Studies of Iron(II) and -(III) Metallocarboranes Derived from *nido*-$C_2B_4H_8$ and *closo*-$C_2B_5H_7$

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Abstract: Ferracarborane cyclopentadienyl and carbonyl complexes of Fe(II) and Fe(III) containing three to five boron atoms, having both open- and closed-cage structures, have been prepared *via* several different synthetic routes in solution and in the vapor phase. The reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ with $NaC_2B_4H_7$ yields $\mu\text{-}[(\pi\text{-}C_5H_5)Fe(CO)_2]C_2B_4H_7$, which on uv irradiation produces the sandwich compounds $(\pi\text{-}C_5H_5)Fe^{II}H(\pi\text{-}2,3\text{-}C_2B_4H_6)$ and $(\pi\text{-}C_5H_5)Fe^{III}(\pi\text{-}2,3\text{-}C_2B_4H_6)$. The latter two complexes are reversibly interconverted *via* an intermediate ionic species by acid–base and redox processes. Treatment of $2,4\text{-}C_2B_5H_7$ with sodium naphthalide, $FeCl_2$, NaC_5H_5, and O_2 produces $(\sigma\text{-}2,4\text{-}C_2B_5H_6)\text{-}(\pi\text{-}2,4\text{-}C_2B_4H_5)Fe^{III}(\pi\text{-}C_5H_5)$, with smaller quantities of $(\pi\text{-}C_5H_5)Fe^{II}H(\pi\text{-}2,4\text{-}C_2B_4H_6)$, $(\sigma\text{-}C_{10}H_7)\text{-}(\pi\text{-}2,4\text{-}C_2B_4H_5)Fe^{III}(\pi\text{-}C_5H_5)$, and $(\pi\text{-}C_5H_5)Fe^{III}(\pi\text{-}2,4\text{-}C_2B_4H_6)$. Treatment of $(\sigma\text{-}2,4\text{-}C_2B_5H_6)\text{-}(\pi\text{-}2,4\text{-}C_2B_4H_5)Fe^{III}(\pi\text{-}C_5H_5)$ with sodium amalgam followed by HCl generates primarily $(\pi\text{-}2,4\text{-}C_2B_4H_6)Fe^{II}H(\pi\text{-}C_5H_5)$ and a lesser amount of $(\sigma\text{-}2,4\text{-}C_2B_4H_6)\text{-}(\pi\text{-}2,4\text{-}C_2B_4H_5)Fe^{II}H(\pi\text{-}C_5H_5)$. The gas-phase reaction of $2,3\text{-}C_2B_4H_8$ with $Fe(CO)_5$ at 215° yields $(\pi\text{-}2,3\text{-}C_2B_4H_6)Fe(CO)_3$ and $(\pi\text{-}2,3\text{-}C_2B_5H_7)Fe(CO)_3$. The gas-phase copyrolysis of $2,4\text{-}C_2B_5H_7$ and $Fe(CO)_5$ at 280° yields $(\pi\text{-}2,4\text{-}C_2B_4H_6)Fe(CO)_3$ and $(\pi\text{-}C_2B_5H_7)Fe(CO)_3$. The structures have been elucidated from ^{11}B and ^1H nmr, infrared, and mass spectra and from an X-ray diffraction investigation of $(\pi\text{-}2,3\text{-}C_2B_3H_7)Fe(CO)_3$.

In earlier reports we have described the preparation of several individual small metallocarboranes of the transition and main-group metals from the open-cage carboranes $CH_3C_3B_3H_6$,[1] $C_2B_4H_8$,[2] and $C_2B_3H_7$.[3] These syntheses have employed either direct gas-phase reactions of neutral carboranes or interactions of carborane anions in solution. In recent studies, we have attempted to develop general synthetic routes to small metallocarboranes, which would permit the synthesis of particular cage systems and even specific isomers. The principal starting materials in this work have been polyhedral $2,4\text{-}C_2B_5H_7$[4] and the open-cage species $2,3\text{-}C_2B_4H_8$, which are the most accessible small carboranes and also offer the advantage that the former compound leads to metallocarboranes having nonadjacent cage carbon atoms while the latter species generates adjacent-carbon isomers. We report elsewhere[5] the preparation of a series of cobaltacarboranes having three to six boron atoms from $C_2B_5H_7$ and $C_2B_4H_6$. This paper deals with the synthesis and chemistry of a family of structurally related small ferracarboranes in which several different synthetic approaches have been employed.[6,7]

Results and Discussion

Preparation of Ferracarboranes from $NaC_2B_4H_7$. Previous work[8] has disclosed that the $C_2B_4H_7^-$ anion, obtained from $2,3\text{-}C_2B_4H_8$ by treatment with NaH, undergoes bridge-insertion reactions with group IV organohalides to produce $\mu\text{-}MR_3C_2B_4H_7$ species in which the M atom (Si, Ge, Sn, or Pb) is attached to the carborane cage *via* a three-center, two-electron B–M–B bond.[9] It appeared likely that similar bridge-insertions of transition metals could be effected with suitable reagents. We have reported in a communication[6b] that the reaction of π-cyclopentadienyliron dicarbonyl iodide with $Na^+C_2B_4H_7^-$ in tetrahydrofuran (THF) at 25° proceeds readily to give $\mu\text{-}[(\pi\text{-}C_5H_5)Fe(CO)_2]C_2B_4H_7$ (I). The proposed structure of I, a light yellow solid which survives brief exposure to air but hydrolyzes over a period of several hours, is given in Figure 1. The mass spectrum contains a cutoff at *m/e* 252 corresponding to the $^{12}C_9{}^{11}B_4{}^{56}Fe{}^{16}O_2{}^1H_{12}^+$ parent ion with groupings at 28 and 56 mass units below the parent group, indicating the loss of two CO fragments. The intensities in the parent region are close to those calculated for a FeB_4 species based on natural isotopic abundances. The 32.1-MHz ^{11}B nmr spectrum (Table I) exhibits a set of four doublets, two of which are nearly superimposed, arising from nonequivalent BH groups. The chemical shifts indicate that the essential cage structure of $C_2B_4H_8$ is present (*e.g.*, the resonance near δ +50 ppm is characteristic of the apex boron in $C_2B_4H_8$ derivatives[10]), and the absence of a singlet assignable to a terminal B–Fe bond locates the iron atom in a bridging position. The 100-MHz proton nmr spectrum of I (Table II) contains the expected cage C–H, C_5H_5, and $B\text{-}H_t$

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(1) J. W. Howard and R. N. Grimes, *Inorg. Chem.*, **11**, 263 (1972).

