Organotransition-Metal Metallacarboranes. 5.[1a] Studies on (η^6-Arene)(carborane)iron Complexes of Benzene and Biphenyl. Crystal Structures of (η^6-C_6H_5–C_6H_5)Fe($Et_2C_2B_4H_4$) and 1,2-[(η^6-C_6H_6)Fe($Et_2C_2B_4H_3$)]$_2$CH(CH_3)CH_2, a Hydrocarbon-Linked Bis(ferracarborane)

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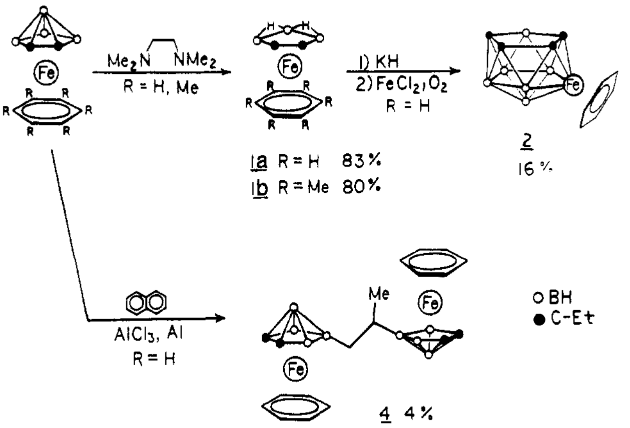
The reaction of *closo*-1,2,3-(η^6-C_6R_6)Fe($Et_2C_2B_4H_4$) (R = H, Me) with 1,2-$(NMe_2)_2(CH_2)_2$ gave *nido*-(η^6-C_6R_6)Fe($Et_2C_2B_3H_5$) species in high yield. Bridge deprotonation of the nido product (R = H) with KH followed by metal-promoted oxidative fusion formed (η^6-C_6H_6)Fe($Et_4C_4B_6H_6$), which was structurally characterized from two-dimensional (2-D) ^{11}B–^{11}B NMR spectra and X-ray evidence as an 11-vertex FeC_4B_6 cage. Treatment of (η^6-C_6H_6)Fe($Et_2C_2B_4H_4$) with naphthalene over Al and $AlCl_3$ gave several low-yield products, one of which was characterized by X-ray diffraction as a 1,2-bis((arene)ferracarboranyl)propane derivative. The reaction of (η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$) with biphenyl in vacuo at 200 °C gave (η^6-C_6H_5–C_6H_5)Fe($Et_2C_2B_4H_4$) in 44% yield; the same complex was also obtained in lower yield via ligand exchange in hexane over Al and $AlCl_3$. The structure of the biphenyl complex was established via X-ray crystallography. Treatment of this compound with a second equivalent of (η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$) at 180 °C in vacuo gave ($Et_2C_2B_4H_4$)Fe(η^6-C_6H_5)(η^6-C_6H_5)Fe($Et_2C_2B_4H_4$), characterized spectroscopically. Crystal data for 1,2-[(η^6-C_6H_6)Fe($Et_2C_2B_4H_3$)]$_2$CH(CH_3)CH_2: M_r = 567, space group $P2_1/n$, $Z = 2$, a = 8.062 (2) Å, b = 15.335 (3) Å, c = 12.661 (3) Å, β = 105.99 (2)°, V = 1504 Å^3, R = 0.050 for 2254 reflections for which $F_o^2 > 3\sigma(R_o^2)$. Crystal data for (η^6-C_6H_5-C_6H_5)Fe($Et_2C_2B_4H_4$): M_r = 339, space group $P2_1/c$, $Z = 4$, a = 9.906 (2) Å, b = 12.678 (3) Å, c = 14.495 (4) Å, β = 100.94 (2)°, V = 1787 Å^3, R = 0.047 for 3053 reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Transition-metal sandwich complexes in which one ligand is an arene[2] or other aromatic system (e.g., $C_8H_8^{2-}$)[3] and the other is a carborane or borane form a bridge between two well-established areas of organometallic chemistry. These two families—metal–arene sandwiches and metallacarboranes/metallaboranes—have both found application in synthesis,[4,5] but their chemistry is quite different. Hence it is worthwhile to explore the possibilities for creating novel synthetic reagents which combine the characteristics of metal–arene and metal–boron systems. Of even greater potential interest would be complexes manifesting new chemistry not reflective of either "parent" class. Some encouragement for the idea that metal–(organic) ligand bonding can be markedly influenced by a carborane ligand coordinated to the same metal is given by the remarkably air-stable (η^8-C_8H_8)M($Et_2C_2B_nH_n$) compounds in which M is V or Ti.[1a,3] Previously known complexes containing (η^8-C_8H_8)Ti were highly O_2 sensitive,[6] and the vanadium counterparts were (and are) unknown.

Scheme I



Earlier papers in this series have described the synthesis and structural characterization of several (η^6-arene)Fe($Et_2C_2B_4H_4$) complexes via ligand exchange with the very useful precursor (η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$).[1a,2d,e,3a] Recently, we have begun to examine the reactivity of these species with respect to (1) the hydrocarbon ligand, (2) the carborane cage, and (3) the metal center. This paper reports some chemistry of (η^6-C_6R_6)Fe($Et_2C_2B_4H_4$) complexes involving stepwise transformations of the carborane cage, as well as the preparation, structure, and metal complexation of an (η^6-biphenyl)ferracarborane.

Results and Discussion

Conversion of *closo*-(Arene)FeC_2B_4 to *nido*-(Arene)FeC_2B_3 Cage Systems via Base Attack. Previous work has shown that the apex BH unit [B(7)] in closo 7-vertex MC_2B_4 metallacarborane cages (where M = Co or Fe) can be extracted by Lewis bases[2e,7] or via pyrolysis

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[1] (a) Part 4: Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* **1984**, *3*, 599. (b) Present address: PPG Industries, Inc., Fiber Glass Research Center, Pittsburgh, Pa. (c) University of Virginia. (d) Howard University.

[2] (a) Garcia, M. P.; Green, M.; Stone, F. G. A.; Somerville, R. G.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 871. (b) Hanusa, T. P.; Huffman, J. C.; Todd, L. J. *Polyhedron* **1982**, *1*, 77. (c) Micciche, R. P.; Sneddon, L. G. *Organometallics* **1983**, *2*, 674. (d) Maynard, R. B.; Swisher, R. G.; Grimes, R. N. *Ibid.* **1983**, *2*, 500. (e) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Ibid.* **1983**, *2*, 506.

[3] (a) Swisher, R. G.; Sinn, E.; Brewer, G. A.; Grimes, R. N. *J. Am. Chem. Soc.* **1983**, *105*, 2079. (b) Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* **1976**, *15*, 2872.

[4] For a recent review, see: Davies, S. G. "Organotransition Metal Chemistry: Applications to Organic Synthesis"; Pergamon Press: Oxford, 1982.

[5] Behnken, P. E.; Belmont, J. A.; Busby, D. C.; Delaney, M. S.; King, R. E. III; Kreimendahl, C. W.; Marder, T. B.; Wilczynski, J. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 3011 and references therein.

[6] See ref 1a, footnote 5 for list of references

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Table I. 115.8-MHz ^{11}B FT NMR Data

compound	δ (J_{BH}, Hz)[a]	rel area
$(C_6H_6)Fe(Et_2C_2B_3H_5)$ (**1a**)[b]	2.38 (147), B(4,6); −0.21 (145), B(5)	2:1
$(C_6Me_6)Fe(Et_2C_2B_3H_5)$ (**1b**)[b]	5.19 (141), B(4,6); 1.62 (137), B(5)	2:1
1b[c]	4.34 (141), B(4,6); 0.36 (134), B(5)	2:1
$(C_6H_6)Fe(Et_4C_4B_6H_6)$ (**2**)[b]	1.28 (149), B(6);[d] −7.27 (174), B(3); −8.86 (169), B(4); −16.09 (147), B(11); −17.58 (172), B(5); −31.30 (128), B(1)	equal areas
2[e,f]	1.02, −6.75, −9.22, −16.35, −17.97, −32.12	equal areas
$[(C_6H_6)Fe(Et_2C_2B_4H_3)]_2CH(CH_3)CH_2$ (**4**)[e]	24.67,[g] 21.35,[g] 6.19 (133), −0.02[h]	1:1:2:4
$(C_6H_5)(C_6H_5)Fe(Et_2C_2B_4H_4)$ (**5**)[e]	6.25 (161), 4.65 (170), 1.04 (147)	1:1:2

[a] $BF_3.O(C_2H_5)_2$ shift is zero, positive shifts downfield. [b] *n*-Hexane solution. [c] THF solution. [d] Assignments based on 2-D spectrum (see text). [e] CH_2Cl_2 solution. [f] Proton-decoupled spectrum. [g] Singlet in proton-coupled spectrum; assigned to C-substituted boron. [h] Signal is broadened in proton-coupled spectrum, but *J* is not measurable.

