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Oxidative Fusion of Carborane Ligands in Iron and Cobalt Complexes: A Systematic Study[1]

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Abstract: The conversion of the red, diamagnetic sandwich complexes $(R_2C_2B_4H_4)_2FeH_2$ or $(R_2C_2B_4H_4)_2CoH$ to the corresponding $R_4C_4B_8H_8$ carborane (R = alkyl) via oxidative fusion of the formal $R_2C_2B_4H_4^{2-}$ ligands was investigated in detail. The reaction is intramolecular with respect to the ligands; in mixtures of $(R_2C_2B_4H_4)_2FeH_2$ and $(R'_2C_2B_4H_4)_2FeH_2$ where $R \neq R'$, no evidence of ligand exchange was found. In the absence of O_2 or other oxidizers, the iron and cobalt complexes are stable indefinitely in diethyl ether solution. In tetrahydrofuran (THF) solution, however, slow conversion to a purple, paramagnetic *diiron* complex is observed. From X-ray and other evidence (following paper) the purple complex is formulated as $(R_2C_2B_4H_4)_2Fe_2(THF)_2$. This species on exposure to O_2 rapidly forms $R_4C_4B_8H_8$ and hence is an intermediate in the oxidative fusion of the monoiron complex. The disproportionation of $(R_2C_2B_4H_4)_2FeH_2$ to $(R_2C_2B_4H_4)_2Fe_2(THF)_2$ and $R_4C_4B_8H_8$ is catalyzed by traces of $FeCl_3$ in THF solution but does not take place at a significant rate in diethyl ether even in the presence of excess $FeCl_3$. However, at $FeCl_3/(R_2C_2B_4H_4)_2FeH_2$ mole ratios of 2.0 or greater in THF, $R_4C_4B_8H_8$ is produced essentially quantitatively. Implications of these findings with respect to the fusion process are discussed.

The metal-promoted face-to-face fusion of two pyramidal carborane cages to form a single polyhedral cluster has been observed in several reaction systems, as reported in a series of papers from this laboratory.[2] The most clearly documented examples involve, as intermediates, dicarboranyl complexes of iron and cobalt, i.e., $(R_2C_2B_4H_4)_2Fe^{II}H_2$ and $(R_2C_2B_4H_4)_2Co^{III}H$, where R is an alkyl group (Figure 1). The overall process for the iron system[2b,3] can be represented as in eq 1 and 2 (R = CH_3, C_2H_5, n-C_3H_7). The analogous cobalt complexes yield identical carborane products.[2c]

$$2Na^+R_2C_2B_4H_5^- + FeCl_2 \xrightarrow[-30\ °C]{THF} \underset{80\%}{(R_2C_2B_4H_4)_2FeH_2} + 2NaCl \quad (1)$$

$$(R_2C_2B_4H_4)_2FeH_2 \xrightarrow{THF} R_4C_4B_8H_8 \text{ (colorless air-stable solid) } 80\text{–}90\% + \text{solvated iron complexes} + H_2 \quad (2)$$

The red intermediate $[(CH_3)_2C_2B_4H_4]_2FeH_2$ and its fusion product $(CH_3)_4C_4B_8H_8$ have been fully characterized by multinuclear NMR[2b] and X-ray diffraction[2d,4,5] studies, and the rich chemistry of these species and others derived from them has been explored in some detail.[2e,2f] The nature of the fusion process itself, however, has remained something of a mystery, although various kinds of empirical evidence concerning the scope of the reaction have accumulated.[2f–i]

The present investigation, centered for convenience primarily on the iron system, addressed three basic questions: (1) Is the fusion process truly intramolecular, as previously assumed? (2) Is it solvent dependent? (3) Can species intermediate between $(R_2C_2B_4H_4)_2FeH_2$ and $R_4C_4B_8H_8$ be isolated and characterized? In addition to providing affirmative answers to these queries, this work uncovered some remarkable and unsuspected facets of the fusion process.