(2) R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan, and P. T. Greene, *J. Amer. Chem. Soc.*, **94**, 1865 (1972).

(3) D. A. Franz, V. R. Miller, and R. N. Grimes, *ibid.*, **94**, 412 (1972).

(4) The numbering system employed in this paper is that formulated by the IUPAC Commission on Nomenclature of Inorganic Chemistry: *Pure Appl. Chem.*, **30**, 683 (1972). This system clearly states the principle that cage heteroatoms (*e.g.*, carbon atoms in carboranes) are given the lowest possible numbers based on the parent boron skeleton (see Rule 7.1), and supersedes an earlier system (*Inorg. Chem.*, 7, 1945 (1968)) which is similar but has been subject to conflicting interpretations.

(5) (a) V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, **95**, 2830 (1973); (b) D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, and G. J. Palenik, *ibid.*, **95**, 3046 (1973).

(6) Preliminary communications on portions of this work have appeared: (a) R. N. Grimes, *ibid.*, **93**, 261 (1971); (b) L. G. Sneddon and R. N. Grimes, *ibid.*, **94**, 7161 (1972).

(7) Substantial work on large ferracarboranes has been reported by Hawthorne and coworkers: M. F. Hawthorne and G. B. Dunks, *Science*, **178**, 462 (1972); M. F. Hawthorne, *Pure Appl. Chem.*, **29**, 547 (1973), and references therein.

(8) (a) M. L. Thompson and R. N. Grimes, *Inorg. Chem.*, **11**, 1925 (1972); (b) A. Tabereaux and R. N. Grimes, *ibid.*, **12**, 792 (1973).

(9) Analogous insertions into the $C,C'\text{-}(CH_3)_2C_2B_4H_5^-$ ion to give Si- or Ge-bridged species have been described: C. G. Savory and M. G. H. Wallbridge, *Chem. Commun.*, 622 (1971); C. G. Savory and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 8/9, 918 (1972).

(10) T. P. Onak and J. Spielman, *J. Magn. Resonance*, **3**, 122 (1970).

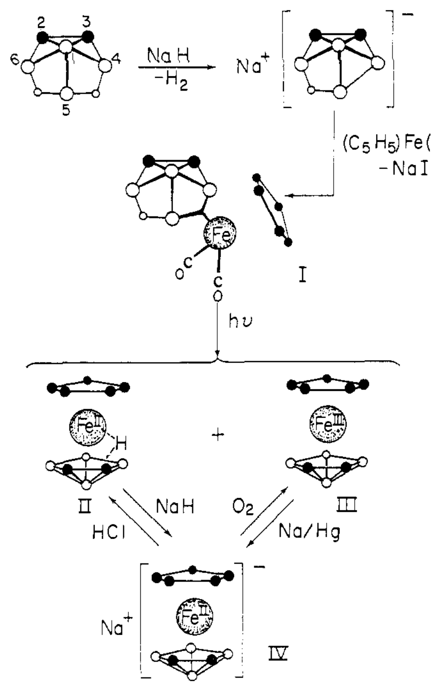

Figure 1. Reaction scheme for the synthesis and interconversion of sandwich complexes of the 2,3-$C_2B_4H_6^{2-}$ ligand, showing proposed structures of I–IV. The solid circles represent CH and the open circles BH groups. The location of the iron hydride hydrogen in II is suggested schematically; the presence of an Fe–H bond will probably cause the C_5H_5 and carborane rings to be skewed relative to each other.

Table I. 32.1-MHz ^{11}B Nmr Data

Compd	δ, ppm (J, Hz)[a]	Relative areas
I[b]	−16.4 (139), −3.2 (165), −1.6 (178), +52.0 (181)	1, 1, 1, 1
II[b]	+8.5 (167), +20.0 (153)	3, 1
III[b]	+154,[c] +281[d]	∼1.7, 1[e]
V[f]	−20.0 (170), −14.1 (180), −7.5 (163), +27.4 (173), +242, +314, +408	1, 1, 1, 2, 1, 1, 1.5[g]
VI[h]	−7.7 (162), +10.2 (155), +15.3 (161)	1, 1, 2
VII[h]	+221, +352, +489	∼1, 1, 1[e]
X[b]	−18.9 (160), −5.16 (150), +17.7 (160)	1, 2, 1
XI[b]	−4.90 (∼135)	
XII[i]	−17.8 (144), −10.9 (144)	1, 3
XIII[i]	−49.9 (142), −15.6 (140), −6.2 (140), +0.3 (145), +6.5 (130)	1, 1, 1, 1, 1

[a] Chemical shifts in ppm relative to $BF_3 \cdot O(C_2H_5)_2$. [b] CCl_4 solution. [c] $w_{1/2}$ = ∼375 Hz. [d] $w_{1/2}$ = ∼900 Hz. [e] Areas of extremely broad peaks could not be accurately measured. [f] Hexane solution. [g] Areas of three broad high-field peaks, assigned to $Fe^{III}C_2B_4$ cage, are approximate. [h] CH_2Cl_2 solution. [i] $CDCl_3$ solution.

Table II. 100-MHz ^1H Nmr Data

	δ, ppm (J, Hz)[a]				
Compd	C_5H_5	Carborane CH	H_{bridge}	Other	Relative areas
I	−4.83	−6.52	+0.91	−3.27 (147)[b] +0.98 (169)[b]	5, 2, 1[c]
II	−4.10	−4.82		+14.40[d]	5, 2, 1
III	−12.35[e]	+7.35		−3.35[f] −5.5[f] +10.6[f]	5, 2[c]
V	−14.4	−4.9 +57 +75		−1.9[f] +8.0[f]	5, 1, 1, 1[c]
VI	−3.80	−3.22		+7.80[d]	5, 2, 1
X		−5.58		−6.30 (152)[b] −4.87 (152)[b] −0.24 (160)[b]	2, 2, 1, 1
XI		−5.38	+3.7	−7.42 (126)[b] −3.70 (135)[b]	2, 2, 1, 2
XII[g]		−3.5			

[a] Chemical shifts relative to $(CH_3)_4Si$. All spectra except XII were obtained in CCl_4 solution. Except where otherwise indicated, H–^{11}B quartets are weak and/or masked by H–C resonances. [b] Quartet assigned to terminal H–^{11}B group. [c] Areas of H–B_t resonances not included. [d] Singlet assigned to Fe–H (or Fe–H–B) group. [e] $w_{1/2} \approx$ 300 Hz. [f] Broad humps assigned to Fe(III)-decoupled H–^{11}B resonances. [g] $CDCl_3$ solution.