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

1a	3100 w, 2980 vs, 2930 s, 2880 s, 2530 s, 2510 vs, 1880 m, 1618 m, 1547 s, 1478 w, 1450 s, 1370 w, 1315 w, 1150 w, 1115 w, 1060 w, 1050 w, 1012 w, 998 m, 933 s, 894 w, 840 w, 811 m, 780 s, 750 m, 710 w, 595 m, 540 w, 480 s, 433 w, 410 m, 390 w
1b	3040 w, 2980 s, 2940 s, 2880 m, 2550 s, 2480 vs, 1873 m, 1600 w, 1522 m, 1575 vw, 1560 m, 1390 s, 1075 m, 1060 w, 1020 m, 978 w, 935 s, 915 w, 790 s, 755 m, 600 w, 550 w, 490 m, 445 w
2	3140 w, 3030 s, 3000 s, 2940 m, 2660 s, 2580 vvs, 1670 w, br, 1500 w, 1475 s, 1410 m, 1360 w, 1255 w, 1230 w, 1190 w, 1105 w, 1055 m, 1021 w, 980 s, 926 m, 865 m, 805 w, 700 w, 670 w
4	3080 w, 2980 s, 2940 vs, 2880 s, 2550 s, 1745 m, br, 1645 m, br, 1615 w, 1460 m, 1390 m, 1160 w, 1130 w, 1070 w, 990 w, 890 w, 870 w, 820 m, 755 m, 710 m, 620 w, 495 w, 430 w
5	3100 w, 3055 w, 2980 s, 2950 s, 2890 m, 2550 vs, 1650 m, br, 1510 m, 1460 s, 1420 w, 1385 m, 1160 w, 1080 w, 1050 w, 1020 w, 990 m, 968 m, 928 m, 880 s, 840 m, 830 m, 775 s, 790 m, 703 s, 620 w, 560 m, 490 m, 430 m
6	2950 s, 2920 s, 2860 m, 2520 s, 1720 m, br, 1630 m, br, 1450 m, 1380 m, 1290 w, 1070 w, 1010 w, 960 w, 920 w, 880 m, 835 m, 730 w, 700 w, 660 w, 625 w, 610 w, 490 w, 430 w

[a] KBr pellets.

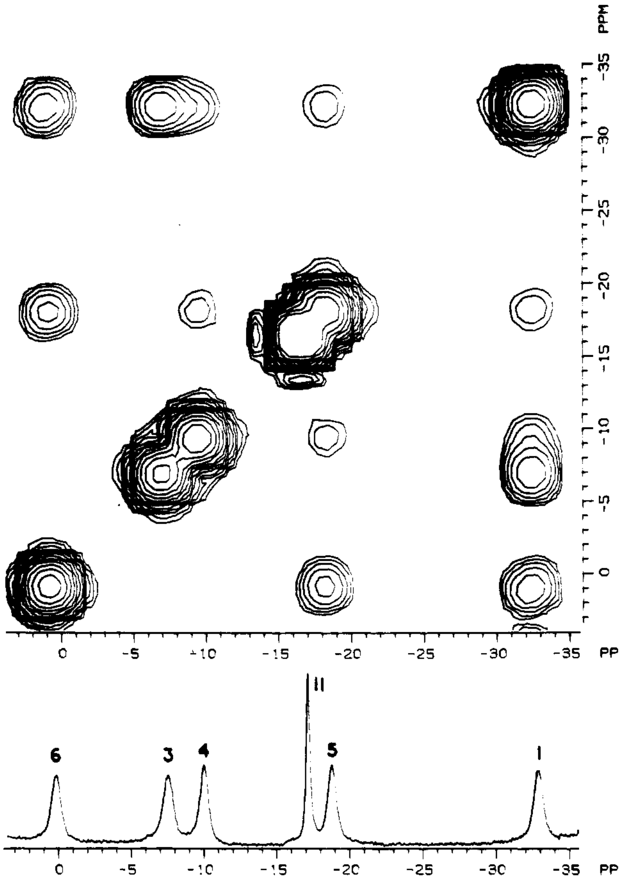

Figure 1. Two-dimensional (2-D) proton-decoupled ^{11}B–^{11}B NMR spectrum (115.8 MHz) of $(\eta^6\text{-}C_6H_6)Fe(Et_4C_4B_6H_6)$ (**2**) in CH_2Cl_2. One-dimensional (1-D) spectrum, with resonances assigned to boron atoms in cage (see Figure 2), is shown at bottom.

in vacuo,[8] to give nido MC_2B_3 species which contain a cyclic $R_2C_2B_3H_5^{2-}$ ligand analogous to $C_5H_5^-$. The base-degradation approach has also been employed in the conversion of certain large metallacarborane systems (e.g., MC_2B_{10} and MC_2B_9 cages) to species with one less boron atom.[9] For 7-vertex MC_2B_4 species, facile removal of the apex boron while leaving the complex otherwise intact is a crucial step leading to multidecked polymetallic complexes containing alternating metal and *cyclo*-$R_2C_2B_3H_3^{4-}$ units[7] and to face-to-face oxidative fusion of two MC_2B_3 cages to give "carbon-rich" $M_2C_4B_6$ systems.[10] In order to determine whether such processes can be conducted on (arene)Fe($R_2C_2B_4H_4$) complexes, $(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_4)$ and its hexamethylbenzene counterpart were treated with 1,2-bis(dimethylamino)ethane. In both cases the desired *nido*-ferracarborane products (**1a,b**) were obtained in good yield, although the hexamethylbenzene complex required more vigorous conditions (Scheme I). The products were isolated via chromatography in air as bright yellow solids and characterized as *nido*-1,2,3-$(\eta^6\text{-}C_6R_6)Fe(Et_2C_2B_3H_5)$ species via high-resolution ^{11}B NMR (Table I), infrared (Table II), and mass spectra. Both complexes exhibit strong parent envelopes in the mass spectra, with intensities corresponding to those calculated from natural isotope abundances. The presence of B–H–B hydrogen bridges is indicated by IR absorptions between 1800 and 1900 cm^{-1} as well as by a broad resonance at δ −6 in the ^1H spectrum of **1a**.

Preparation of $(\eta^6\text{-}C_6H_6)FeEt_4C_4B_6H_6$ (2). In an attempt to achieve metal-promoted oxidative fusion[11] of two FeC_2B_3 cages to form an $Fe_2C_4B_6$ system, **1a** was bridge-

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(7) (a) Grimes, R. N.; Beer, D. C.; Sneddon, L. G.; Miller, V. R.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 1138. (b) Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *Ibid.* **1976**, *98*, 4818.

(8) Sneddon, L. G.; Beer, D. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1973**, *95*, 6623.

(9) Jones, C. J.; Francis, J. N.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1972**, *94*, 8391.

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

(11) Maynard, R. B.; Grimes, R. N. *J. Am. Chem. Soc.* **1982**, *104*, 5983 and references therein.