Results and Discussion

Synthesis of the $(R_2C_2B_4H_4)_2FeH_2$ Complexes. The *C,C'*-dialkylcarboranes $R_2C_2B_4H_6$ (R = CH_3, C_2H_5, or n-C_3H_7) were prepared by a previously described method[6] involving the reaction of B_5H_9, $(C_2H_5)_3N$, and RC≡CR at 0 °C without solvent. The syntheses of the diethyl and dipropyl carboranes are straightforward and proceed analogously; for reasons not entirely understood, the diethylcarborane synthesis from 3-hexyne[7] is less sensitive to temperature and other reaction conditions and gives more consistent results (isolated yields 30–35%) than does the dimethylcarborane preparation from 2-butyne. Conversion of the $R_2C_2B_4H_6$ carboranes to their respective $R_2C_2B_4H_5^-$ anions via reaction with NaH in THF,[8] and complexation with Fe^{2+} ion as in eq 1[2b,3] is routine.

Oxidative Fusion of $(R_2C_2B_4H_4)_2FeH_2/(R'_2C_2B_4H_4)_2FeH_2$ Mixtures: Tests for Ligand Exchange. The fusion reaction as depicted in Figure 1 implies an intramolecular process in which there is no interchange of carborane ligands between complexes. This assumption is certainly consistent with the general observation that carborane ligands in metallacarborane complexes are nonlabile, although examples of exchange of dicarbollide ($R_2C_2B_9H_9^{2-}$) ligands in certain complexes have been reported.[9] Several experiments were conducted in order to establish whether the $R_2C_2B_4H_4^{2-}$ ligands do in fact exchange under the conditions of fusion.

(a) Equimolar mixtures of $(R_2C_2B_4H_4)_2FeH_2$ and $(R'_2C_2B_4H_4)_2FeH_2$ (R = C_2H_5, R' = n-C_3H_7, diethyl ether solution; R = CH_3, R' = C_2H_5, no solvent) were recovered unchanged with no evidence of formation of mixed-ligand complexes $(R_2C_2B_4H_4)(R'_2C_2B_4H_4)FeH_2$.

(b) Reaction of an equimolar mixture of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ and $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ with O_2 in THF produced only $(CH_3)_4C_4B_8H_8$ and $(C_2H_5)_4C_4B_8H_8$; the mixed-ligand fusion product, $(CH_3)_2(C_2H_5)_2C_4B_8H_8$, was not observed.

As a control experiment, the $(CH_3)_2C_2B_4H_5^-$ and $(C_2H_5)_2C_2B_4H_5^-$ ions were allowed to react simultaneously with $FeCl_2$ as in eq 3, thereby demonstrating that the mixed complex is in fact formed when both ligands are available in solution.

$$FeCl_2 + (CH_3)_2C_2B_4H_5^- + (C_2H_5)_2C_2B_4H_5^- \xrightarrow[THF]{O_2} [(CH_3)_2C_2B_4H_4]_2FeH_2 + [(C_2H_5)_2C_2B_4H_4]_2FeH_2 + [(CH_3)_2C_2B_4H_4][(C_2H_5)_2C_2B_4H_4]FeH_2 \quad (3)$$

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(1) Presented in part at the 182nd National Meeting of the American Chemical Society, New York, Aug 1981; INOR 10.

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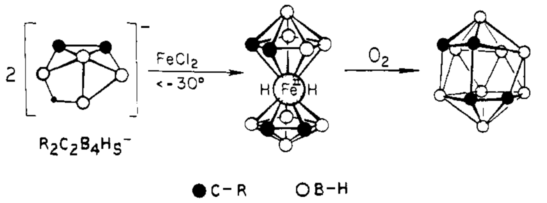
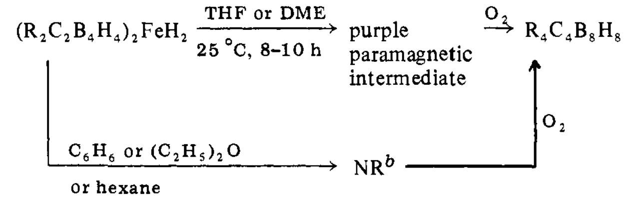


Figure 1. Conversion of $(R_2C_2B_4H_4)_2FeH_2$ to $R_4C_4B_8H_8$ via oxidative fusion (R = CH_3, C_2H_5, or n-C_3H_7).

Scheme I[a]



[a] R = CH_3, C_2H_5. [b] No reaction.

(c) Treatment of $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ with $(CH_3)_2C_2B_4H_5^-$ ion in THF solution, followed by acidification with HCl and exposure to oxygen, gave $(C_2H_5)_4C_4B_8H_8$ as the only carborane product. Analogous experiments with $[(C_2H_5)_2C_2B_4H_4]_2CoH$ yielded the same result.