Table III. Infrared Absorptions (cm^{-1})[a]

I	3120(w), 3025(m), 2580(s), 2010(vs), 1965(vs), 1450(s), 1420(s), 1395(m), 1350(m), 1320(m), 1265(m), 1070(m), 1055(s), 1000(s), 965(w), 945(w), 910(m), 890(s), 860(m), 830(s), 665(s), 640(s)
II	3100(w), 3050 (w), 2570 (vs), 1800(w), 1735(w), 1665 (w), 1410(m), 1265(s), 1210(w), 1150(sh, w), 1120(s), 1020(m, sh), 1005(s), 995(s), 950(m), 870(w), 865(m), 690(m), 677(s), 620(m)
III	3105(w), 3020(w), 2550(vs), 1820(w), 1750(w), 1670(w), 1420(s), 1350(w), 1260(s), 1195(m), 1107(m), 1005(s), 970(m), 900(w), 685(m), 670(s)
V[b]	3118(w), 3100(w), 3045(w), 2600(vs), 1831(w), 1766(w), 1681(w), 1384(m, sh), 1355(s), 1186(m), 1113(m), 1048 (m), 1034(m), 1011(m), 911(m), 864(m), 832(s), and 639(w)
VI[b]	3090(w), 3040(w), 2590(vs), 1815(w), 1670(w), 1460(m), 1360(m), 1240(w), 1210(w), 1130(m), 1110(w), 1012(s), 963(m), 910(w), 865(w), 835(m)
X	2590(vs), 2076(vs), 2017(vs), 1700(m), 1535(m, b), 1270 (s), 1180(m), 1090(m), 980(m, b)
XI	3008(m), 2570(vs), 1890(m–s), 1700(m), 1600(m), 1350 (m), 1050(m)
XII[c]	2590(s), 2090(vs), 2040(vs), 1160(m), 1050(m), 920(w), 870(m), 710(m), 610(m)
XIII	2580(s), 2080(vs), 2030(vs), 1160(w), 1105(m), 1065(w), 1035(w)

[a] CCl_4 solution *vs.* CCl_4, except where otherwise indicated. [b] CH_2Cl_2 solution *vs.* CH_2Cl_2. [c] Gas phase.

and B–H–B resonances. The C–H peak is a broad singlet rather than the doublet expected for nonequivalent cage CH groups, an effect which has been frequently observed in the proton nmr spectra of $C_2B_4H_8$ derivatives.[8,9] The infrared spectrum presented in Table III contains the expected terminal BH, bridging BH, terminal CH, and CO stretching bands.

Ultraviolet irradiation of I produces two new complexes in comparable quantity, with a total yield of >90%. These compounds have been formulated as "sandwich" complexes, $(\pi\text{-}C_5H_5)Fe^{II}H(\pi\text{-}2,3\text{-}C_2B_4H_6)$ (II) and $(\pi\text{-}C_5H_5)Fe^{III}(\pi\text{-}2,3\text{-}C_2B_4H_6)$ (III), depicted in Figure 1. The mass spectra of II and III contain parent ion peaks at *m/e* 196 and 195, respectively, and intensity profiles consistent with FeB_4 species. The spectrum of II reflects some hydrogen abstraction from the parent ion, as does its isomer $(\pi\text{-}C_5H_5)$-$Fe^{II}H(\pi\text{-}2,4\text{-}C_2B_4H_6)$, discussed below. Confirmation of the empirical formulas is given by an exact mass measurement of III (calcd for $^{56}Fe^{12}C_7{}^{11}B_4{}^1H_{11}$, 195.058; found, 195.060). The ^{11}B nmr spectrum of II (Table I) is typical of metallocarboranes containing a pentagonal pyramidal $C_2B_4H_6^{2-}$ ligand π bonded to the metal, but the spectrum is consistent with either of two isomeric structures incorporating the 2,3-

$C_2B_4H_6^{2-}$ or 2,4-$C_2B_4H_6^{2-}$ ligands. However, II is unambiguously identified as the 2,3 isomer based on its derivation from 2,3-$C_2B_4H_8$ and the fact that the alternative isomer, (π-C_5H_5)FeH(π-2,4-$C_2B_4H_6$), with nonadjacent cage carbon atoms has been prepared from 2,4-$C_2B_5H_7$ as described below. The ^1H nmr spectrum of II exhibits the expected C_5H_5 and carborane CH peaks as well as a broad resonance at higher field which is attributed to a proton associated with the iron atom. This high-field peak is in the region typical of transition metal–hydrogen bonds and is further upfield from tetramethylsilane than resonances arising from B–H–B bridging protons normally occur. However, some degree of interaction between the hydrogen bonded to the iron and the carborane cage ligand seems intuitively likely, possibly involving rapid proton tautomerism between four-center bridge bonds utilizing the two FeB_2 triangles on the polyhedral surface. Some chemical consequences of this proton are described below.

Compound III, a brown crystalline odd-electron species having one electron fewer than the diamagnetic II, is regarded as a complex of iron(III) and as expected is paramagnetic. The epr spectrum at −196° contains a very broad single peak which has not been unambiguously interpreted, but a measurement of the magnetic moment has given $\mu = 2.1$, corresponding to a low-spin d^5 system, with a temperature dependence typical of Fe(III) complexes of near-octahedral symmetry.[11] The ^{11}B and ^1H nmr spectra contain widely separated broad singlets indicative of collapse of the H–B coupling, typical of paramagnetic boron cage compounds. Although these spectra *per se* are not particularly informative, the proposed sandwich structure of III (Figure 1) is supported by the facile and reversible interchange of II and III as reported in the following section.

Interconversion of Fe(II) and Fe(III) Sandwich Complexes. The reaction of II with sodium hydride in THF releases a mole equivalent of H_2 and yields an orange solution of $Na^+[(\pi\text{-}C_5H_5)Fe^{II}(C_2B_4H_6)]^-$ (IV) which on air-oxidation generates III rapidly and in high yield. These processes are reversible, since treatment of III with sodium amalgam and subsequent addition of HCl regenerates II as shown in Figure 1. The orange intermediate IV has not been isolated, but a sandwich structure analogous to II and III can be inferred from its redox and acid–base relationship to these species. Although direct air-oxidation of II to III in the solid state has not been observed, some III is formed during thin-layer chromatography of II on basic silica gel. Both compounds may be handled in air for periods of a few hours without noticeable decomposition, but exposure for several days results in degradation, that of III being the more rapid.