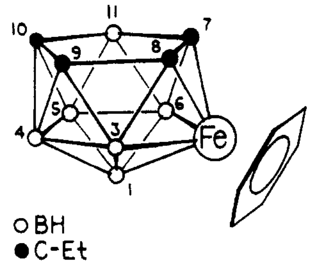

Figure 2. Structure of (η^6-C_6H_6)Fe($Et_4C_4B_6H_6$) (2).

deprotonated via treatment with KH to form the $(C_6H_6)Fe(Et_2C_2B_4H_5)^-$ anion (designated $(1a)^-$), which was in turn exposed to a solution of $FeCl_2$. Following the reaction, chromatography of the mixture on silica in air gave only one isolable product, red crystalline 2 (Scheme I), characterized from its ^{11}B and ^1H NMR, IR, and mass spectra. The composition is clearly established from the mass spectrum, whose parent group has a $C_{18}B_6Fe$ pattern and cuts off at *m/e* 371 (^{13}C peak), and it is clear from the ^{11}B spectrum (Table I) and Figure 1, bottom) as well as the 360-MHz ^1H NMR data (Experimental Section) that the cage structure has no symmetry. From the polyhedral skeletal electron-counting rules,[12] one can predict a nido 11-vertex geometry consisting of an icosahedron missing a vertex. The two-dimensional (2-D) ^{11}B–^{11}B NMR spectrum[13] (Figure 1) contains several off-diagonal "cross" peaks which reveal scalar coupling between specific boron nuclei, but other cross peaks may be obscured by overlap of resonances on the diagonal. This NMR information does not identify a unique structure for 2, but the cage geometry has been established from X-ray diffraction data collected on a low-quality crystal. Although an accurate structure determination has not been possible (refinement proceeding only to $R = 0.20$), the non-hydrogen atoms were unambiguously located and the polyhedral cage is depicted in Figure 2.

We assume that 2 is formed via oxidative fusion of two $(1a)^-$ units (with concomitant loss of hydrogen) in a sequence such as eq 1 which would be analogous to the

$$2(C_6H_6)Fe(Et_2C_2B_3H_4)^- + Fe^{2+} \rightarrow \underset{\text{(not isolated)}}{[(C_6H_6)Fe(Et_2C_2B_3H_3)]_2FeH_2} \rightarrow \underset{2}{(C_6H_6)FeEt_4C_4B_6H_6}$$

synthesis of $R_4C_4B_8H_8$ carboranes via oxidation of $(R_2C_2B_4H_4)_2FeH_2$,[11] except that in the present case the formation of 2 involves net loss of a $(C_6H_6)Fe$ unit. In principle this could occur before or after fusion, a question which was not examined in this study. The cage structure of 2 suggests that it may have formed by face-to-face fusion of a C_2B_3 ring onto a pyramidal FeC_2B_3 substrate, with subsequent migration of one C–Et unit [C(10)] in such a way as to leave all four skeletal carbons on the open face, a highly favored arrangement.[14]

From the known cage geometry, we can interpret the 2-D ^{11}B–^{11}B NMR spectrum and assign the resonances in the 1-D spectrum (Figure 1, bottom) to specific boron nuclei. In this scheme, all adjacent borons give rise to observed cross peaks in the 2-D spectrum except for those between the 3–4, 5–11, and 6–11 nuclei. The apparent absence of these peaks may be due either to overlap of closely spaced resonances or to unusually rapid relaxation of one or more of these nuclei (especially B(11)); such effects are discussed elsewhere.[13] It should be noted that the unusual sharpness of the B(11) 1-D resonance (together with the apparent absence of coupling of B(11) to B(5) and B(6), just mentioned) correlates with the semiisolation of B(11) on the open rim between two carbon atoms.

Table III. Experimental Parameters and Crystal Data on 4

M_r	567	*B*	0.35
space group	$P2_1/n$	trans coeff (max)[a]	0.700
a, Å	8.062 (2)	trans coeff (min)	0.599
b, Å	15.335 (3)	2*θ* range, deg	1–50
c, Å	12.661 (3)	reflectns obsd	2612
β, deg	105.99 (2)	reflectns refined	2254
V, Å^3	1504	*R*	0.050
μ, cm^{-1}	10.1	R_w	0.051
D(calcd), g cm^{-3}	1.25	esd unit wt	2.0
A	0.60	*Z*	2
		radiatn	Mo K*α*

[a] Crystal dimensions (mm from centroid): $10\bar{1}$ (0.21), $\bar{1}01$ (0.21), $0\bar{2}1$ (0.275), $0\bar{2}\bar{1}$ (0.275), $02\bar{1}$ (0.30), $0\bar{2}1$ (0.30), 001 (0.29), $00\bar{1}$ (0.29).

Treatment of (η^6-C_6H_6)Fe($Et_2C_2B_4H_4$) with Al/$AlCl_3$ and Naphthalene. In an attempt to synthesize the naphthalene complex (η^6-$C_{10}H_8$)Fe($Et_2C_2B_4H_6$) via ligand exchange, (η^6-C_6H_6)Fe($Et_2C_2B_4H_4$) and naphthalene were combined with aluminum powder and $AlCl_3$ in hexane at 80 °C. The desired complex was not found (it has subsequently been obtained via a different route[15b]), but two minor products were isolated (Scheme I). Yellow 3 has a mass spectrum indicating a three-boron species of mass 430, but except for recording its ^1H NMR spectrum this compound was not further characterized. In one experiment, a golden yellow solid product, 4, was isolated in low yield and characterized both spectroscopically and via X-ray diffraction. The mass spectrum of 4 exhibits a parent grouping with a cutoff at *m/e* 569 (^{13}C peak) and more intense envelopes with local cutoffs at *m/e* 491 and 413, corresponding to the loss of one and two C_6H_6 units, respectively; each group exhibits intensities consistent with an eight-boron pattern. From this information it is apparent that 4 contains two $(C_6H_6)Fe(Et_2C_2B_4H_x)$ units, but the NMR data (Table I and Experimental Section) indicate an absence of overall symmetry in the molecule. In order to elucidate its structure, 4 was examined by X-ray diffraction.

Crystallographic Study of 4. Tables III–VI list data collection and unit cell parameters, atomic positions, and bond distances and angles, and a table of calculated mean planes is available as supplementary material. Figures 3 and 4 depict the molecular structure and unit cell packing. The molecule consists of two (η^6-C_6H_6)Fe($Et_2C_2B_4H_3$) ferracarborane units linked by a $-CH(CH_3)CH_2-$ chain which connects the B(5) and B(5′) boron atoms on the respective cages. Although the individual molecules have no symmetry, there is a crystallographic inversion center which is produced by disorder of the methyl group C(BM) between the two equivalent positions on the hydrocarbon chain; this was handled in refinement by assigning each C(BM) position a weight of 0.5. As a consequence, the asymmetric unit contains only one ferracarborane cage.

The parameters of the $(C_6H_6)Fe(Et_2C_2B_4H_3)$ moiety are closely comparable to those found earlier for the monomeric benzene complex,[2e] as can be seen in Table V. Unlike

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(12) O'Neill, M. E.; Wade, K. In "Metal Interactions with Boron Clusters"; Grimes, R. N., Ed.; Plenum Press: New York, 1982; Chapter 1 and references therein.

(13) Homonuclear ^{11}B 2D NMR spectroscopy is described by: Venable, T. L.; Hutton, W. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 29.

(14) Grimes, R. N. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 55.

(15) Swisher, R. G.; Sinn, E.; Grimes, R. N., (a) second of three papers in this issue. (b) third of three papers in this issue.

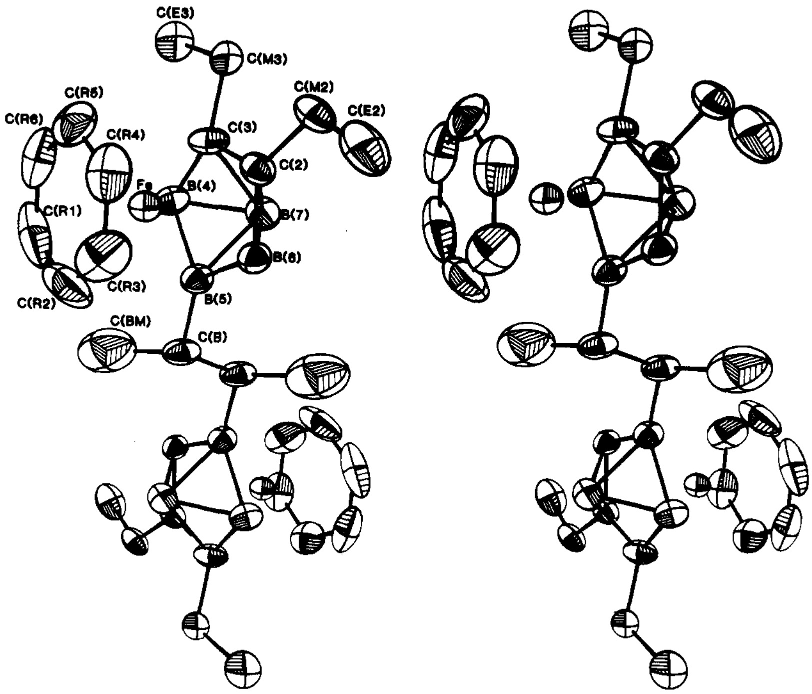

Figure 3. Stereoview of the molecular structure of $[(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_3)]_2CH(CH_3)CH_2$ (4). The methyl carbon C(BM) is shown in both disordered positions.

