the proton NMR spectrum.[3]

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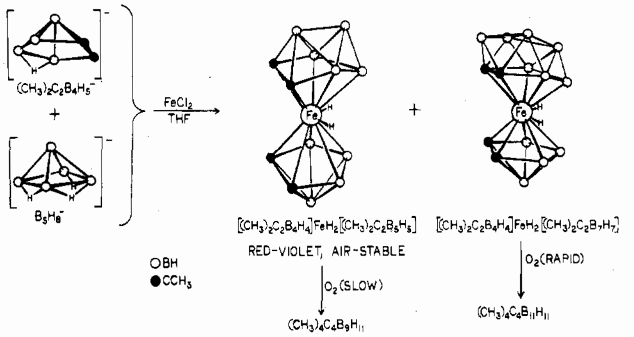

Figure 3. Formation of mixed-ligand ferracarboranes and conversion to tetracarbon carboranes.

vealed the presence of $[(CH_3)_2C_2B_4H_4]FeH_2[(CH_3)_2C_2B_7H_7]$ (IV), the probable precursor of III via oxidative fusion; complex IV proved to be extremely air sensitive (in curious contrast to its cobalt analogue I, described above) and was not isolated.

Very small amounts of white crystalline carboranes, identified as $[(CH_3)_2C_2B_8H_8]_2$ and $[(CH_3)_4C_4B_8H_7]_2$ from their mass spectra, were recovered in the HPLC separation of the products but could not be further characterized. Spectroscopic data on III, however, were obtained, as described in a later section.

Figure 3 depicts the proposed structures of II and IV. The mass spectrum of II contains a cutoff at *m/e* 274 corresponding to the parent ion (^{56}Fe isotope), as well as an intense peak group having a local cutoff at *m/e* 262, indicating facile loss of BH in the mass spectrometer to form the known[3] complex $[(CH_3)_2C_2B_4H_4]_2FeH_2$. The proton-decoupled ^{11}B NMR spectrum (Table I) contains four identifiable resonances whose range of chemical shifts is consistent with the presence of $(CH_3)_2C_2B_5H_5^{2-}$ and 2,3-$(CH_3)_2C_2B_4H_4^{2-}$ ligands[15] and with the structure postulated in Figure 3, but which cannot be unequivocally assigned. The ^{1}H spectrum (Table II) contains only two methyl peaks, demonstrating that each of the ligands per se contains equivalent C–CH_3 units related by a mirror plane; as in the case of the cobalt species I, discussed above, the NMR data do not establish the orientation of the ligands relative to each other. Also present in the ^{1}H spectrum is a broad resonance at δ −12.4 arising from the FeH_2 protons.

The formal $(CH_3)_2C_2B_5H_5^{2-}$ ligand in II has not previously been observed, the only other examples of C_2B_5M-type metallacarboranes being 3,1,7-$(\eta^5\text{-}C_5H_5)CoC_2B_5H_7$[17] and 3,1,7-$(CO)_3FeC_2B_5H_7$,[18] in both of which the cage carbon atoms have been assigned nonadjacent positions in the cage. From electron-counting considerations,[6] $(CH_3)_2C_2B_5H_5^{2-}$ is expected to have a nido 7-vertex structure so that the metal atom completes a closo 8-vertex polyhedron, as shown in Figure 3.

Reaction of $B_3H_8^-$, 2,3-$(CH_3)_2C_2B_4H_5^-$, and $FeCl_2$. When the preceding experiment was repeated with $(CH_3)_4N^+B_3H_8^-$ in place of $Na^+B_5H_8^-$, *the isolated products were again II, III, and $(CH_3)_4C_4B_8H_8$ and in nearly identical yields.* These findings indicate that both $B_3H_8^-$ and $B_5H_8^-$ are capable of attacking the $(CH_3)_2C_2B_4H_5^-$ group in the presence of $FeCl_2$[19] with net addition of three BH units to generate the unstable $[(CH_3)_2C_2B_4H_4]FeH_2[(CH_3)_2C_2B_7H_7]$ complex (IV), which in turn degrades to form the stable, isolable species $[(CH_3)_2C_2B_4H_4]FeH_2[(CH_3)_2C_2B_5H_5]$ (II). In principle, the replacement of $B_5H_8^-$ by $B_3H_8^-$ as a borane reagent is highly advantageous (if the ultimate products are the same) because of the accessibility and ease of handling of $B_3H_8^-$ salts, which are air stable and can be easily prepared[20] from $NaBH_4$ or obtained commercially. The present work is evidently the first instance in which $B_3H_8^-$ has been employed as a source of boron in polyhedral metallaborane or metallacarborane syntheses, although we have recently reported the multistep, one-pot preparation of the nido carborane 2,3-$(CH_3)_2C_2B_4H_6$ from $(C_2H_5)_3N^+B_3H_8^-$ via B_5H_9 generated in situ.[21] Many metal chelate (nonpolyhedral) complexes of $B_3H_8^-$ are, of course, known.[22]