Preparation of Ferracarboranes from 2,4-$C_2B_5H_7$. In a recent study in this laboratory[5a] it was found that the reaction of 2,4-$C_2B_5H_7$ with sodium naphthalide, cobaltous chloride, and sodium cyclopentadienide with subsequent air-oxidation (a procedure originally developed by Hawthorne, *et al.*, for large metallocarboranes[7]) yields an extensive series of cobaltacarborane sandwich complexes. In contrast, we find that an analogous procedure employing ferrous chloride in place of the cobalt salt forms primarily (σ-2,4-$C_2B_5H_6$)-(π-2,4-$C_2B_4H_5$)Fe^{III}(π-C_5H_5) (V) with smaller quantities of (π-C_5H_5)Fe^{II}H(π-2,4-$C_2B_4H_6$) (VI, isomer of II) and (σ-$C_{10}H_7$)-(π-2,4-$C_2B_4H_5$)Fe^{III}(π-C_5H_5) (VII), a naphthyl-substituted species. The reaction is illustrated schematically in Figure 2. Surprisingly, the parent iron(III) species, (π-2,4-$C_2B_4H_6$)-Fe^{III}(π-C_5H_5) (VIII, an isomer of III), is obtained only in trace quantity. Since VIII may reasonably be assumed to form initially in substantial amount, the formation of the linked-cage complex V is attributed to a subsequent cage-coupling process involving VIII and a $C_2B_5H_6^-$ ion produced by deprotonation of the $C_2B_5H_7$ starting material.[12] Coupling reactions of this sort have been encountered in cobaltacarborane chemistry[5a] also, suggesting that this may be a general phenomenon deserving further investigation.

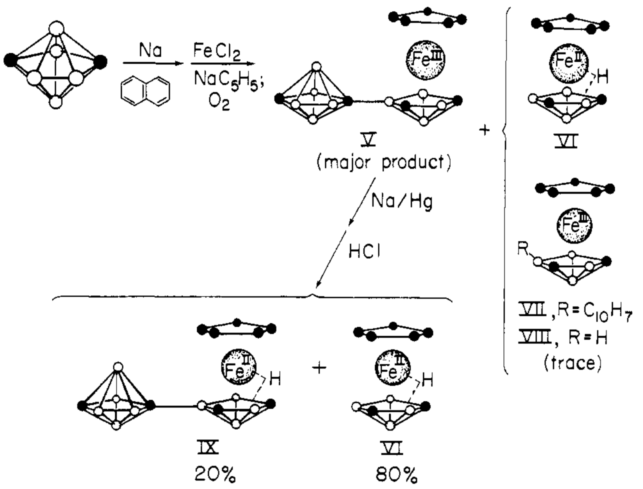

Figure 2. Reaction scheme for the synthesis of sandwich complexes of the 2,4-$C_2B_4H_6^{2-}$ ligand. The position of ligand attachment in VII has not been established, and the structure of IX has been inferred from mass spectroscopic evidence and its formation from V.

The products V–VII have been characterized from their nmr, infrared, and mass spectra, but only mass spectra are available for the trace product VIII, for which the structure having nonadjacent cage carbons (Figure 2) is presumed on the basis of its synthesis from 2,4-$C_2B_5H_7$. The mass spectra of VI and VIII are nearly identical with those of their respective isomers II and III, described above, and the spectra of all of the compounds contain strong parent peaks and intensity patterns consistent with the compositions indicated. The spectra of the iron hydride complexes II and VI exhibit substantial hydrogen loss in the parent region (Figure 3, bottom), in contrast to the normal metallocarborane spectra in which the intensities reflect isotope distribution but little or no hydrogen abstraction, as illustrated for VIII (Figure 3, top).

The ^{11}B nmr spectrum of V (Figure 4) is interesting in that, while the expected paramagnetism is manifested by the broad, widely separated resonances

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[11] We thank Professor Arthur Brill and Dr. Nick Hill for the epr spectrum and Professor Ekkehard Sin for the magnetic susceptibility measurements, which were obtained in the laboratory of Professor Harry Gray at the California Institute of Technology.

[12] R. R. Olsen and R. N. Grimes, *J. Amer. Chem. Soc.*, **92**, 5072 (1970).

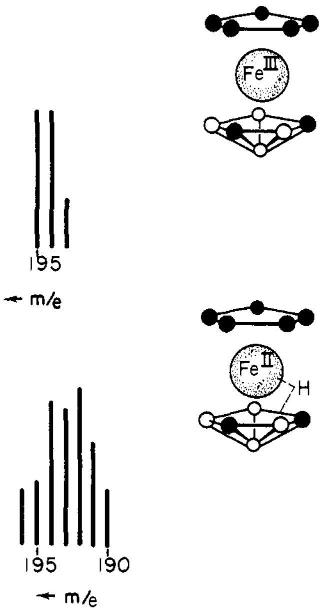

Figure 3. Partial mass spectra of (π-C_5H_5)Fe^{III}(π-2,4-$C_2B_4H_6$) (VIII, top) and (π-C_5H_5)$Fe^{II}H$(π-2,4-$C_2B_4H_6$) (VI, bottom).

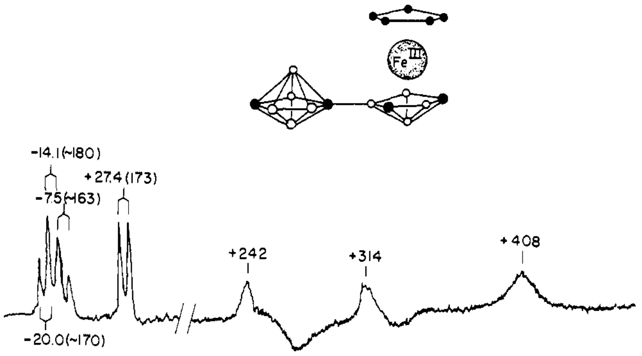

Figure 4. A 32.1-MHz ^{11}B nmr spectrum of (σ-2′,4′-$C_2B_5H_6$)-(π-2,4-$C_2B_4H_5$)Fe^{III}(π-C_5H_5) (V) in hexane solution. Chemical shifts are in ppm relative to $BF_3 \cdot O(C_2H_5)_2$ and coupling constants are in parentheses.

arising from the boron atoms in the metallocarborane cage, the BH groups in the σ-bonded $C_2B_5H_6$ ligand give peaks of normal width and chemical shift values, closely resembling the spectrum of 2,4-$C_2B_5H_7$. Thus, the resonance-broadening and decoupling effects of the paramagnetic iron(III) atom are confined to its own cage system, and the ligand cage is insulated from the metal by the intercage σ bond. The ^{11}B nmr spectrum indicates that all boron atoms in the $C_2B_5H_6$ ligand are bonded to terminal hydrogens and that the FeC_2B_4 cage contains at least three different boron environments as shown by the three high-field peaks. The ^1H nmr spectrum exhibits two singlets at very high field, attributed to nonequivalent CH groups in the ferracarborane polyhedron; the singlet at low field is assigned to a CH unit in the $C_2B_5H_6$ ligand. These observations suggest the structure indicated in Figure 4, which is analogous to a previously prepared[5a] linked-cage cobalt complex, (σ-$C_2B_5H_6$)-(π-2,4-$C_2B_4H_5$)Co^{III}(π-C_5H_5).