These findings clearly demonstrate that the carborane ligands in our complexes do not significantly dissociate under the conditions examined and that the formation of $R_4C_4B_8H_8$ products via ligand fusion must be an intramolecular process as previously assumed.[2a,b,f]

Properties of $(R_2C_2B_4H_4)_2FeH_2$ in Solution. The conversion of THF solutions of $(R_2C_2B_4H_4)_2FeH_2$ complexes (R = CH_3 or C_2H_5) to $R_4C_4B_8H_8$ carboranes occurs very rapidly, almost instantaneously, on exposure to O_2 or other oxidizing agents. In the absence of oxidizers, the complexes appear to be stable over short time periods; however, on standing several hours at room temperature, even rigorously pure solutions of $(R_2C_2B_4H_4)_2FeH_2$ in THF or dimethoxyethane (DME), which are deep red at the start (maximum ν 470 nm), gradually acquire a deep purple color owing to the formation of a nw complex with absorption maxima at ν 516 and 640 nm. The conversion is quite slow, but in the presence of $FeCl_3$ it occurs rapidly, as discussed below.

The purple paramagnetic[10] solutions appear to undergo no further change provided oxidizing agents are excluded; even a trace of O_2, however, induces formation of $R_4C_4B_8H_8$. So sensitive is the purple material that exposure to medium-purity commercial N_2 gas with an O_2 concentration of a few parts per million leads to rapid conversion to the carborane.

In deoxygenated nonpolar solvents such as benzene, diethyl ether, or hexane, the red $(R_2C_2B_4H_4)_2FeH_2$ complexes appear to be stable, remaining unchanged for periods of days to weeks with no evidence of formation of the purple species. On exposure to O_2, the solutions are rapidly decolorized and generate the $R_4C_4B_8H_8$ carborane. Scheme I summarizes these observations.

Characterization of the Purple Complexes. Solutions of the purple species derived from the $(R_2C_2B_4H_4)_2FeH_2$ precursors, where R is CH_3 or C_2H_5, exhibit no detectable ^{11}B NMR signal at the 115.5-MHz irradiating frequency. The 360-MHz proton NMR spectrum of the methyl complex contains a series of peaks (see Experimental Section) but is basically uninterpretable. Mass spectra of the purple solids are essentially indistinguishable from those of $R_4C_4B_8H_8$, indicating that conversion to the carborane occurs in the spectrometer before the spectrum of the complex can be recorded. The IR spectrum of the tetramethyl complex contains a distinctive feature: the B–H stretching absorption near 2500 cm^{-1} is a doublet, in contrast to the sharp singlet exhibited by $[(CH_3)_2C_2B_4H_4]_2FeH_2$. Unfortunately, the extreme air-sensitivity of the purple complexes prevented satisfactory microanalyses; however, usable crystals of the tetramethyl compound were obtained, and an X-ray structural analysis was performed (see following paper.[11] The completely unanticipated structure was found to contain *two* iron atoms (Figure 2), an observation fully consistent with the Mössbauer spectrum.[11] From available evidence, the formula of the complex obtained in DME solvent can be given as $[(CH_3)_2C_2B_4H_4]_2Fe_2[(OCH_3)_2C_2H_4]$; the analogous compound prepared in THF exhibits nearly identical spectroscopic properties and is formulated as $[(CH_3)_2C_2B_4H_4]_2Fe_2[O(CH_2)_4]_2$, with two THF molecules in place of the bidentate DME ligand in Figure 2. As expected, when the THF complex is placed in DME solvent the more weakly basic THF ligands are displaced, forming the DME complex.

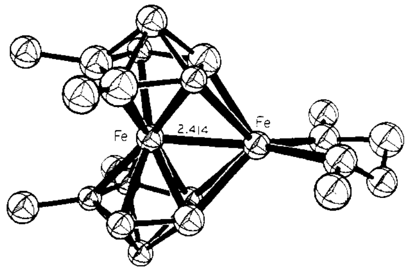


Figure 2. Structure[11] of $[(CH_3)_2C_2B_4H_4]_2Fe_2[(OCH_3)_2C_2H_4]$.