Reaction of BH_4^-, 2,3-$(CH_3)_2C_2B_4H_5^-$, and $FeCl_2$. As an extension of the work involving $B_3H_8^-$ and $B_5H_8^-$, $FeCl_2$ was treated with a THF solution containing a mixture of BH_4^- and $(CH_3)_2C_2B_4H_5^-$ ions. The sole carborane product was the known dark red complex[3] $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$, obtained in 97% yield. Clearly no incorporation of boron from BH_4^- took place, but the nearly quantitative yield of ferracarborane was significantly higher than we have previously obtained[3] in the absence of BH_4^- (~80–90%). The probable explanation is that trace oxidants present in the THF, which survive drying and distillation and reduce the yield of the ferracarborane complex, are removed by the BH_4^- (which does not attack the ferracarborane itself). However, the role of BH_4^- in this reaction was not further explored.

Reaction of $B_5H_8^-$ and $FeCl_2$ Followed by $(CH_3)_2C_2B_4H_5^-$. The preceding experiments did not establish whether the observed metallacarborane products formed via attack of the carborane ligand on a ferraborane species produced initially, attack of $B_5H_8^-$ or $B_3H_8^-$ on a metallcarborane intermediate, or both. In order to investigate the actual sequence, we allowed $FeCl_2$ and a 2:1 excess of $Na^+B_5H_8^-$ in THF to react, forming a brown nonvolatile complex which was not isolated. After treatment of this dark solution with excess $Na^+(CH_3)_2C_2B_4H_5^-$ followed by workup with CCl_4 as described above, the sublimable products were found on mass spectroscopic analysis to consist of a complex mixture of species including II, $(CH_3)_4C_4B_8H_8$, and $[(CH_3)_2C_2B_5H_5]_2FeH_2$ (V), a product which was not observed to form in the "simultaneous" $B_5H_8^-$–$(CH_3)_2C_2B_4H_5^-$–$FeCl_2$ reaction described above. Complex V unfortunately did not survive column chromatography on silica, even when conducted in an oxygen- and water-free chamber, and was not isolated. The observation that V forms in this reaction but is absent when both $B_5H_8^-$ and $(CH_3)_2C_2B_4H_5^-$ are present initially suggests that $FeCl_2$ reacts more rapidly with the carborane anion than with $B_5H_8^-$; this question will be discussed further in the concluding section.

Mass spectra of the product mixture following exposure to air for 16 h revealed the presence of a new carborane species, $(CH_3)_4C_4B_{10}H_{10}$, whose formation can be attributed to oxidative fusion of the $(CH_3)_2C_2B_5H_5^{2-}$ ligands in V. Also present were $(CH_3)_4C_4B_8H_8$ and traces of a compound assigned as $[(CH_3)_2C_2B_8H_8]_2$.

Reaction of $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$ with B_5H_9. From earlier work it was known that the $(CH_3)_2C_2B_4H_5^-$ ion and $FeCl_2$ rapidly form the red complex $[(CH_3)_2C_2B_4H_4]_2FeH_2$ in nearly quantitative yield. This compound was detected only in traces in the present study, implying that it undergoes further attack by borane reagents during the course of the

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(15) Observed ^{11}B shifts for $(CH_3)_2C_2B_4H_4^{2-}$ complexes range from +10.8 to −18.3[3,4,10] and for complexes of $C_2B_7H_9^{2-}$ range from +21.0 to −25.2.[12,16]

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(19) Control experiments demonstrate that the $(CH_3)_2C_2B_4H_5^-$ and $B_5H_8^-$ ions do not interact significantly with each other in THF at room temperature, in the absence of a transition metal reagent.