The ^{11}B and ^1H nmr spectra of VI closely resemble, but are not identical with, the spectra of the isomeric complex II. As is usual among carboranes and metallocarboranes, the isomer having nonvicinal carbon atoms, VI, is more volatile than II, presumably reflecting the smaller dipole moment which is expected for VI. The ^{11}B nmr spectrum of VII consists of extremely broad singlets exhibiting large chemical shifts, as expected for a paramagnetic species, and the signals in the ^1H nmr spectrum were so broad as to be virtually undetectable. The position of naphthyl substitution on the cage cannot be uniquely established from these data, but in the analogous cobalt(III) compound[5a] the most probable location is at B(5) as indicated in Figure 2.

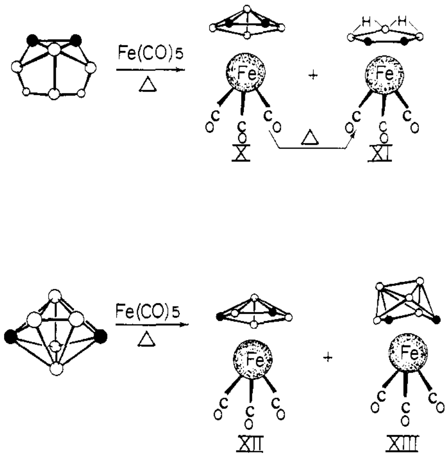

Figure 5. Reaction scheme for the synthesis of ferracarborane carbonyls from $C_2B_4H_8$ and $C_2B_5H_7$.

Reaction of (σ-2,4-$C_2B_5H_6$)-(π-2,4-$C_2B_4H_5$)Fe^{III}(π-C_5H_5) with Sodium Amalgam and HCl. The reduction of the linked iron(III) species V with sodium amalgam in THF followed by treatment with anhydrous HCl yields a minor product whose mass spectrum is consistent with the expected iron(II) hydride linked complex (σ-$C_2B_5H_6$)-(π-2,4-$C_2B_4H_5$)$Fe^{II}H$(π-C_5H_5) (IX), but the reduction is accompanied by extensive cleavage of the intercage link, leading to the previously described parent species VI as the principal product (Figure 2).

Synthesis of Ferracarborane Carbonyls from $C_2B_4H_8$ and $C_2B_5H_7$. The volatility and high reactivity of iron pentacarbonyl suggested that gas-phase reactions of this material with volatile open-cage carboranes such as $C_2B_4H_8$ would be a likely route to iron carborane cage compounds. Initial attempts involving copyrolysis of $Fe(CO)_5$ with $C_2B_4H_8$ in sealed bulbs failed due to rapid decomposition of the $Fe(CO)_5$ before significant reaction with the carborane could occur. However, when $C_2B_4H_8$ is heated at 240° in a vertical hot–cold reactor containing a pool of liquid $Fe(CO)_5$ maintained at 25°, substantial quantities of two volatile ferracarboranes are obtained (Figure 5). The mass spectra of these materials identify them as (π-$C_2B_4H_6$)$Fe(CO)_3$ (X) and (π-$C_2B_3H_7$)$Fe(CO)_3$ (XI), with cutoffs at *m/e* 214 and 204, respectively, and intensity patterns corresponding to the natural isotope distributions for FeB_4 and FeB_3 species. The successive loss of three CO groups is clearly evident in each spectrum.[6a]

The ^{11}B and ^1H nmr spectra of X are typical of pentagonal bipyramidal (π-$C_2B_4H_6$)M complexes[2,5a,6] and support the structure suggested in Figure 6. As was the case with the isomers of (π-C_5H_5)Fe(π-C_2-

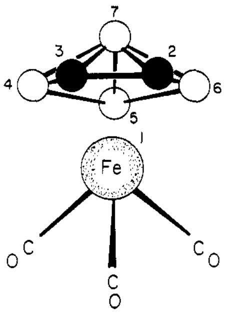

Figure 6. Proposed structure of (π-2,3-$C_2B_4H_6$)Fe$(CO)_2$ (X).

B_4H_6), discussed above, X can be unambiguously identified as the 2,3 (adjacent carbon) isomer by virtue of the fact that the 2,4 isomer has been prepared independently from 2,4-$C_2B_5H_7$ (*vide infra*).

The indicated formula of ($C_2B_3H_7$)Fe$(CO)_3$ for XI was intriguing and appeared to represent a new class of metallocarboranes containing cyclocarboranyl ligands. Since a formal $C_2B_3H_7^{2-}$ ligand would be isoelectronic with the cyclic planar $C_5H_5^-$ ion, a metallocene-like structure containing a cyclic $C_2B_3H_7^{2-}$ unit with two B–H–B bridges and π-bonded to a Fe$(CO)_3^{2+}$ moiety was postulated.[6a] The ^{11}B and ^{1}H nmr spectra support such a geometry, particularly in view of the absence of a distinct ^{11}B resonance which would normally be expected for an apex boron atom. This structure, depicted in Figure 7, has been confirmed in an X-ray diffraction study[13] which established that the C_2B_3 ring is completely planar with all ring–metal distances equal. This geometry is consistent with metallocene-type bonding in which the $C_2B_3H_7^{2-}$ ligand contains six delocalized electrons in bonding molecular orbitals extending around the five-membered ring; indeed, XI is an isostructural as well as isoelectronic analog of the (π-C_5H_5)Fe$(CO)_3^+$ ion.

Compound XI is more thermally stable than the polyhedral species X, as shown by the partial conversion of X to XI at 250° in the mass spectrometer. This is an unusual observation since closo borane and carborane systems normally exhibit higher stability than the open-cage or nido systems. However, a similar situation exists in cobaltacarborane chemistry, in that a main product of the degradation of (π-$C_2B_4H_6$)Co(π-C_5H_5) in aqueous base is (π-$C_2B_3H_7$)Co(π-C_5H_5)[14] presumably a structural analog of XI. Although a $C_2B_3H_7^{2-}$ ion has not been isolated, when complexed to metals this ligand and its bridge-deprotonated derivative[5b] $C_2B_3H_5^{4-}$ are particularly stable ring systems which are expected to play an extensive role in the chemistry of small metallocarboranes.