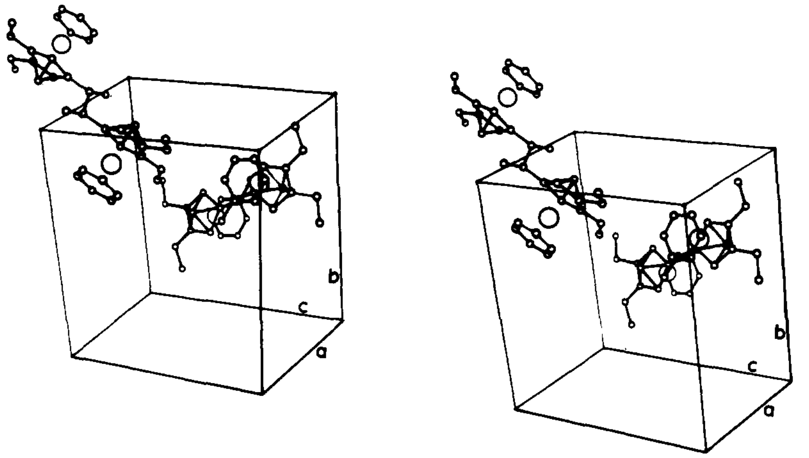

Figure 4. Stereoview of the unit cell in 4.

the monomer, which contains two rotameric forms in the crystal (one form having the C–C bond of the carborane ligand nearly parallel to an edge of the C_6H_6 ring and the other a "staggered" orientation), the arrangement in 4 is roughly "eclipsed", i.e., with the C(2)–C(3) and C(R4)–C(R5) edges almost parallel. The C(2)–C(3)–B(4)–B(5)–B(6) and benzene rings are both planar within experimental error and approximately centered over the metal atom, and the vector distances of iron from the carborane and benzene planes (Table VII) are virtually identical with the corresponding values in the analogous benzene,[2e] toluene,[2c] 1,3,5-trimethylbenzene,[2e] and hexamethylbenzene[2e] complexes. The distances and angles in the exo-polyhedral hydrocarbon chain are normal.

The structure determination on 4 furnishes a more accurate set of molecular parameters than did our earlier study of monomeric $(C_6H_6)Fe(Et_2C_2B_4H_4)$,[2e] for which R = 0.069. Although the two FeC_2B_4 units in 4 are crystallographically equivalent, in solution they are inequivalent since the $-CH(CH_3)CH_2-$ chain is asymmetric; this is seen in the ^{11}B NMR spectrum, which would be incompatible with a single FeC_2B_4 cage substituted at B(5). We can offer no plausible mechanism for the formation of 4, but the three-carbon chain may originate in a $C–C_2H_5$ unit of the starting carborane, which undergoes extensive decomposition under the reaction conditions.

Synthesis of Mono- and Bis(ferracarboranyl) Complexes of Biphenyl. As a part of our investigation of (arene)(carborane)iron complexes, we sought to prepare and study species having metal-bound hydrocarbon ligands with more than one arene ring. Not only are such complexes of interest in their own right in terms of electronic structure and chemical properties,[16] but also one might hope to use them to prepare extended polymetallic systems in which two or more complex units are connected via metal–arene–metal and/or metal–carborane–metal arrays.[15a] Multiring complexes could be constructed either from fused-ring systems such as naphthalene or from linked arenes like biphenyl. Examples of the former type are described elsewhere;[15b] here we report on the synthesis and structures of complexes containing biphenyl, which represent a logical extension of the $(C_6R_6)Fe(Et_2C_2B_4H_6)$ species discussed up to this point.

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[16] Morrison, W. H., Jr.; Ho, E. Y.; Hendrickson, D. N. *J. Am. Chem. Soc.* 1974, *96*, 3603; *Inorg. Chem.* 1975, *14*, 500.

Table IV. Positional Parameters for $[(C_6H_6)Fe(Et_2C_2B_4H_3)]_2CH_2CHMe$ (4)

atom	x	y	z
Fe	−0.21291 (8)	0.17269 (4)	0.22705 (5)
C(R1)	0.0098 (8)	0.1469 (5)	0.1876 (7)
C(R2)	−0.0944 (9)	0.2015 (6)	0.1092 (5)
C(R3)	−0.1497 (9)	0.2757 (5)	0.1422 (6)
C(R4)	−0.1117 (8)	0.2983 (4)	0.2501 (6)
C(R5)	−0.0134 (8)	0.2451 (5)	0.3289 (5)
C(R6)	0.0483 (8)	0.1691 (5)	0.2981 (7)
C(2)	−0.4310 (6)	0.1850 (3)	0.2795 (3)
C(E2)	−0.5889 (8)	0.3283 (4)	0.2775 (5)
C(3)	−0.3195 (7)	0.1146 (3)	0.3376 (3)
C(B)	−0.4135 (7)	0.0254 (3)	0.0177 (4)
C(BM)	0.2640 (14)	0.5252 (7)	0.5210 (8)
C(M3)	−0.303 (1)	0.1142 (6)	0.4621 (7)
C(M32)	−0.225 (1)	0.1057 (7)	0.4664 (9)
C(E31)	−0.181 (2)	0.0378 (12)	0.5123 (14)
C(E32)	−0.276 (2)	0.0280 (13)	0.5179 (15)
C(E33)	−0.367 (3)	0.0529 (14)	0.5079 (17)
C(M2)	−0.4979 (7)	0.2539 (4)	0.3419 (4)
B(4)	−0.2829 (8)	0.0446 (4)	0.2583 (5)
B(5)	−0.3923 (7)	0.0768 (4)	0.1310 (4)
B(6)	−0.4856 (7)	0.1698 (4)	0.1534 (4)
B(7)	−0.4993 (8)	0.0773 (4)	0.2338 (5)
H(B)	0.080 (5)	0.427 (3)	0.457 (3)
H(R1)	0.046 (6)	0.098 (3)	0.170 (4)
H(R2)	−0.117 (6)	0.174 (3)	0.036 (4)
H(R3)	−0.222 (6)	0.309 (3)	0.092 (4)
H(R4)	−0.158 (6)	0.353 (3)	0.275 (4)
H(R5)	0.019 (6)	0.259 (3)	0.406 (4)
H(R6)	0.114 (6)	0.128 (3)	0.354 (4)
H(M21)	−0.561 (5)	0.230 (3)	0.372 (3)
H(M22)	−0.413 (4)	0.272 (2)	0.390 (3)
H(E21)	−0.516 (5)	0.350 (3)	0.238 (3)
H(E22)	−0.625 (5)	0.378 (3)	0.325 (3)
H(E23)	−0.692 (5)	0.311 (3)	0.228 (4)
H(4)	−0.195 (5)	−0.015 (3)	0.296 (3)
H(6)	−0.565 (5)	0.224 (3)	0.092 (3)
H(7)	−0.621 (5)	0.053 (3)	0.254 (3)

The biphenyl complex 5 was prepared from $(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)$ and biphenyl, either in hexane solution over $AlCl_3$ or in a vapor phase reaction at 200 °C without solvent (Scheme II); the latter is the preferred route. The product 5 was obtained as an air-stable orange solid and characterized as $(\eta^6\text{-}C_6H_5\text{–}C_6H_5)Fe(Et_2C_2B_4H_4)$ from its NMR, IR, and mass spectra and an X-ray crystal structure analysis, described below. The mass spectrum exhibits a strong parent envelope at m/e 341 closely matching the calculated pattern based on natural isotopes, with a less intense group at m/e 265 (P − 76) corresponding to net loss of C_6H_4. The 360-MHz ^1H NMR spectrum (Figure 5a and Experimental Section) is particularly informative, in that all types of CH protons can be readily assigned; the 90-MHz ^{13}C spectrum (Figure 5b) exhibits resonances for the ethyl and ring carbons, but peaks attributable to the cage carbon nuclei and the tertiary carbons in the biphenyl ligand are not observed. In both the ^1H and ^{13}C NMR spectra, the nuclei of the biphenyl ring coordinated to iron resonate at higher field than those of the uncomplexed ring, as has been previously observed in $(\eta^6\text{-}C_6H_5\text{–}C_6H_5)Fe(C_5H_5)^+$ and in arene–transition-metal complexes generally.[17]