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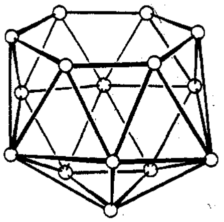

Figure 4. Possible geometry of a 15-vertex nido cage corresponding to $(CH_3)_4C_4B_{11}H_{11}$, derived from a T_d closo 16-vertex polyhedron[23] by removal of a high-coordinate vertex.

reaction. As a direct test, a sample of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ was treated with an equimolar quantity of B_5H_9 in THF at room temperature, giving as sublimable products only the mixed-ligand complex II and the carboranes $(CH_3)_4C_4B_{11}H_{11}$ (III) and $(CH_3)_4C_4B_8H_8$; no starting metallacarborane was recovered.

Formation of C_4B_n Carboranes by Oxidative Fusion. The reactions described above produced several species lacking metal atoms and having the formulas $(CH_3)_4C_4B_nH_m$, where $n - 2 \le m \le n + 2$ and n has values from 8 to 16. Of these, the known compound $(CH_3)_4C_4B_8H_8$ was obtained in largest yield (up to 64%); since this carborane is known to form by fusion of two $[(CH_3)_2C_2B_4H_4]^{2-}$ ligands in transition-metal complexes,[2-4] it can be assumed that the new C_4B_n species originate in similar fashion, either by fusion to produce a single large cage or by coupling to generate bis(carboranes) in which two discrete polyhedra are linked by single B–B bonds. Where $m < n$ (as in $[(CH_3)_4C_4B_8H_7]_2$, mentioned above), a linked-cage structure is almost certain, but when $m \ge n$, a single polyhedral system is more likely; this conclusion is strengthened by the crystallographic characterizations of $(CH_3)_4C_4B_8H_8$[5] and the $Co_2C_4B_6$ fusion products[8,9] mentioned earlier. The parent–daughter relationship between the bis(carboranyl)metal complexes and the observed tetracarbon carborane products is further supported by experimental evidence in the case of the C_4B_{11} and C_4B_9 systems, as follows.

$(CH_3)_4C_4B_{11}H_{11}$. The white, air-stable, surprisingly volatile crystalline solid (III) was characterized from its unit- and high-resolution mass spectra and ^{11}B and ^1H FT NMR spectra (Tables I and II). The mass spectrum exhibits an intense parent grouping (cutoff at *m/e* 240) with no other major peaks, indicating little fragmentation or hydrogen abstraction; this spectrum is compatible with a compact polyhedral species lacking bridge hydrogens. Thus, although III could be formulated as a linked-cage molecule, e.g., $(CH_3)_2C_2B_4H_4$–$H_7B_7C_2(CH_3)_2$ with a B–H–B bridge on each cage (terminal hydrogens being absent on the boron atoms involved in the B–B linkage), such a structure appears inconsistent with the mass spectrum. The NMR spectra are complex, despite the mass spectroscopic purity of the sublimed product, and suggest that more than one isomer is present in solution. However, at 110 °C in C_6D_6 solution the original species, III, rearranged to a new isomer (IIIA) whose ^{11}B NMR spectrum was considerably simpler than that of III (Table I); the mass spectrum of the new isomer was essentially unchanged from that of III.

All efforts at obtaining crystals of III or IIIA suitable for X-ray analysis have thus far been unsuccessful, but if we are in fact dealing with a C_4B_{11} cage as suggested above, electron-counting arguments[6] predict that it should be of the nido class, and specifically should resemble a 16-vertex closo polyhedron with one missing vertex. No known examples of either 16-vertex closo or 15-vertex nido cages have been structurally established (or even postulated prior to the present study), but Brown and Lipscomb[23] have predicted a unique stable geometry for *closo*-$B_{16}H_{16}^{2-}$, consisting of a tetracapped tetratruncated tetrahedron of T_d symmetry, i.e., a tetrahedron whose four corners have been truncated, each of whose four hexagonal faces is capped by an additional vertex. Removal of one of the high-coordinate vertices yields an open basket (Figure 4) which may represent the gross geometry of the C_4B_{11} species; there are, of course, many possible ways of arranging the four carbons on this framework consistent with the NMR spectra (i.e., unsymmetrical), and a unique assignment is not possible at present.

Evidence that III is generated from an unstable precursor $[(CH_3)_2C_2B_4H_4]FeH_2[(CH_3)_2C_2B_7H_7]$ (IV) is given by the mass spectrum of the product mixture *prior to workup in air*, which revealed a strong peak grouping with a cutoff at *m/e* 298 corresponding to IV; on exposure to air this material disappeared, and III, not previously present, was observed.