The reaction of *closo*-2,4-$C_2B_5H_7$ with Fe$(CO)_5$ in a hot–cold reactor at 270/25° produces (π-2,4-$C_2B_4H_6$)Fe$(CO)_3$ (XII), isomeric with X, in substantial yield, as well as a smaller amount of (π-$C_2B_5H_7$)Fe$(CO)_3$ (XIII). This synthesis is a rare example of the direct insertion of a metal into a polyhedral cage without a prior discrete cage-opening step such as base degradation or reduction with sodium[15] and can be described as a gas-phase polyhedral expansion.[16] In addition to XII and XIII, trace quantities of several other products are obtained, which have been tentatively identified from mass spectral analysis as ($C_2B_5H_7$)$Fe_2(CO)_6$, ($C_2B_6H_8$)$Fe_2(CO)_6$, and $(C_2B_5H_7)_2$FeH. Further study of these materials has been precluded by the extremely small yields. Compound XII has been characterized from its mass spectrum, which contains a cutoff at *m/e* 214 and is nearly identical with that of X, and its ^{11}B and ^{1}H nmr spectra, which support the structure as depicted in the reaction scheme (Figure 5). The mass spectrum of XIII exhibits a cutoff at *m/e* 226, corresponding to the $^{12}C_5{}^{11}B_5{}^{56}Fe{}^{16}O_3{}^1H_7^+$ parent peak, and a pattern of intensities corresponding closely to those calculated for a B_5Fe species. The ^{11}B nmr spectrum suggests a cage structure containing five magnetically nonequivalent boron atoms, one of which is assigned to a four-coordinate vertex adjacent to the metal.[5a] The ^{1}H nmr spectrum is basically uninformative, consisting of overlapped broad humps in which the H–C resonances cannot be clearly identified. Assuming a dodecahedral cage similar to other eight-atom carborane and metallocarborane polyhedra, the structure of XIII is proposed to be (π-(4)-1,8-$C_2B_5H_7$)Fe$(CO)_3$, as shown in Figure 8. This compound is thus an apparent structural analog of (π(4)-1,8-$C_2B_5H_7$)(Co)(π-C_5H_5),[5a] whose ^{11}B nmr spectrum is in fact strikingly similar to that of XIII.

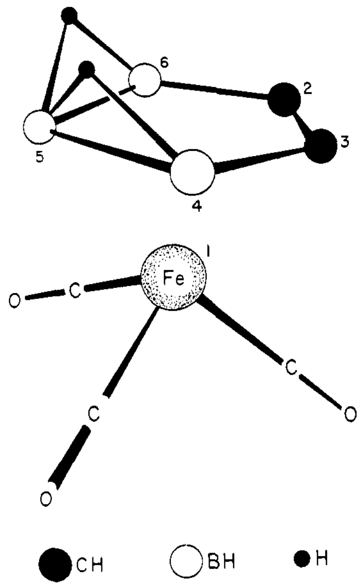

Figure 7. Established structure of (π-2,3-$C_2B_3H_7$)Fe$(CO)_3$ (XI).

Summary. This work describes several different synthetic routes to small ferracarboranes, employing the open-cage $C_2B_4H_8$ and polyhedral $C_2B_5H_7$ systems and utilizing both direct gas-phase reactions and metal ion insertion into carborane anions. The emphasis in this investigation has been on synthesis and structural characterization of novel metallocarborane species and no attempt has been made to optimize yields or to develop large-scale syntheses. Of the metallocarboranes produced, those containing the formal

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(13) J. P. Brennan, R. N. Grimes, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, in press.

(14) V. R. Miller and R. N. Grimes, manuscript in preparation.

(15) Direct insertion of Ni, Pd, and Pt into *closo*-$(CH_3)_2C_2B_9H_9$ in toluene solution has been reported: J. L. Spencer, M. Green, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1178 (1972).

(16) Recent work has shown that similar gas-phase metal insertions occur with other closo carboranes: L. G. Sneddon and R. N. Grimes, to be submitted for publication.

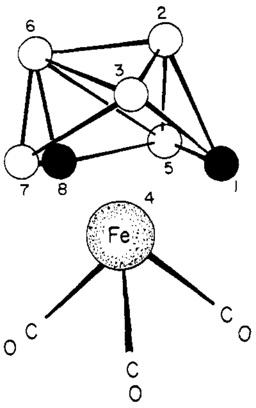

Figure 8. Proposed structure of $[\pi\text{-}(4)\text{-}1,8\text{-}C_2B_5H_7)]Fe(CO)_3$ (XIII).

2,3- and 2,4-$C_2B_4H_6^{2-}$ ligands or their derivatives are dominant, with the 2,3 isomers formed from $C_2B_4H_8$ and the 2,4 species from $C_2B_5H_7$. The ferracarborane carbonyls obtained in these studies are potential precursors to a variety of other complexes since metal-bonded carbonyl groups typically are readily replaced by other ligands;[17] indeed, preliminary studies[18] indicate that $(C_2B_3H_7)Fe(CO)_3$ reacts easily with butadiene to give a series of $(C_2B_3H_7)Fe(C_4H_6)_m(CO)_n$ species in which m = 1–3 and n = 0–2. In addition, it is reasonable to expect that the $(C_2B_4H_6)Fe(C_5H_5)$ complexes can be converted by base hydrolysis to $(C_2B_3H_7)Fe(C_5H_5)$, and probably to triple-decked $(C_5H_5)Fe(C_2B_3H_5)Fe(C_5H_5)$ species also, since such transformations occur readily with the analogous $(C_2B_3H_7)Co(C_5H_5)$ system.[5b] Thus, an extensive and versatile small ferracarborane chemistry seems accessible, and, by the choice of appropriate carborane starting materials, ligands, and synthetic route, it should be possible to systematically prepare specifically designed ferracarborane organometallic derivatives. Such extensions of the present work are under active investigation.

Experimental Section

Materials. Dicarbahexaborane(8) $(C_2B_4H_8)$ and solutions of $NaC_2B_4H_7$ in tetrahydrofuran (THF) were prepared as described elsewhere.[19,20] Dicarba-*closo*-heptaborane (7) $(C_2B_5H_7)$ was obtained from Chemical Systems, Inc., and purified by glpc (30% Apiezon-L on Chromosorb-W at 41°). Cyclopentadienyliron tricarbonyl iodide (Alfa), hydrogen chloride (Matheson), iron pentacarbonyl (Alfa), and naphthalene (Fisher) were used as received. Anhydrous iron(II) chloride was prepared from chlorobenzene and iron(III) chloride by a procedure described earlier.[21] Cyclopentadiene was distilled from dicyclopentadiene (Aldrich). All solvents were reagent grade, and THF was dried over lithium hydride before use.