Scheme II

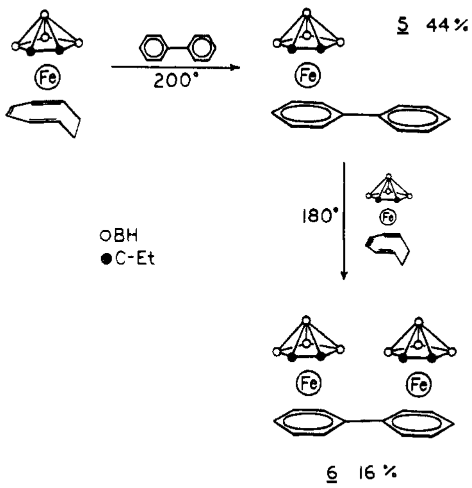

Table V. Bond Distances (Å) in 4 and 5

	4	5	$(C_6H_6)Fe(Et_2C_2B_4H_4)$[a,b]		4	5	$(C_6H_6)Fe(Et_2C_2B_4H_4)$[a,b]
Fe–C(R1)[c]	2.030 (4)	2.120 (3)	2.040 (5)	Fe–B(5)	2.182 (3)	2.157 (4)	2.162 (4)
Fe–C(R2)[c]	2.030 (4)	2.083 (4)	2.074 (6)	Fe–B(6)	2.139 (3)	2.121 (4)	2.132 (5)
Fe–C(R3)[c]	2.052 (3)	2.051 (4)	2.071 (6)	C(2)–C(3)	1.466 (4)	1.458 (5)	1.466 (6)
Fe–C(R4)[c]	2.080 (3)	2.076 (4)	2.076 (6)	C(2)–C(M2)	1.505 (4)	1.516 (5)	1.521 (7)
Fe–C(R5)[c]	2.084 (3)	2.082 (4)	2.048 (7)	C(M2)–C(E2)	1.474 (5)	1.455 (7)	1.335 (14)
Fe–C(R6)[c]	2.050 (3)	2.095 (4)	2.048 (7)	C(2)–B(6)	1.554 (3)	1.555 (5)	1.555 (7)
⟨Fe–C⟩	2.054	2.085	2.060	C(2)–B(7)	1.786 (4)	1.750 (6)	1.778 (6)
C(R1)–C(R2)	1.390 (7)	1.422 (5)	1.404 (10)	C(3)–C(M3)	1.545 (5)	1.522 (6)	1.514 (6)
C(R2)–C(R3)	1.331 (7)	1.399 (6)	1.372 (10)	C(3)–C(M32)[d]	1.605 (7)		
C(R3)–C(R4)	1.360 (6)	1.382 (6)	1.343 (10)	C(M3)–C(E31)[d]	1.546 (11)	1.319 (8)	1.474 (8)
C(R4)–C(R5)	1.361 (5)	1.392 (6)	1.357 (10)	C(M3)–C(E32)[d]	1.486 (13)		
C(R5)–C(R6)	1.366 (6)	1.401 (5)	1.338 (11)	C(M3)–C(E33)[d]	1.287 (12)		
C(R6)–C(R1)	1.390 (7)	1.401 (5)	1.358 (11)	C(M32)–C(E32)[d]	1.469 (13)		
⟨C–C(ring)⟩	1.366	1.400	1.362	C(M32)–C(E33)[d]	1.607 (13)		
C(A1)–C(B1)		1.471 (5)		C(3)–B(4)	1.552 (4)	1.547 (16)	1.555 (7)
C(B1)–C(B2)		1.376 (5)		C(3)–B(7)	1.762 (4)	1.734 (5)	1.774 (6)
C(B2)–C(B3)		1.385 (6)		B(4)–B(5)	1.684 (4)	1.646 (6)	1.673 (8)
C(B3)–C(B4)		1.370 (7)		B(4)–B(7)	1.759 (5)	1.752 (7)	1.748 (9)
C(B4)–C(B5)		1.366 (7)		B(5)–B(6)	1.671 (4)	1.665 (6)	1.651 (8)
C(B5)–C(B6)		1.377 (6)		B(5)–B(7)	1.749 (4)	1.722 (7)	1.688 (8)
C(B6)–C(B1)		1.384 (5)		B(6)–B(7)	1.766 (5)	1.777 (6)	1.749 (8)
⟨C–C(B ring)⟩		1.376		C(B)–C(B)′	1.551 (6)		
Fe–C(2)	2.052 (2)	2.063 (3)	2.039 (5)	C(B)–C(BM)	1.618 (6)		
Fe–C(3)	2.037 (3)	2.041 (4)	2.035 (4)	⟨C–H⟩	0.94	0.94	1.00
Fe–B(4)	2.111 (3)	2.108 (4)	2.129 (5)	⟨B–H⟩	1.17	1.11	1.14

[a] See ref 2e. [b] Average values in two independent molecules.[2e] [c] In complex 5, carbon atoms of Fe-bonded C_6 ring are labeled C(A1)–C(A6); in $(C_6H_6)Fe(Et_2C_2B_4H_4)$ they are labeled C(1R)–C(6R).[2e] [d] C(M32), C(E31), C(E32), and C(E33) represent carbon atoms of disordered ethyl group attached to C(3) (see Experimental Section).

Table VI. Bond Angles (deg) for $[(C_6H_6)Fe(Et_2C_2B_4H_3)]_2CH_2CHMe$ (4)

C(R2)-C(R1)-C(R6)	119.7 (4)	Fe-C(3)-C(M32)	124.2 (3)	C(3)-C(M32)-C(E33)	101.1 (6)
C(R1)-C(R2)-C(R3)	118.6 (5)	Fe-C(3)-B(7)	92.63 (15)	Fe-B(4)-B(7)	90.3 (2)
C(R2)-C(R3)-C(R4)	122.1 (5)	C(2)-C(3)-C(M3)	112.6 (3)	C(3)-B(4)-B(5)	105.9 (2)
C(R3)-C(R4)-C(R5)	120.6 (4)	C(2)-C(3)-C(M32)	128.8 (3)	Fe-B(5)-B(7)	88.2 (2)
C(R4)-C(R5)-C(R6)	119.0 (4)	C(2)-C(3)-B(4)	112.6 (2)	Fe-B(5)-C(8)	136.1 (2)
C(R1)-C(R6)-C(R5)	119.9 (4)	C(M3)-C(3)-B(4)	132.7 (3)	B(4)-B(5)-B(6)	103.3 (2)
Fe-C(2)-C(M2)	134.2 (2)	C(M3)-C(3)-B(7)	125.6 (3)	B(4)-B(5)-C(B)	127.6 (2)
Fe-C(2)-B(7)	91.44 (15)	C(M32)-C(3)-B(4)	118.4 (3)	B(6)-B(5)-C(B)	128.9 (2)
C(M2)-C(2)-C(3)	120.9 (2)	C(M32)-C(3)-B(7)	142.5 (3)	B(7)-B(5)-C(B)	135.6 (2)
C(M2)-C(2)-B(6)	127.2 (3)	C(3)-C(M3)-C(E31)	106.9 (5)	Fe-B(6)-B(7)	89.2 (2)
C(M2)-C(2)-B(7)	134.1 (2)	C(3)-C(M3)-C(E32)	116.7 (6)	C(2)-B(6)-B(5)	106.8 (2)
C(3)-C(2)-B(6)	111.4 (2)	C(3)-C(M3)-C(E33)	122.0 (7)	B(5)-C(B)-C(B)′	111.8 (3)
C(2)-C(M2)-C(E2)	116.7 (3)	C(3)-C(M32)-C(E31)	124.2 (7)	B(5)-C(B)-C(BM)	109.7 (3)
Fe-C(3)-C(M3)	140.1 (3)	C(3)-C(M32)-C(E32)	114.1 (6)	C(B)′-C(B)-C(BM)	119.0 (3)

Table VII. Experimental Parameters and Crystal Data on 5

M_r	339	B	0.35
space group	$P2_1/c$	trans coeff (max)[a]	0.630
a, Å	9.906 (2)	trans coeff (min)	0.593
b, Å	12.678 (3)	2θ range, deg	3.8-64
c, Å	14.495 (4)	reflectns obsd	5972
β, deg	100.94 (2)	reflectns refined	3053
V, Å^3	1787	R	0.047
μ, cm^{-1}	8.6	R_W	0.049
D(calcd), g cm^{-3}	1.26	esd unit wt	1.0
A	0.60	Z	4
		radiatn	Mo Kα

[a] Crystal dimensions (mm from centroid): 110 (0.475), $\bar{1}\bar{1}0$ (0.475), $1\bar{1}0$ (0.475), $\bar{1}10$ (0.475), 010 (0.475), $0\bar{1}0$ (0.475), 001 (0.55), $00\bar{1}$ (0.55).