Since each carborane ligand is formally dinegative, the two iron atoms must carry a total 4+ charge *provided there are no "extra" hydrogen atoms*[12] that might be present as H^+ or H^-. Subsequent magnetic susceptibility and ESR measurements,[11] combined with the Mössbauer work, are consistent with an assignment of oxidation state 2+ for each iron atom, consistent with the above formula; one of the metals is present in a high-spin configuration and is the source of the paramagnetic behavior.

Interaction of the $(R_2C_2B_4H_4)_2FeH_2$ Complexes with $FeCl_3$. The structural characterization of the purple species raised a number of questions concerning the synthetic origin of the second iron atom and its role in the conversion of the diiron species to the tetracarbon carborane. Comparison of the known structures[4,11] of red $(R_2C_2B_4H_4)_2FeH_2$ and purple $(R_2C_2B_4H_4)_2Fe_2L_2$ (R = alkyl; L_2 = DME or 2THF) suggested that the diiron species forms simply by introduction of a second metal ion into a wedging location on the monoiron complex. Accordingly, the diethylcarborane monoiron complex was found to react rapidly with an equimolar quantity of $FeCl_3$ in THF to generate the purple diiron compound together with $(C_2H_5)_4C_4B_8H_8$. In this reaction, which is conducted under rigorously oxygen-free conditions, the $FeCl_3$ functions as an oxidizing agent:

$$\underset{1.0\ \text{mmol}}{(R_2C_2B_4H_4)_2FeH_2} + \underset{1.0}{FeCl_3} \xrightarrow[R\,=\,C_2H_5]{THF} \underset{0.58}{(R_2C_2B_4H_4)_2Fe_2(THF)_2} + \underset{\sim 0.4}{R_4C_4B_8H_8} + H_2 \quad (4)$$

From the observed stoichiometry, it is clear that part of the metal in the diiron product is derived from the $FeCl_3$ reagent. The reaction is more complex than eq 4 suggests, since uncharacterized solids were also produced.

In the presence of *excess* $FeCl_3$, oxidative fusion occurs to give $R_4C_4B_8H_8$ quantitatively. In order to prove that the carborane

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[10] Magnetic susceptibility measurements are reported in the accompanying article.[11]

[11] Grimes, R. N.; Maynard, R. B.; Sinn, E.; Brewer, G. A.; Long, G. J., following paper in this issue.

[12] In early stages of this work, we tentatively formulated the complexes as $(R_2C_2B_4H_4)_2Fe^{III}{}_2H_2L_2$, containing two H^- ligands.[13] Subsequent magnetic susceptibility and ESR measurements[11] demonstrated that both iron atoms are in the 2+ oxidation state, and there is no evidence for the presence of "extra" hydrogens.

[13] (a) Maynard, R. B.; Grimes, R. N. "Abstracts of Papers", 182nd National Meeting of the American Chemical Society, New York, American Chemical Society: Washington, DC, 1981; INOR 10. (b) Grimes, R. N. *Pure Appl. Chem.* **1982**, *54*, 43.

product does in fact form from the attack of $FeCl_3$ on the diiron complex, we conducted a 1:1 reaction as in eq 5, producing the carborane as expected.

$$(R_2C_2B_4H_4)_2Fe_2(THF)_2 + FeCl_3 \xrightarrow{THF} R_4C_4B_8H_8 \quad (5)$$

Even catalytic amounts of $FeCl_3$ promote formation of the purple complex (eq 6). Reactions 4 and 6 proceed rapidly,

$$\underset{0.73\ \text{mmol}}{(R_2C_2B_4H_4)_2FeH_2} + \underset{0.05}{FeCl_3} \xrightarrow[R = C_2H_5]{THF} \underset{0.36\ (92\%\ \text{based on Fe})}{(R_2C_2B_4H_4)_2Fe_2(THF)_2} + R_4C_4B_8H_8 \quad (6)$$

reaching completion within minutes at room temperature; reaction 5 is virtually instantaneous. In the remarkable catalytic process (6), the net effect is a disproportionation of two molecules of the monoiron species to form the diiron complex and carborane.