$(CH_3)_4C_4B_9H_{11}$. The red mixed-ligand $[(CH_3)_2C_2B_4H_4]$-$FeH_2[(CH_3)_2C_2B_5H_5]$ (II), obtained as described earlier, is moderately air stable and does not appreciably degrade as a solid on exposure to air for several hours. In THF solution, however, treatment with a stream of O_2 gas did effect oxidative ligand fusion over an 18-h period, forming a new tetracarbon carborane, $(CH_3)_4C_4B_9H_{11}$ (V). This compound was purified by sublimation and obtained in 42% yield as a colorless crystalline air-stable solid (mp 65 °C). The mass spectrum of V exhibits a strong parent envelope and a more intense grouping corresponding to $(CH_3)_4C_4B_8H_8^+$ (*m/e* 204); the latter species must form by loss of BH_3 from V in the mass spectrometer, since contamination of the product by $(CH_3)_4C_4B_8H_8$ is excluded by the ^{11}B and ^1H NMR spectra. The ^1H FT NMR spectrum reveals only two methyl environments, consistent with the presence of either a C_2 axis or, more probably, a mirror plane. The carborane skeleton is a formal 32-electron ($2n + 6$) system (taking into account the two "extra" hydrogens), on the basis of which we would expect a C_4B_9 arachno cage corresponding to a 15-vertex closo polyhedron with two vacant vertices. Elucidation of the structure clearly will require an X-ray crystallographic study.

Conclusions

Scheme I outlines the observed reactions, proposed intermediates, and probable sequences of product formation in the iron–borane–carborane system. While the tetracarbon carborane products other than $(CH_3)_4C_4B_8H_8$ have not yet been structurally characterized, the origin of these compounds from bis(carborane)iron complexes is clearly indicated. These results, combined with studies previously reported, further demonstrate that metal-promoted fusion and coupling[24] of borane and carborane substrates are a general phenomenon that can be exploited as a useful synthetic tool.

Observations regarding mechanism(s) have been presented elsewhere,[9,25] and it has been noted that fusion of carborane ligands seems to be associated with the presence of hydrogen atoms bound to the metal; significantly, this empirical correlation still holds true on the basis of the work reported here. However, we have established that the presence of an external oxidant (such as O_2) is not an absolute requirement for fusion to take place. Thus, while $[(CH_3)_2C_2B_4H_4]_2FeH_2$ converts rapidly to $(CH_3)_4C_4B_8H_8$ on exposure to air with concomitant formation of an iron oxide–hydroxide mixture, the carborane

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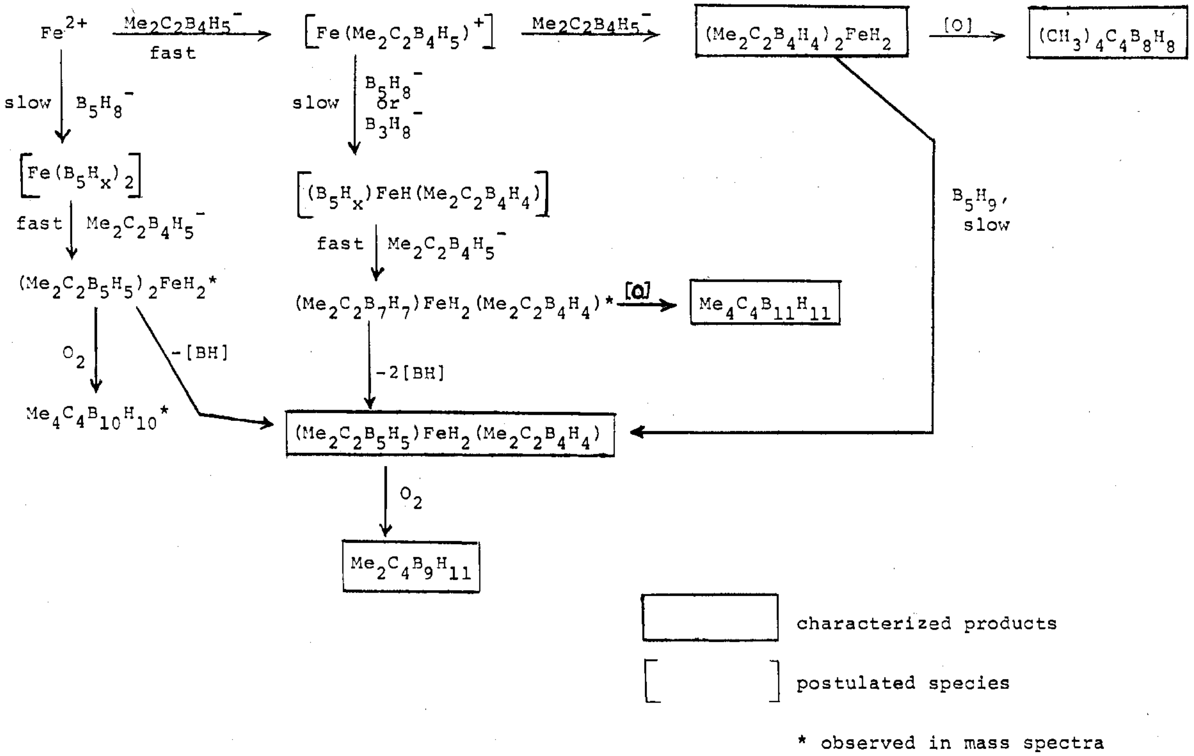
(23) Brown, L. D.; Lipscomb, W. M. *Inorg. Chem.* **1977**, *16*, 2989.