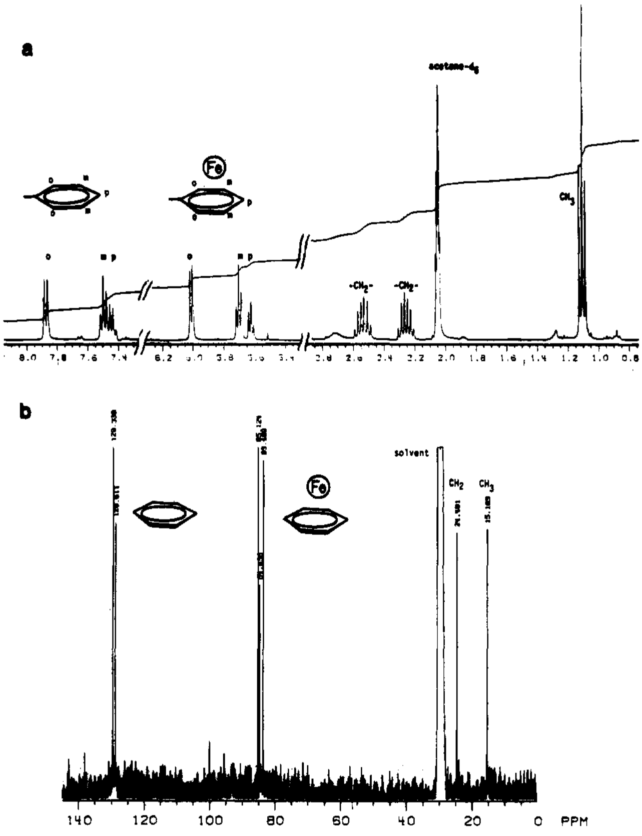

Figure 5. (a) 360-MHz ^1H NMR spectrum $(\eta^6\text{-}C_6H_5\text{–}C_6H_5)Fe(Et_2C_2B_4H_4)$ (5) in acetone-d_6. (b) 90-MHz ^{13}C NMR spectrum of 5 in acetone-d_6.

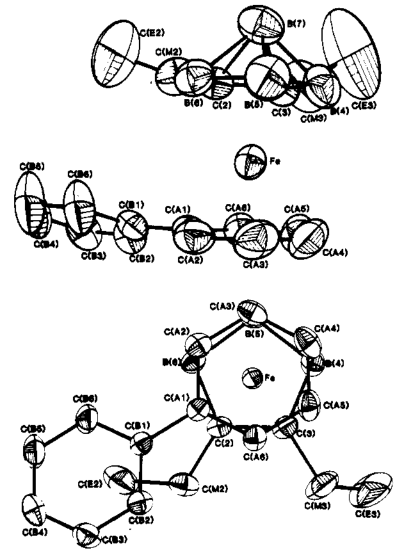

Figure 6. Two views of the molecular structure of 5. (Atom B(7) is omitted in bottom drawing, which is projected down the Fe–B(7) axis.)

Coordination of a second $Fe(Et_2C_2B_4H_4)$ group to the uncomplexed ring of 5 was achieved by heating 5 with $(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)$ in a sealed tube at 180 °C. Compound 6 was isolated as pale yellow crystals and characterized spectroscopically as $[(\eta^6\text{-}C_6H_5)Fe(Et_2C_2B_4H_4)]_2$. The mass spectrum of 6 contains a parent grouping with a cutoff at m/e 527 and an intensity pattern consistent with the calculated spectrum. The assigned structure (Scheme II) is also supported by the high-resolution ^1H NMR spectrum which exhibits a single set of resonances in the aryl region between δ 5.7 and 6.3 characteristic of Fe-coordinated aryl rings; significantly, no resonances are observed at lower field, in the region typical of uncoordinated phenyl group protons (see the spectrum of 5 in Figure 5a for comparison). The NMR data on 6 imply equivalence of the two $(C_6H_5)Fe(Et_2C_2B_4H_4)$ units, but no conclusions can be drawn regarding their relative orientation; however, the barrier to rotation on the inter-ring C–C bond is not expected to be large.

Crystallographic Study of 5. Tables VII–IX list crystallographic and cell parameters, atom coordinates, and bond angles, while bond distances are contained in Table V; a table of calculated mean planes is included in the supplementary material. Figures 6 and 7 present views of the molecular structure and crystal packing. The geometry of the closo FeC_2B_4 cluster is normal and compares closely with those in 4 and in $(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_4)$ (Table V), as well as in other (arene)$Fe(R_2C_2B_4H_4)$ complexes.[2c,2e,15]

The biphenyl ligand in 5 is of particular interest, since 5 is to our knowledge the first biphenyl complex of iron to be characterized by X-ray diffraction although a number of such species, including $(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_5\text{-}C_6H_5)^+$, have

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(17) Steele, B. R.; Sutherland, R. G.; Lee, C. C. *J. Chem. Soc., Dalton Trans.* **1981**, 529.

Table VIII. Positional Parameters for $(C_6H_5)(C_6H_5)Fe(Et_2C_2B_4H_4)$ (5)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Fe	0.22940 (5)	0.12811 (4)	0.40154 (3)	H(A2)	0.027 (4)	−0.027 (3)	0.401 (2)
C(A1)	0.0649 (3)	0.0718 (3)	0.2978 (2)	H(A3)	0.249 (4)	−0.077 (3)	0.458 (2)
C(A2)	0.0980 (4)	−0.0010 (3)	0.3734 (3)	H(A4)	0.428 (4)	−0.018 (3)	0.382 (2)
C(A3)	0.2336 (5)	−0.0336 (3)	0.4061 (3)	H(A5)	0.380 (4)	0.098 (3)	0.261 (2)
C(A4)	0.3381 (4)	0.0009 (4)	0.3626 (3)	H(A6)	0.154 (3)	0.155 (2)	0.210 (2)
C(A5)	0.3086 (4)	0.0715 (4)	0.2879 (3)	H(B2)	−0.055 (4)	0.160 (3)	0.139 (2)
C(A6)	0.1735 (4)	0.1062 (3)	0.2560 (2)	H(B3)	−0.275 (4)	0.223 (3)	0.085 (3)
C(B1)	−0.0764 (3)	0.1097 (3)	0.2653 (2)	H(B4)	−0.443 (4)	0.211 (3)	0.182 (3)
C(B2)	−0.1173 (4)	0.1550 (3)	0.1782 (3)	H(B5)	−0.372 (4)	0.140 (3)	0.332 (3)
C(B3)	−0.2500 (5)	0.1913 (4)	0.1470 (3)	H(B6)	−0.150 (4)	0.072 (3)	0.377 (3)
C(B4)	−0.3444 (4)	0.1847 (5)	0.2047 (4)	H(M21)	0.041 (4)	0.338 (3)	0.311 (2)
C(B5)	−0.3065 (4)	0.1399 (6)	0.2914 (4)	H(M22)	0.100 (4)	0.425 (3)	0.376 (2)
C(B6)	−0.1746 (4)	0.1033 (5)	0.3215 (3)	H(E21)	−0.030 (4)	0.404 (3)	0.475 (3)
C(2)	0.1643 (4)	0.2779 (3)	0.4275 (2)	H(E22)	−0.129 (4)	0.414 (3)	0.370 (3)
C(M2)	0.0605 (5)	0.3544 (3)	0.3739 (3)	H(E23)	−0.112 (4)	0.301 (3)	0.421 (3)
C(E2)	−0.0665 (6)	0.3713 (5)	0.4085 (4)	H(M31)	0.359 (5)	0.317 (4)	0.295 (3)
C(3)	0.3073 (4)	0.2775 (3)	0.4158 (2)	H(M32)	0.299 (5)	0.401 (3)	0.331 (3)
C(M3)	0.3595 (5)	0.3534 (4)	0.3491 (3)	H(E31)	0.525 (4)	0.459 (3)	0.362 (3)
C(E3)	0.4770 (8)	0.4041 (6)	0.3737 (6)	H(E32)	0.540 (5)	0.351 (4)	0.366 (3)
B(4)	0.3989 (5)	0.2033 (4)	0.4860 (3)	H(E33)	0.505 (4)	0.405 (3)	0.441 (3)
B(5)	0.2954 (5)	0.1523 (4)	0.5506 (3)	H(4)	0.521 (4)	0.202 (3)	0.494 (2)
B(6)	0.1408 (5)	0.2020 (3)	0.5072 (3)	H(5)	0.322 (3)	0.102 (3)	0.615 (2)
B(7)	0.2864 (5)	0.2864 (4)	0.5317 (3)	H(6)	0.047 (3)	0.198 (3)	0.535 (2)
				H(7)	0.314 (3)	0.356 (3)	0.568 (2)