In light of these findings, it seemed possible that the slow conversion of "pure" $(R_2C_2B_4H_4)_2FeH_2$ to the purple $(R_2C_2B_4H_4)_2Fe_2(THF)_2$ (Scheme I), which occurs on a time scale of hours in the absence of oxygen, might be triggered by traces of solvated Fe^{3+} in samples of the monoiron complex. However, even *freshly sublimed* $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ when dissolved in THF is quantitatively converted to the diiron complex and $(C_2H_5)_4C_4B_8H_8$ in 10 h at 25 °C; in contrast, this reaction does *not* take place in diethyl ether solution, even in the presence of excess ferric chloride:

$$[(C_2H_5)_2C_2B_4H_4]_2FeH_2 + FeCl_3 \xrightarrow{(C_2H_5)_2O} NR \quad (7)$$

These facts suggest that the red monoiron complex, when placed in THF, undergoes slow, solvent-induced decomposition that liberates traces of solvated Fe^{3+} that in turn catalyze the formation of the diiron complex.

Conclusions

It is clear that the fusion of $R_2C_2B_4H_4^{2-}$ carborane ligands via $(R_2C_2B_4H_4)_2FeH_2$ complexes is intramolecular with respect to the ligands but, in at least one pathway, is *inter*molecular in terms of the metal. The route outlined in Scheme I involving the $(R_2C_2B_4H_4)_2Fe_2{\cdot}L_2$ purple intermediate may not be the only one leading to $R_4C_4B_8H_8$, although no evidence for other intermediates has been observed. In the reaction of $(R_2C_2B_4H_4)_2FeH_2$ in THF with equivalent or excess quantities of $FeCl_3$, the purple (diiron) intermediate is not observed, since in the presence of $FeCl_3$ that species is immediately converted to $R_4C_4B_8H_8$; thus, the formation of the diiron species from the monoiron precursor, a slower process, is rate limiting in the overall scheme.

Solvent properties are clearly important in these reaction systems. In the absence of O_2, moderately basic media such as THF are required to promote the conversion of the monoiron species to the diiron intermediate and the carborane product; the failure of diethyl ether to induce this reaction suggests that fairly strong solvation of the $(R_2C_2B_4H_4)_2FeH_2$ reagent is part of the sequence. However, in the presence of oxygen the solvent makes little difference in the final result; even in $(C_2H_5)_2O$ or hexane, the monoiron complex is rapidly oxidized to carborane, implying that a different fusion mechanism (bypassing the diiron intermediate) may be operating in such cases.

The structure of $[(CH_3)_2C_2B_4H_4]_2Fe_2(DME)$ unfortunately provides no direct information on the manner in which linkage of the two carborane ligands actually takes place; isolation of an intermediate representing an early stage in the fusion process itself remains elusive, although certain metallacarboranes have "partially fused" structures[14] that may be related to such intermediates. However, it is possible to speculate that the attack of an oxidizer on the diiron complex severs the "outer" iron from the rest of the molecule, leaving the four borons (formerly attached to the outer iron) in a state of coordinative unsaturation. The two B–B edges defined by the four boron atoms would be induced to join, initiating ligand fusion and expulsion of the remaining iron. In essence, the second (outer) iron atom in this scheme serves to lower the activation energy for linkage of the B–B edges on the carborane ligands.

The structure of the dimetallic complex suggests numerous follow-up studies, including the possibility of substituting other elements in place of iron as the "second" metal. Aside from its involvement in the ligand fusion process, the highly exposed outer metal atom is expected to be reactive to a variety of electron-donating substrates and may well be an active catalyst precursor. We are investigating these possibilities.

Experimental Section

Except where noted, all reactions were conducted under a dry nitrogen atmosphere by using Schlenk, glovebox, or high vacuum techniques.

Known compounds including $(R_2C_2B_4H_4)_2FeH_2$, $(R_2C_2B_4H_4)_2CoH$, and $R_4C_4B_8H_8$ (R = alkyl) were identified from their characteristic mass spectra, which exhibit strong peak profiles in the parent region.[2b,c,3,6]

Materials. 2,3-Dialkyl-2,3-dicarbahexaboranes ($R_2C_2B_4H_6$, R = CH_3, C_2H_5, *n*-C_3H_7) were prepared from the appropriate symmetrical alkyne and pentaborane(9) as previously described.[6,7] The compounds $[R_2C_2B_4H_4]_2FeH_2$ (where R = CH_3, C_2H_5, or *n*-C_3H_7) and $[(C_2H_5)_2C_2B_4H_4]_2CoH$ were synthesized by literature procedures.[2b,c,3] Anhydrous $FeCl_3$ was prepared from $FeCl_3{\cdot}6H_2O$ via dehydration with $SOCl_2$.[15] Tetrahydrofuran (THF), diethyl ether, and benzene were dried by reflux over sodium benzophenone ketyl. Hexane was dried by reflux over calcium hydride.