(24) An example of oxidative *coupling* (single-bond linkage of two cages) in a bis(carboranyl)metal complex is the thermal conversion of μ,μ'-$[(CH_3)_2C_2B_4H_5]_2Hg$ to 5,5′-$[(CH_3)_2C_2B_4H_5]_2$ and elemental mercury: Hosemane, N. S.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 2886.

(25) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 263.

(26) The order of addition of reagents is also important in the cobalt system, which under certain conditions (reaction of $CoCl_2$ with $B_5H_8^-$ prior to addition of carborane anion) generates mixed borane–carborane complexes of Co(III): Borodinsky, L.; Grimes, R. N., to be submitted for publication.

Scheme I



forms slowly even when oxygen is rigorously excluded; in this case metallic iron is produced (see the Experimental Section). The net process involves a two-electron transfer from two carborane ligands to Fe^{2+} (eq 5). The reaction is accompanied by color changes corresponding to intermediate iron–carborane complexes (including the known red compound $[(CH_3)_2C_2B_4H_4]_2FeH_2$). It should be emphasized that this reaction is extremely slow in comparison to the very rapid (minutes) conversion of the red complex to $(CH_3)_4C_4B_8H_8$ in the presence of oxidants such as O_2 or $PbBr_2$.[3,14]

$$2Na^+(CH_3)_2C_2B_4H_5^- + FeCl_2 \xrightarrow[25\,°C,\ 24\ h]{THF} \underset{90\%}{(CH_3)_4C_4B_8H_8} + Fe + H_2 + 2NaCl \quad (5)$$

Current investigations in our laboratory are concerned with mixed-ligand complexation and fusion involving large anions including $C_2B_9H_{12}^-$ and will be reported at a later time.

Experimental Section

Materials. 2,3-Dimethyl-2,3-*nido*-dicarbahexaborane(8), 2,3-$(CH_3)_2C_2B_4H_6$, was prepared by the reaction of 2-butyne with pentaborane(9) in the presence of triethylamine as described elsewhere.[21] Pentaborane(9) was obtained from the Callery Chemical Co., Callery, Pa. All other reagents were commercially obtained and used as received. Tetrahydrofuran (THF) was dried over lithium aluminum hydride before use.

Spectra. Boron-11 and proton pulse Fourier transform NMR spectra at 32.1 and 100 MHz, respectively, were recorded on a JEOL PS-100P spectrometer interfaced to a JEOL-Texas Instruments EC-100 computer system. Unit-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer, while high-resolution mass measurements were conducted on an AEL MS-902 double-focusing instrument equipped with an SRI chemical ionization source. All high-resolution spectra were recorded under chemical ionizing conditions in methane or argon–water. Infrared spectra were obtained on a Beckman IR-8 instrument.

Reaction of $B_5H_8^-$, $[(CH_3)_2C_2B_4H_5^-]$, and $CoCl_2$. A solution of $Na^+B_5H_8^-$ and $Na^+[(CH_3)_2C_2B_4H_5]^-$ was prepared by distillation of B_5H_9 (0.25 g, 3.87 mmol) and $(CH_3)_2C_2B_4H_6$ (0.40 g, 3.85 mmol) together onto NaH (0.553 g, 24.0 mmol) in 50 mL of THF. This solution was filtered in vacuo onto anhydrous $CoCl_2$ (0.63 g, 4.85 mmol) in a 250-mL round-bottom flask cooled in dry ice. The solution was allowed to warm to −30 °C and stirred for 4 h at that temperature, during which it turned dark brown and gas was evolved. After cooling of the reaction flask in liquid nitrogen, the noncondensable gas (5.0 mmol) was pumped off. The solvent (THF) was distilled out at −30 °C over a period of 2 h, leaving a dark brown residue. Dry N_2 was introduced into the flask, and a vacuum sublimator was attached to the vessel. On heating of the flask at 70 °C, no material was collected on the cold finger, which was maintained at −78 ° by dry ice.