Table IX. Bond Angles (deg) for $(C_6H_5)(C_5H_5)Fe(Et_2C_2B_4H_4)$ (5)

C(A2)-C(A1)-C(A6)	116.9 (3)	C(B1)-C(B2)-C(B3)	122.3 (4)	C(2)-C(M2)-C(E2)	117.7 (4)
C(A2)-C(A1)-C(B1)	121.7 (3)	C(B2)-C(B3)-C(B4)	119.7 (4)	Fe-C(3)-C(M3)	133.6 (3)
C(A6)-C(A1)-C(B1)	121.5 (3)	C(B3)-C(B4)-C(B5)	119.1 (4)	C(2)-C(3)-C(M3)	121.7 (4)
C(A1)-C(A2)-C(A3)	121.2 (4)	C(B4)-C(B5)-C(B6)	120.7 (5)	C(2)-C(3)-B(4)	112.8 (3)
C(A2)-C(A3)-C(A4)	120.4 (4)	C(B1)-C(B6)-C(B5)	121.6 (4)	C(M3)-C(3)-B(4)	125.1 (4)
C(A3)-C(A4)-C(A5)	119.6 (4)	Fe-C(2)-C(M2)	134.5 (3)	C(M3)-C(3)-B(7)	133.8 (4)
C(A4)-C(A5)-C(A6)	120.3 (4)	C(M2)-C(2)-C(3)	121.5 (3)	C(3)-C(M3)-C(E3)	121.7 (6)
C(A1)-C(A6)-C(A5)	121.5 (4)	C(M2)-C(2)-B(6)	126.4 (3)	C(3)-B(4)-B(5)	105.2 (3)
C(A1)-C(B1)-C(B2)	121.8 (3)	C(M2)-C(2)-B(7)	133.9 (3)	B(4)-B(5)-B(6)	105.3 (3)
C(A1)-C(B1)-C(B6)	121.7 (3)	C(3)-C(2)-B(6)	111.7 (3)	C(2)-B(6)-B(5)	105.0 (3)
C(B2)-C(B1)-C(B6)	116.5 (4)				

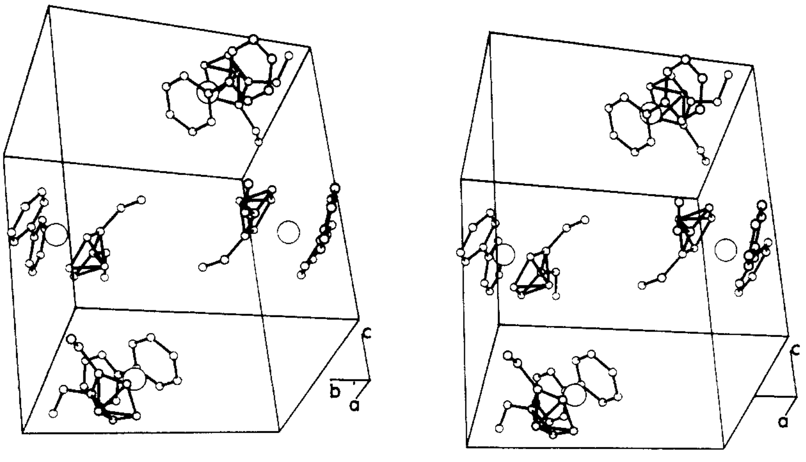

Figure 7. Stereoview of the unit cell in 5.

been prepared.[17,18] The metal-bound aryl ring (ring A) is planar within experimental error and essentially centered over the iron atom; moreover, it is nearly parallel with the carboranyl binding face [C(2)–C(3)–B(4)–B(5)–B(6)]. The vector distances of iron from the C_6 and C_2B_3 planes, 1.545 and 1.617 Å, respectively, are comparable to those in other arylferracarboranes.[2] The uncomplexed C_6H_5 ring (B) is planar, but not parallel with ring A, forming a dihedral angle of 19.3°. However, the two rings are nearly aligned along a common C(A4)–C(A1)–C(B1)–C(B4) axis (thus, the C(A4)–C(A1)–C(B4) angle is 178.8°, and atoms C(A1) and C(B1) are each coplanar with their three neighboring carbon atoms). As expected, the C–C distances in the metal-bound ring are significantly longer than the corresponding distances in ring B [mean values 1.400 (5) Å vs. 1.376 (5) Å], reflecting the weakening of the carbon–carbon interactions in ring A due to complexation with the metal. There is some perturbation of the rings in the vicinity of the connecting C(A1)–C(B1) link, as seen in the C(A2)–C(A1)–C(A6) and C(B2)–C(B1)–C(B6) angles which are 116.8° and 116.6°, respectively; in comparison, the average value of the other five internal C–C–C angles in each ring is 121.6°.

These features can be compared with the solid-state structure of biphenyl, $(C_6H_5)_2$, as determined independently by two groups.[19] In biphenyl the two rings are

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(18) (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Dokl. Akad. Nauk SSSR* **1966**, *166*, 607. (b) Lee, C. C.; Sutherland, R. G.; Thomson, B. J. *J. Chem. Soc., Chem. Commun.* **1972**, 907.

entirely coplanar, in contrast to **5**, and the internal C–C–C angles are nearly uniform, the smallest (at the substituted carbon atom) being 118.8° and the largest 121.4°. The ring–C–C distances in biphenyl range from 1.35 to 1.41 Å, with no clear pattern although the C(2)–C(3) and C(5)–C(6) bonds appear slightly longer. The central C–C bond in biphenyl is long [1.51 (3) Å], implying an absence of conjugation between the rings;[19b] in **5** this distance [1.469 (5) Å] is not significantly different, indicating that here, too, there is no inter-ring π-interaction. This conclusion is supported by the mutually twisted conformation of the phenyl rings in **5** and is evidenced indirectly by the fact that a second ferracarborane unit can be coordinated to **5** to give **6** as described above. Were there substantial deactivation of the uncomplexed phenyl ring in **5**, one would expect **6** to form only with difficulty, if at all.

Experimental Section

Materials and Instrumentation. $(\eta^6\text{-}C_6R_6)Fe(Et_2C_2B_4H_4)$ (R = H or Me) and $(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)$ were prepared by previously reported methods.[2d,e] Other reagents and solvents were reagent grade and were used as received, except where otherwise indicated. ^{11}B (115.8-MHz), ^1H (360-MHz), and ^{13}C (90.9-MHz) pulse Fourier transform NMR spectra were recorded on a Nicolet Magnetics Corp. NT-360/Oxford spectrometer, and data manipulation utilized standard Nicolet software with a 1280/293B data system. Broad-band heteronuclear coupling was employed. Two-dimensional (2-D) ^{11}B–^{11}B NMR spectra were produced on selected samples via procedures described elsehwere.[13] Unit resolution mass spectra in the electron-impact (EI) or chemical ionization (CI) mode were obtained on a Finnigen MAT Model 4610 GC/MS spectrometer in the Department of Chemistry or by Harvey Laboratories, Inc., Charlottesville, VA. Calculated mass spectra based on natural isotopic abundances were generated with program MASSPEAK (R. N. Grimes, 1982).[20] Infrared spectra were recorded on a Perkin-Elmer Model 1430 spectrometer.