Instrumentation. Boron-11 and proton nmr spectra were obtained on a Varian HA-100 nmr spectrometer, infrared spectra were obtained on a Beckman IR-8 instrument, and mass spectra were recorded on Hitachi Perkin-Elmer RMU-6E and AEI MS-902 mass spectrometers.

Procedure. Except where otherwise indicated, all reactons were run in high-vacuum systems or in an inert atmosphere. Thin-layer and column chromatography were conducted on silica gel in air.

μ-[(π-C_5H_5)Fe(CO)$_2$]$C_2B_4H_7$. In a typical reaction, a solution of 2.6 mmol of $NaC_2B_4H_7$ in 10 ml of THF was added dropwise under nitrogen to a solution of 2.6 mmol of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ in 10 ml of THF. The mixture was allowed to react for 4 hr at 25°. The reaction was then exposed to the air and filtered, and the solvent was removed. The residue was chromatographed on a silica gel column. Hexanes eluted $\mu\text{-}[(\pi\text{-}C_5H_5)Fe(CO)_2]C_2B_4H_7$, a bright yellow moderately air-sensitive solid. Due to decomposition on the column, precise yield data could not be obtained, but the estimated yield was at least 50%.

(π-C_5H_5)FeH(π-2,3-$C_2B_4H_6$) and (π-C_5H_5)Fe(π-2,3-$C_2B_4H_6$). A solution of *ca.* 0.7 mmol of $\mu\text{-}[(\pi\text{-}C_5H_5)Fe(CO)_2]C_2B_4H_7$ in 10 ml of THF was added to a quartz reaction flask under vacuum and irradiated for 12 hr with stirring at 30°. The flask was opened, the solvent removed, and the residue chromatographed on a silica gel column. Carbon tetrachloride eluted two bands: red-orange $(\pi\text{-}C_5H_5)FeH(\pi\text{-}C_2B_4H_6)$ (45.3 mg, 0.23 mmol) and brown $(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_2B_4H_6)$ (82.1 mg, 0.42 mmol). No other products were detected.

Conversion of (π-C_5H_5)FeH(π-2,3-$C_2B_4H_6$) to (π-C_5H_5)Fe(π-2,3-$C_2B_4H_6$). A solution of $(C_5H_5)FeH(C_2B_4H_6)$ (45.3 mg, 0.23 mmol) in THF was added dropwise to a solution of sodium hydride (0.50 mmol, 56% mineral oil dispersion) in THF (5 ml) under nitrogen. Vigorous bubbling occurred at once and the solution changed from red-orange to light orange. After 10 min this solution was filtered under nitrogen. Upon exposure to air the solution immediately turned a dark brown color characteristic of $(C_5H_5)Fe(\pi\text{-}2,3\text{-}C_2B_4H_6)$. Purification of the product on a silica gel column yielded 33.1 mg (0.17 mmol, 73% yield) of $(\pi\text{-}C_5H_5)Fe(\pi\text{-}2,3\text{-}C_2B_4H_6)$, identified from its ir spectrum and tlc R_f value.

Conversion of (π-C_5H_5)Fe(π-2,3-$C_2B_4H_6$) to (π-C_5H_5)FeH(π-2,3-$C_2B_4H_6$). A solution of $(\pi\text{-}C_5H_5)Fe(\pi\text{-}2,3\text{-}C_2B_4H_6)$ (72.6 mg, 0.37 mmol) in 10 ml of THF was added to 2 ml of sodium amalgam containing 1.70 mmol of Na, under an atmosphere of nitrogen. Within 20 min the solution had changed from dark brown to light orange. The solution was then decanted and filtered under nitrogen. The solvent was removed under vacuum and 0.60 mmol of HCl was added. After a reaction period of 10 min, fractionation of the volatiles showed that 0.34 mmol of HCl remained. The residue was chromatographed on a silica gel column to yield 23.3 mg (0.12 mmol, 31%) of $(\pi\text{-}C_5H_5)FeH(\pi\text{-}2,3\text{-}C_2B_4H_6)$ which was identified from its ir and boron-11 nmr spectra and its tlc R_f value.

Preparation of Cyclopentadienyl Ferracarborane Complexes from 2,4-$C_2B_5H_7$. In a typical experiment, 22 mmol of cyclopentadiene was distilled *in vacuo* into a 100-ml flask containing 20 mmol of finely divided sodium in 20 ml of THF and the mixture was stirred at room temperature for 4 hr, during which all of the sodium was consumed. $C_2B_5H_7$ (5.0 mmol) was distilled *in vacuo* into a separate 100-ml flask containing 10 mmol of sodium and 10 mmol of naphthalene in 15 ml of THF, and the mixture was allowed to react at 25° for 10 hr. The carborane and NaC_5H_5 solutions were taken into a drybox and transferred to a pressure-equalized addition funnel. The addition funnel was fitted to a 100-ml two-neck flask containing 12.5 mmol of $FeCl_2$ in 20 ml of THF, and the solution was added dropwise over 20 min. Almost immediately the iron chloride–THF slurry turned dark and gas evolved. The reaction was stirred overnight at 25° under a nitrogen atmosphere, after which the reaction was opened to air for 1–2 hr and the solvent removed *in vacuo*. The resulting residue was extracted with hexane followed by benzene. After removal of solvent from the hexane extract, the resulting crude dark orange reaction product was applied to a 2.25 cm × 50 cm liquid-phase chromatographic column packed with 70–230 mesh silica gel and eluted with hexane. The first red band, $(\pi\text{-}C_5H_5)FeH(\pi\text{-}2,4\text{-}C_2B_4H_6)$ (VI), was collected, and the solvent was removed. The product was further purified (to remove naphthalene impurity) by thin-layer chromatography using pentane as the eluent, with 10 mg of pure red-orange compound ultimately obtained.