Instrumentation. ^{11}B (115.5 MHz) and ^{1}H (360 MHz) pulse Fourier transform NMR spectra were recorded on a Nicolet NT-360 spectrometer equipped with a 1180E/293B data processor, with broad-band heteronuclear decoupling of protons for the ^{11}B spectra. Unit resolution mass spectra (EI) were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer at 70 eV. Visible–ultraviolet spectra were recorded on a Varian 634 UV–visible recording spectrophotometer, and infrared spectra were obtained on a Beckman IR-8 grating instrument.

Mixed-Ligand Experiments on $(R_2C_2B_4H_4)_2FeH_2$ Complexes. (a) Equimolar quantities of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ (a red solid) and $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ (a dark red oil) were mixed together in the absence of solvent. After several hours at room temperature, a mass spectrum of the mixture contained only peaks arising from the starting materials (parent envelopes with cutoffs at *m/e* 262 and 318, respectively). No evidence of the mixed-ligand species $[(CH_3)_2C_2B_4H_4]FeH_2[(C_2H_5)_2C_2B_4H_4]$ (*m/e* 290) was observed.

(b) Equimolar quantities of $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ and $[(n\text{-}C_3H_7)_2C_2B_4H_4]FeH_2$ were dissolved together in 30 mL of diethyl ether and stirred at room temperature overnight. After removal of the solvent in vacuo, mass spectrometric analysis revealed only starting materials.

(c) Equimolar quantities of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ and $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ were dissolved in 30 mL of THF and stirred overnight. The dark purple solution was exposed to the air and stirred for ~1 h. The THF was stripped off, and the residue was extracted with CH_2Cl_2 and filtered through a layer of silica gel on a glass frit. Following solvent removal by rotary evaporation, a mass spectrum of the residue exhibited parent ion envelopes with high-mass cutoffs at *m/e* 260, corresponding to $(C_2H_5)_4C_4B_8H_8$, and 204, indicative of $(CH_3)_4C_4B_8H_8$. No significant peaks were observed in the *m/e* 232 region corresponding to $(CH_3)_2(C_2H_5)_2C_4B_8H_8$.

Reaction of $(CH_3)_2C_2B_4H_5^-$, $(C_2H_5)_2C_2B_4H_5^-$, and $FeCl_2$. A THF solution of $Na^+(CH_3)_2C_2B_4H_5^-$ and $Na^+(C_2H_5)_2C_2B_4H_5^-$ was prepared by distillation of $(CH_3)_2C_2B_4H_6$ (0.075 g, 0.72 mmol) and addition of $(C_2H_5)_2C_2B_4H_6$ (0.094 g, 0.72 mmol) via a sidearm tipper onto NaH (0.080 g, 3.3 mmol) in 25 mL of THF. This solution was filtered in vacuo onto anhydrous $FeCl_2$ (0.107 g, 0.84 mmol) into a 50-mL round-bottom flask cooled in liquid nitrogen. The solution was allowed to warm to 0 °C and stirred for ~1 h. The THF was removed in vacuo and the residue transferred to a drybox. The red-brown residue was rinsed with hexane through a layer of silica gel until the washings were colorless. Following removal of THF, a mass spectrum of the mixture exhibited the following parent ion envelopes (high-mass *m/e*, ^{13}C peaks ignored): 262, $[(CH_3)_2C_2B_4H_4]_2FeH_2$; 290, $[(CH_3)_2C_2B_4H_4][(C_2H_5)_2C_2B_4H_4]FeH_2$; 318, $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$. No attempt was made to effect separation of these complexes.

Reactions of $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ with $(CH_3)_2C_2B_4H_5^-$. (a) A THF solution of $Na^+(CH_3)_2C_2B_4H_5^-$ was prepared by distillation of $(CH_3)_2C_2B_4H_6$ (0.048 g, 0.46 mmol) onto an excess of NaH in 20 mL of THF.