To the brown residue was added 100 mL of an equal-volume mixture of CH_2Cl_2 and hexane, and the solution was stirred in air for 1 h. The dark brown solution was filtered, and the solvent was distilled away from the filtrate. This residue was placed in a 200-mL flask, and a vacuum sublimator was attached. On heating of the solution at 30 °C in vacuo, a yellow sublimate condensed on the dry-ice-filled cold finger. This material was characterized as $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_7H_7]$ (I) (mp 79 °C, 0.12 g (0.43 mmol), 22% yield on the basis of carborane consumed). Mass measurement: calcd for $^{59}Co^{12}C_8{}^{11}B_{11}{}^1H_{25}{}^+$ (P + 1 peak), 301.231; found, 301.235. IR (CCl_4 vs. CCl_4): C–H bands at 3050 (m), 3018 (vs), 2845 (s); B–H, 2570 (vs); other bands at 1450 (m), 1370 (m), 1100 (w, br).

When the reaction was conducted at room temperature (all other conditions being the same as described above), the results were identical except that the yield of I was slightly lower (15%).

Reaction of $B_5H_8^-$, $(CH_3)_2C_2B_4H_5^-$, and $FeCl_2$ (Simultaneous Addition of Reagents). A solution of $Na^+B_5H_8^-$ and $Na^+[(CH_3)_2C_2B_4H_5]^-$ in THF was prepared as described in the preceding experiment, from 1.48 g (23.1 mmol) of B_5H_9, 2.39 g (23.0 mmol) of $(CH_3)_2C_2B_4H_6$, and 1.50 g (62.5 mmol) of NaH in 50 mL of THF. This solution was filtered in vacuo onto anhydrous $FeCl_2$ (4.44 g 35.0 mmol) in a 250-mL round-bottom flask cooled in dry ice. The solution was allowed to warm to room temperature and stirred for 24 h, during which it became purple and gas was evolved. The vessel was cooled in liquid nitrogen, and the noncondensable gas (7.0 mmol) was expelled. The solvent (THF) was removed over a period of 2.0 h, leaving a dark red-brown residue. Fractionation of the volatile products gave B_2H_6 (10.0 mmol) and BH_3·THF, identified from their IR spectra. Dry N_2 was introduced, and a vacuum sublimator was attached to the vessel; however, heating the reaction residue at 70 °C produced no sublimate on the dry-ice-cooled finger.

A few milliliters of liquid CCl_4 was condensed into the flask at −196 °C, and the mixture was allowed to warm to room temperature and stirred for 30 min, during which the solution was at first green and then turned to reddish brown; there was considerable heat and gas evolution. After cooling of the flask in liquid nitrogen, the noncondensable gas (2.50 mmol) was expelled, the flask was warmed once again to room temperature, and the solvent was removed in vacuo. Heating of the reaction residue at 80 °C for 6 h caused a mixture of red and white crystalline solids to collect on the −78 °C cold finger. A mass spectrum of this mixture disclosed the presence of perchloroethane (C_2Cl_6) together with $[(CH_3)_2C_2B_7H_7]FeH_2[(CH_3)_2C_2B_4H_4]$, $(CH_3)_4C_4B_{11}H_{11}$, $(CH_3)_4C_4B_8H_8$, $[(CH_3)_2C_2B_4H_4]FeH_2[(CH_3)_2C_2B_5H_5]$, and $[(CH_3)_2C_2B_4H_4]_2FeH_2$.

The sublimed mixture was fractionated in vacuo through a trap at 0 °C, which allowed the C_2Cl_6 (0.21 g) to pass through but retained the other materials. These substances were separated in air on a Waters Prep/500 high-pressure liquid chromatograph (HPLC) with two 500-mL silica gel columns employed in sequence and pure hexane as eluant. The pure products obtained included red $[(CH_3)_2C_2B_4H_4]FeH_2[(CH_3)_2C_2B_5H_5]$ (II) (0.351 g (1.28 mmol), 11% yield, retention time (R_T) = 4.0 min, mp 71 °C). Mass measurement: calcd for $^{56}Fe^{12}C_8{}^{11}B_9{}^1H_{23}{}^+$, 274.1987; found, 274.1981. IR($CDCl_3$ vs. $CDCl_3$): C–H, 2950 (m), 2920 (vs), 2850 (m); B–H, 2570 (vs). The previously reported compound $(CH_3)_4C_4B_8H_8$[3,5a] appeared with R_T = 7.6 min (1.51 g (7.40 mmol), 64% yield). The new carborane $(CH_3)_4C_4B_{11}H_{11}$ eluted with R_T = 10.0 min as colorless crystals (mp 68 °C, 63.8 mg (0.27 mmol), 2.3% yield). Mass measurement: calcd for $^{12}C_8{}^{11}B_{11}{}^1H_{23}{}^+$, 240.2824; found, 240.2820.