The benzene extract from above was applied to a silica gel column and eluted with hexane. An orange band that proved to be ferrocene eluted first followed by a bright green band, $(\sigma\text{-}2,4\text{-}C_2B_5H_6)\text{-}(\pi\text{-}2,4\text{-}C_2B_4H_5)Fe(\pi\text{-}C_5H_5)$ (V), and a slower moving brown band containing $(\sigma\text{-}C_{10}H_7)\text{-}(\pi\text{-}2,4\text{-}C_2B_4H_5)Fe(\pi\text{-}C_5H_5)$ (VII) and $(\pi\text{-}C_5H_5)Fe(\pi\text{-}2,4\text{-}C_2B_4H_6)$ (VIII). Compounds V, VII, and VIII were further purified by repeated thin-layer chromatography with hexane, giving ultimately 30 mg of pure lime green V, ~1 mg of green VII, and <1 mg of brown VIII, Substantial losses of products were incurred during the chromatographic separation, so that the yields of pure products do not in this case represent an accurate indication of the actual reaction yields.

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Reaction of (σ-2,4-$C_2B_4H_6$)-(π-2,4-$C_2B_4H_5$)Fe^{III}(π-C_5H_5) with Na/Hg and HCl. Under a nitrogen atmosphere a tenfold excess of sodium amalgam was added *via* a pressure-equalized addition funnel to 12 mg (0.04 mmol) of compound V in 10 ml of THF. Upon agitation the lime green solution turned light orange. After 30 min the THF layer was separated and reduced in volume to give a dull orange residue. Excess anhydrous gaseous HCl was then expanded into the reaction flask and the reaction was allowed to proceed for 30 min. After removal of HCl, the resulting crude product was extracted with pentane and solvent was removed at reduced pressure. The compounds IX and VI reported above were obtained from this residue by thin-layer chromatography. Compound VI eluted before compound IX in hexane. The relative yields of VI and IX were estimated as 4:1.

Reaction of 2,3-$C_2B_4H_8$ with $Fe(CO)_5$. Typically, 3.24 mmol of $Fe(CO)_5$ was distilled into an evacuated cylindrical Pyrex reactor which was 24 mm in diameter and connected to the vacuum line by a greaseless Teflon stopcock containing a Viton O-ring. While a liquid nitrogen trap was maintained on the reactor, 3.10 mmol of $C_2B_4H_8$ was added by distillation and the stopcock was closed. The reactor was warmed to room temperature, a heating tape controlled by a Variac was wrapped around the central portion of the reactor, and the reactor was clamped in a vertical position such that the bottom section containing a pool of liquid $Fe(CO)_5$ was immersed in a dewar flask of water at 25°. The heating tape was maintained at 215–245° for 24 hr during which substantial dark nonvolatile deposits, including metallic iron, were deposited on the reactor walls. Following the reaction the reactor was cooled to $-196°$; noncondensables ($\sim$3 mmol) were pumped off and the remaining volatiles were distilled through a $-45°$ trap which allowed $Fe(CO)_5$, $C_2B_5H_7$, and unreacted $C_2B_4H_8$ to pass through. The $-45°$ condensate consisted of two components which were separated by repeated fractionation through a $-23°$ trap. The condensate at $-23°$ consisted of (π-2,3-$C_2B_4H_6$)$Fe(CO)_3$ (X), a yellow-orange liquid, and the more volatile fraction was (π-2,3-$C_2B_3H_7$)$Fe(CO)_3$ (XI), a pale yellow liquid. Owing to the difficulties of separation by trap-to-trap fractionation, yields of the pure compounds have not been determined but are estimated to be 5–10% each.

Conversion of (π-2,3-$C_2B_4H_6$)$Fe(CO)_3$ to (π-2,3-$C_2B_3H_7$)$Fe(CO)_3$ in the Mass Spectrometer. In repeated experiments, nearly pure samples of X vapor (containing <2% XI) were introduced into the gas inlet section of the mass spectrometer, maintained at 250°. The first spectra produced immediately upon introduction of the sample contained a strong parent envelope of X (cutoff at *m/e* 214) with peaks of very weak intensity coresponding to XI (cutoff at *m/e* 204). Spectra taken over the next 10 min on the same gas sample showed a rapid buildup of XI and decline of X, with the last spectra indicting virtually pure XI.

Reaction of 2,4-$C_2B_5H_7$ with $Fe(CO)_5$. A hot–cold reactor of the type described above was charged with 3.2 mmol of $C_2B_5H_7$ and 5.2 mmol of $Fe(CO)_5$, and the central portion heated to 280° for 15 hr during which time the lower end was maintained at 25°. Following removal of noncondensables and unreacted starting materials, the two principal products, which were retained in a $-35°$ trap, were separated by repeated fractionation through a trap at $-23°$ to give 20 mg (0.10 mmol) of orange (π-2,4-$C_2B_4H_6$)-$Fe(CO)_3$ (XII) and 14 mg (0.063 mmol) of orange (π-(4)-1,8-$C_2B_4H_7$)$Fe(CO)_3$ (XIII). A total of 1.0 mmol of $C_2B_5H_7$ was recovered.

Acknowledgment. This work was supported by the Office of Naval Research.

Nuclear Magnetic Resonance Studies of the Stereochemically Nonrigid Molecules B_6H_{10}, 2-$CH_3B_6H_9$, and 2-BrB_6H_9. Tautomerism of Bridging Hydrogens and the Influence of Substituents on the Position of the Basal Boron–Boron Bond in the Static Structures Observed at Low Temperature

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Abstract: Variable-temperature pmr and boron-11 nmr spectra of hexaborane(10), 2-methylhexaborane(10), and 2-bromohexaborane(10) are presented. At sufficiently low temperatures, spectra are observed which establish the presence of structures in which bridge protons are static; furthermore, the hexaborane(10) spectra thus obtained are fully consistent with its known solid-state structure as determined by X-ray diffraction (C_s symmetry) and demonstrate that the chemical shift equivalence of the basal atoms at higher temperatures (consistent with C_{5v} symmetry) is the result of time averaging due to a rapid intramolecular migration of bridging hydrogens about the base of the pyramidal molecule. The structures of 2-$CH_3B_6H_9$ and 2-BrB_6H_9 have been deduced from their nmr spectra which are related to the spectra of B_6H_{10}. The tautomerism of bridging hydrogens is rapid on the nmr time scale at ambient temperature for each derivative and involves all bridging sites; however, at intermediate temperatures, not all sites are involved. At low temperature a static structure with no mirror plane of symmetry is inferred for each derivative. The position of the basal boron–boron bond in the static structure is apparently influenced by the inductive effect of the substituent.

The pmr[1] and boron-11 nmr[2] spectra of B_6H_{10} are consistent with a pentagonal pyramidal structure of C_{5v} symmetry in solution while the solid-state structure I, determined by X-ray diffraction,[3] exhibits only C_s symmetry. Resolving this apparent discrep-

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