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This solution was filtered in vacuo onto $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ (0.147 g, 0.46 mmol). After warming to room temperature, the solution was stirred for 7 h, at which point an excess of anhydrous HCl was added. The solution was stirred for an additional 30 min and exposed to the air. The THF was removed and the residue extracted with CH_2Cl_2 and filtered through a layer of silica gel on a glass frit. Following removal of solvent, a mass spectrum of the residue exhibited only the pattern of $(C_2H_5)_4C_4B_8H_8$ (high-mass cutoff at *m/e* 260).

(b) The same procedure as in (a) was followed, except that the mole ratio of $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ to $Na^+(CH_3)_2C_2B_4H_5^-$ was 1:2. Again, the oxidative fusion product obtained an exposure to air consisted of $(C_2H_5)_4C_4B_8H_8$ only, as shown by mass spectrometry.

Reactions of $[(C_2H_5)_2C_2B_4H_4]_2CoH$ with $(CH_3)_2C_2B_4H_5^-$. (a) A THF solution of $Na^+(CH_3)_2C_2B_4H_5^-$ was prepared by distillation of $(CH_3)_2C_2B_4H_6$ (0.025 g, 0.24 mmol) onto an excess of NaH in 10 mL of THF. This solution was filtered in vacuo onto $[(C_2H_5)_2C_2B_4H_4]_2CoH$ (0.077 g, 0.24 mmol), and the mixture was stirred at room temperature for several hours, at which point an excess of anhydrous HCl was added. The solution was stirred for an additional 30 min and exposed to the air. The THF was stripped off and the residue extracted with CH_2Cl and filtered through a layer of silica gel on a glass frit. After removal of the solvent, a mass spectrum of the solid showed only $(C_2H_5)_4C_4B_8H_8$ (cutoff at *m/e* 260).

(b) An analogous procedure employing a 2:1 mixture of $Na^+[(CH_3)_2C_2B_4H_5]^-$ and $[(C_2H_5)_2C_2B_4H_4]_2CoH$ gave identical results, the only carborane product being $(C_2H_5)_4C_4B_8H_8$.

Conversion of $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ to $[(C_2H_5)_2C_2B_4H_4]_2Fe_2(THF)_2$. A 50-mL Schlenk vessel was charged with 0.173 g (0.55 mmol) of freshly sublimed $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ in 20 mL of THF. The solution was degassed and stirred overnight at room temperature. During this period the wine-red solution turned dark purple. The solvent was removed in vacuo, and the residue was transfered onto a 1 × 10 cm silica gel column in a drybox. The residue was eluted with several column volumes of benzene. The solvent was stripped from this fraction to yield 0.065 g (0.25 mmol) of $(C_2H_5)_4C_4B_8H_8$. The dark purple material was eluted off the column with THF to give 0.134 g (0.26 mmol, 96% yield) of crystalline $[(C_2H_5)_2C_2B_4H_4]_2Fe_2(THF)_2$.

The 360-MHz ^1H FT NMR spectrum of this paramagnetic diiron complex in $CDCl_3$ contains major peaks at δ 4.17, 3.97, 3.67, 2.18, 1.73, and 1.33 (relative to tetramethylsilane) with relative areas of 2.0, 1.0, 1.3, 3.8, 1.6, and 1.2, respectively. The IR spectrum (Nujol mull) exhibits peaks at 2510 (vs), 2480 (m), 1343 (m), 1260 (w), 1245 (w), 1170 (w), 1115 (w), 1050 (sh), 1025 (vs), 915 (m), 860 (vs), 840 (sh), 800 (w), and 695 (m) cm^{-1}. The electronic spectrum in THF contains a major absorption at 560 nm (ϵ 757 L mol^{-1} cm^{-1}) with a shoulder at 640 nm. Mössbauer, electron spin resonance, and magnetic susceptibility data are reported in the following article.[11]

Reactions of $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ with $FeCl_3$. (a) 1:1 Mole Ratio. A 50-mL Schlenk vessel was charged with 152 mg (0.48 mmol) of $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ and 77 mg (0.48 mmol) of anhydrous $FeCl_3$ in 20 mL of THF. The solution was degassed and stirred at room temperature overnight. After the reactor was frozen in liquid nitrogen, the noncondensable gas (H_2) was measured as 0.9 mmol. The solvent was removed and the residue extracted with hexane to remove $(C_2H_5)_4C_4B_8H_8$. Subsequent elution with THF gave 143 mg (0.28 mmol, 58% yield) of dark purple $[(C_2H_5)_2C_2B_4H_4]_2Fe_2(THF)_2$.