Small quantities of colorless products with $R_T > 10$ min were eluted and tentatively identified from their mass spectra as $[(CH_3)_2C_2B_8H_8]_2$ (mass 300) and $[(CH_3)_4C_4B_8H_7]_2$ (mass 406).

Reaction of $B_3H_8^-$, $(CH_3)_2C_2B_4H_5^-$, and $FeCl_2$. Anhydrous ferrous chloride (0.700 g, 5.52 mmol) and $(CH_3)_4N^+B_3H_8^-$ (0.516 g, 4.49 mmol, prepared as described elsewhere)[20] were placed in a greaseless Pyrex reactor which was evacuated on the vacuum line, and 10 mL of dry THF was distilled into the reactor at −196 °C. Separately, $(CH_3)_2C_2B_4H_6$ (4.4 mmol) was condensed onto 0.305 g (12.7 mmol) of NaH in 25 mL of dry THF in vacuo. After reaction, the solution of $Na^+(CH_3)_2C_2B_4H_5^-$ was filtered in vacuo through sintered glass into the $FeCl_2$–$(CH_3)_4N^+B_3H_8^-$ solution, and the mixture was allowed to stand at room temperature for 48 h. After cooling of the solution to −196 °C, the noncondensable gas (4.2 mmol) was pumped off, the THF was removed under vacuum at room temperature over a 2-h period, and 30 mL of dry CCl_4 was added. The mixture was stirred at room temperature for 2 h, during which the color changed from greenish brown to red-brown. Following removal of CCl_4 by vacuum distillation over a 2-h period, a sublimator containing a U-tube was attached to the reactor under an N_2 atmosphere, and the reactor was heated to 70–80 °C while the U-tube was immersed in a −78 °C bath. After materials had ceased collecting in the U-trap, the trap was warmed to 0 °C to permit C_2Cl_6 (see above) to be pumped off. The remaining sublimate was separated via HPLC as described above, and the major products were the same as in the preceding experiment. Yields: $(CH_3)_4C_4B_8H_8$, 0.301 g (1.48 mmol, 67%); $[(CH_3)_2C_2B_4H_4]FeH_2[(CH_3)_2C_2B_5H_5]$ (II), 90.2 mg (0.329 mmol, 15%); $(CH_3)_4C_4B_{11}H_{11}$, 13.2 mg (0.055 mmol, 2.5%).

Reaction of BH_4^-, $(CH_3)_2C_2B_4H_5^-$, and $FeCl_2$. A mixture of $NaBH_4$ (0.21 g, 5.6 mmol) and anhydrous $FeCl_2$ (0.55 g, 4.4 mmol) in a Pyrex bulb was evacuated on the vacuum line for 4 h, and a solution of 3.0 mmol of $Na^+(CH_3)_2C_2B_4H_5^-$ in THF was added through a glass filter in vacuo. After the solution was stirred for 18 h at room temperature in THF, during which a black solid formed and noncondensable gas was evolved, THF was removed by distillation. The reaction residue was heated to 78 °C, causing a bright red solid, identified mass spectroscopically as the known[3] complex $[(CH_3)_2C_2B_4H_4]_2FeH_2$, to sublime into an adjoining U-trap cooled to −78 °C. The yield was 0.38 g (1.45 mmol, 97% yield). No other volatile products were detected.

Reaction of $B_5H_8^-$ and $FeCl_2$ Followed by $(CH_3)_2C_2B_4H_5^-$. Pentaborane(9) (13.9 mmol) was treated with 0.803 g (33.5 mmol) of NaH in 20 mL of THF, and the resulting solution of $Na^+B_5H_8^-$ was filtered in vacuo into a Pyrex bulb containing 0.940 g (7.40 mmol) of anhydrous $FeCl_2$. The mixture was stirred for 1 h at room temperature, during which the solution acquired a dark brown color and gas evolution occurred. At this point a solution of 13.7 mmol of $Na^+[(CH_3)_2C_2B_4H_5]^-$ in 20 mL of THF (prepared as described above) was added by filtration, and the mixture was stirred at room temperature for 24 h. No further color change was detected, but some additional gas evolution occurred. Following removal of THF by distillation in vacuo for 2 h, a U-trap with an attached side arm and bulb was attached to the reactor under a flow of H_2, the apparatus was evacuated, and the reactor was heated to 70–80 °C while the U-trap was cooled to −78 °C. The sublimed material was a mixture of red and white solids which on mass spectroscopic analysis was found to contain II, $(CH_3)_4C_4B_8H_8$, and a new compound, $[(CH_3)_2C_2B_5H_5]FeH_2$ (V), identified from its parent grouping (*m/e* 286) and pattern of peak intensities, which conform to the postulated composition. Attempts to separate and purify this new material by HPLC in air and by column chromatography on silica in an atmosphere of dry N_2 did not succeed due to the instability and small quantity of V. The residue remaining after sublimation was treated with CCl_4 as descried above, which gave additional quantities of the same sublimable red and white products.

When the product mixture containing V was exposed to air for 16 h, the mass spectrum of the material contained a new, intense peak grouping at *m/e* 228 corresponding to $(CH_3)_4C_4B_{10}H_{10}$, together with $(CH_3)_4C_{48}H_8$ (*m/e* 204) and a small grouping at *m/e* 300 assigned to $[(CH_3)_2C_2B_8H_8]_2$.

Reaction of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ with B_5H_9. A 10-mg sample of the iron complex and an equimolar quantity of B_5H_9 were stirred in THF at room temperature for 24 h, after which the solvent was removed by distillation at room temperature and the products were analyzed by mass spectroscopy. The mass spectrum revealed three major components: $[(CH_3)_2C_2B_4H_4]FeH_2[(CH_3)_2C_2B_5H_5]$ (II), $(CH_3)_4C_4B_{11}H_{11}$ (III), and $(CH_3)_4C_4B_8H_8$. The original complex was not present in significant quantity.

Synthesis of $(CH_3)_4C_4B_9H_{11}$ from $[(CH_3)_2C_2B_4H_4]FeH_2[(CH_3)_2C_2B_5H_5]$. A solution of 30 mg (0.11 mmol) of the iron complex in 50 mL of THF was placed in a three-necked 200-mL flask, and O_2 was bubbled through the solution over an 18-h period with 30 mL of THF added every 2 h. During this time the originally violet-red solution changed to pale yellow-orange with some insoluble residue at the bottom of the flask. The solution was filtered and the solvent removed under vacuum at 0 °C over a 40-min period.

A vacuum sublimator was attached to the flask, and the apparatus was evacuated; a white sublimate condensed on the dry-ice-filled cold finger while the reactor was maintained at room temperature. The white compound (mp 65 °C, 10 mg, 0.046 mmol, 42% yield) was characterized as $(CH_3)_4C_4B_9H_{11}$ from its mass spectrum and ^{11}B NMR and ^1H NMR spectra.

Conversion of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ to $(CH_3)_4C_4B_8H_8$ in the Absence of Oxygen. A THF solution of $Na^+[(CH_3)_2C_2B_4H_5]^-$, prepared as descried above from 2.38 mmol of $(CH_3)_2C_2B_4H_6$ and excess NaH, was filtered through sintered glass into an evacuated flask containing 0.816 g of $FeCl_2$ (1.48 mmol) and the mixture was stirred at room temperature over a 24-h period. At the end of this time the solution was dark purple. Following removal of solvent by vacuum distillation, the purple residue was heated at 100 °C, causing white crystalline $(CH_3)_4C_4B_8H_8$ (0.22 g, 1.08 mmol, 90.6% yield) to condense in an adjacent U-trap cooled to 0 °C. The carborane was identified from its mass spectrum by comparison with the spectrum of an authentic sample. The dark solid remaining in the reactor was recognized as metallic iron from its attraction to a bar magnet.

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Registry No. I, 74877-72-8; II, 74893-02-0; IV, 74877-71-7; V, 74877-70-6; $(CH_3)_4C_4B_8H_8$, 58815-26-2; $[(CH_3)_2C_2B_4H_4]_2FeH_2$, 58846-86-9; B_5H_9, 19624-22-7; $(CH_3)_2C_2B_4H_6$, 20741-68-8; $(CH_3)_4N^+B_3H_8^-$, 12386-10-6.