(b) 1.5:1 Mole Ratio. A 50-mL Schlenk vessel was charged with 0.157 g (0.97 mmol) of anhydrous $FeCl_3$ and 0.192 g (0.60 mmol) of $[(C_2H_5)_2C_2B_4H_4)_2FeH_2$ in 15 mL of THF. After stirring at room temperature for 10 h, the nearly colorless solution was filtered in vacuo and the solvent removed, giving a residue which was extracted with hexane and eluted on a silica gel TLC plate to give 0.060 g (0.23 mmol, 38% yield) of $(C_2H_5)_4C_4B_8H_8$.

(c) 2:1 Mole Ratio. A 50-mL Schlenk vessel was charged with 0.093 g (0.29 mmol) of $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ and 0.098 g (0.061 mmol) of $FeCl_3$ in 25 mL of THF. The mixture was evacuated under liquid N_2 and stirred at room temperature overnight, at which point it was nearly colorless (very pale purple), indicating virtually complete conversion to $(C_2H_5)_4C_4B_8H_8$.

(d) 1:15 Mole Ratio. A 50-mL Schlenk vessel was charged with 0.233 g (0.73 mmol) of $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ and 8.0 mg (0.05 mmol) of anhydrous $FeCl_3$ in 20 mL of THF. The vessel was frozen in liquid N_2, evacuated, and stirred at room temperature for 24 h, at which point the solution was dark purple. Following solvent removal, the purple solid was placed on a silica column in a nitrogen-filled drybox and washed with hexane to remove $(C_2H_5)_4C_4B_8H_8$, and the purple complex was eluted with THF to give 184 mg (0.36 mmol) of $[(C_2H_5)_2C_2B_4H_4]_2Fe_2(THF)_2$, corresponding to a 92% yield based on the total amount of iron in the starting materials.

Reaction of $[(C_2H_5)_2C_2B_4H_4]_2Fe_2(THF)_2$ with $FeCl_3$. A 50-mL Schlenk vessel was charged with 0.045 g (0.28 mmol) of anhydrous $FeCl_3$ in 20 mL of THF. To this was added via a solids addition tube 0.143 g (0.28 mmol) of $[(C_2H_5)_2C_2B_4H_4]_2Fe_2(THF)_2$. The solution immediately decolorized, and a white precipitate formed. This was transferred into the drybox and filtered through a medium glass frit, and solvent was removed to give 70 mg (0.27 mmol, 96% yield) of $(C_2H_5)_4C_4B_8H_8$.

Treatment of $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ with $FeCl_3$ in Diethyl Ether. (a) A 50-mL Schlenk vessel was charged with 0.211 g (0.67 mmol) of $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ and 0.108 g (0.67 mmol) of anhydrous $FeCl_3$ in 20 mL of diethyl ether. The dark red solution was stirred overnight at room temperature. The solvent was removed in vacuo, and a mass spectrum of the residue showed $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ exclusively.

(b) In an analogous manner a reaction consisting of a 3:1 mixture of anhydrous $FeCl_3$ to $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$ was conducted. Again only starting materials were recovered.

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Registry No. $[(CH_3)_2C_2B_4H_4]_2FeH_2$, 83096-03-1; $[(C_2H_5)_2C_2B_4H_4][(CH_3)_2C_2B_4H_4]FeH_2$, 83096-04-2; $[(C_2H_5)_2C_2B_4H_4]_2FeH_2$, 83096-05-3; $(C_2H_5)_4C_4B_8H_8$, 83096-06-4; $[(C_2H_5)_2C_2B_4H_4]_2CoH$, 83096-07-5; $[(C_2H_5)_2C_2B_4H_4]_2Fe_2(THF)_2$, 83114-92-5; $(CH_3)_2C_2B_4H_5^-$, 52828-12-3; $(C_2H_5)_2C_2B_4H_5^-$, 83096-08-6; $(CH_3)_2C_2B_4H_6$, 20741-68-8; $(C_2H_5)_2C_2B_4H_6$, 80583-48-8.