Except where otherwise indicated, all syntheses were conducted in vacuo or under an inert atmosphere, and chromatography was carried out on silica plates or columns open to the atmosphere.

Preparation of *nido*-1,2,3-$(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_3H_5)$ (1a). A 30-mg (0.114-mmol) sample of *closo*-1,2,3-$(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_4)$[2e] was dissolved in 15 mL of dry 1,2-$(Me_2N)_2(CH_2)_2$ and refluxed with stirring in vacuo for 45 min. After a spot-*thin-layer chromatogram* (TLC) *of the mixture indicated* no starting material remained, the solution was rotoevaporated to dryness and extracted with CH_2Cl_2, after which an insoluble white residue remained in the reaction flask. The yellow solution was evaporated to dryness and eluted on a silica preparative TLC plate with 25% CH_2Cl_2 in hexane, giving a bright yellow band (R_f 0.90) which was characterized as **1a**: 24 mg (0.945 mmol, 83% yield); mass spectrum, parent envelope cutoff at *m/e* 255 corresponding to $^{13}C^{12}C_{11}{}^{11}B_3{}^1H_{21}{}^{56}Fe^+$, $FeC_{12}B_3$ pattern; 360-MHz proton NMR spectrum in $CDCl_3$ (s = singlet; t = triplet; m = multiplet) δ −6 (B–H–B), 1.25 (t, CH_3), 1.94 (m, CH_2), 4.74 (s, C_6H_6). Only traces of other products were observed.

Preparation of *nido*-1,2,3-$(\eta^6\text{-}C_6Me_3)Fe(Et_2C_2B_3H_5)$ (1b). An 18-mg (0.059-mmol) sample of *closo*-1,2,3-$(\eta^6\text{-}C_6Me_6)Fe(Et_2C_2B_4H_4)$[2e] was dissolved in 1 mL of 1,2-$(Me_2N)_2(CH_2)_2$ and 5 mL of benzene and stirred for 3 days at room temperature, after which spot TLC analysis indicated very little reaction had occurred. An additional 5 mL of benzene and 0.1 mL of water were added, and the mixture was refluxed for 30 h, which still failed to produce more than a trace of new product. The mixture was evaporated to dryness, 10 mL of 1,2-$(Me_2N)_2(CH_2)_2$ was added, and the mixture was refluxed for 3 h. After removal of solvent by evaporation and extraction with CH_2Cl_2, the yellow solution was evaporated to dryness and the residue purified by TLC (25% CH_2Cl_2 in hexane) to give yellow solid **1b**: 14 mg (0.047 mmol, 80%); mass spectrum, parent envelope cutoff at *m/e* 339, corresponding to $^{13}C^{12}C_{17}{}^{11}B_3{}^1H_{33}{}^{56}Fe^+$, $C_{18}B_3Fe$ pattern. Only traces of other products were observed.

Preparation of $(\eta^6\text{-}C_6H_6)Fe(Et_4C_4B_6H_6)$ (2). In an O_2-free atmosphere 111 mg (0.437 mmol) of **1a** was dissolved in 5 mL of dry THF and the solution was added dropwise, with stirring, to a 25-mL flask containing 100 mg (2.5 mmol) of KH. After 30 min of stirring, during which gas was evolved and the orange color darkened slightly, $FeCl_2$ (100 mg, 0.78 mmol) was added and stirring was continued another 30 min. The reaction mixture was filtered to remove unreacted KH and $FeCl_2$, and the solution, now olive green, was removed from the drybox and exposed to the atmosphere. Within a few minutes the color returned to orange. TLC with 25% CH_2Cl_2 in hexane gave only two bands, yellow unreacted starting material (**1a**) (47 mg (0.185 mmol), R_f 0.55) and air-stable, red crystalline $(\eta^6\text{-}C_6H_6)Fe(Et_4C_4B_6H_6)$ (**2**) (R_f 0.48, 10 mg (0.27 mmol, 21.4% based on **1a** consumed)): mp 153–155 °C; mass spectrum, parent envelope cutoff at *m/e* 371 corresponding to $^{13}C_{12}C_{17}{}^{11}B_6{}^1H_{32}{}^{56}Fe^+$, $C_{18}B_6Fe$ pattern; 360-MHZ ^1H NMR spectrum in C_6D_6, triplets (CH_3) at δ 0.945, 1.022, 1.220, 1.368, multiplets (CH_2) at δ 1.68, 1.95, 2.02, 2.31, singlet (C_6H_6) at δ 5.048.

Reaction of $(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_4)$ with Al, $AlCl_3$, and Naphthalene. A 42-mg (0.16-mmol) sample of the ferracarborane was dissolved in 25 mL of hexane, and 18 mg (0.67 mmol) of Al powder and 158 mg (1.23 mmol) of naphthalene were added. $AlCl_3$ (92 mg, 0.69 mmol) was added with stirring, and the mixture was heated to 80 °C in an oil bath for 20 min. After being cooled, the mixture was rotoevaporated to dryness and excess naphthalene was removed by vacuum sublimation. The residue was extracted with CH_2Cl_2 and developed on a silica TLC plate in 1:2 CH_2Cl_2/hexane to give, in addition to unreacted starting carborane, two products. Yellow **3**: R_f 0.64, 3 mg; mass spectrum, parent envelope cutoff at *m/e* 431, pattern corresponding to $C_{26}B_3Fe$, possibly *nido*-1,2,3-$(\eta^6\text{-}C_{10}H_8)FeEt_2C_2B_3H_4\text{-}B\text{-}C_{10}H_7$;[21] the ^1H NMR spectrum exhibits singlets at δ 0.412, 4.482, a triplet at δ 1.252, doublets at δ 3.14, and 3.62, and multiplets at δ 0.90, 2.08, 2.29, 2.62, 2.80, 3.02, and 3.25. Golden **4**: R_f 0.56; mp 148–149 °C; 2 mg; mass spectrum, parent envelope cutoff at *m/e* 569, corresponding to $^{13}C^{12}C_{26}{}^{11}B_8{}^1H_{44}{}^{56}Fe_2{}^{2+}$, $C_{27}B_8Fe_2$ pattern, in agreement with X-ray structure determination (vide infra); ^1H NMR, triplet at δ 1.35, doublet at δ 1.93, multiplets at δ 0.91, 1.72, 2.21, 2.41.

Preparation of $(\eta^6\text{-}C_6H_5\text{–}C_6H_5)Fe(Et_2C_2B_4H_4)$ (5). (a) Vapor-Phase Method. A 73-mg (0.25-mmol) sample of $(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)$ and biphenyl (39 mg, 0.25 mmol) were placed in an evacuated Pyrex tube which was sealed and heated in an oil bath at 200 °C for 15 min. After the mixture was cooled to room temperature, the tube was opened and the contents extracted with CH_2Cl_2 and developed on a TLC plate with 25% CH_2Cl_2 in hexane, giving orange solid **5**: R_f 0.32; 37 mg (0.11 mmol, 44%).

(b) Al/$AlCl_3$ Method. In a 100-mL round-bottom flask were placed 25 mL of dry hexane, 44.5 mg (2.89 mmol) of biphenyl, 23 mg (0.85 mmol) of Al powder, and 160 mg (0.548 mol) of $(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)$. The mixture was brought to reflux under an N_2 atmosphere, and $AlCl_3$ (461 mg, 3.46 mmol) was added with stirring. After the mixture was refluxed for 1 h with stirring under N_2, the solvent was removed by evaporation and 25 mL of 1:1 CH_3OH/H_2O was added slowly. The crude product was extracted with CH_2Cl_2 in four portions, which were reduced in volume by evaporation and placed on a silica gel column (1.5 × 30 cm) which had been charged with hexane. Elution with hexane gave unreacted biphenyl followed by crude **5**, which was purified on silica gel TLC plates in 1:1 CH_2Cl_2/hexane to give 44 mg (0.13 mmol, 24%) of **5**.

The mass spectrum of **5** exhibits a parent group with a cutoff at *m/e* 341, corresponding to $^{13}C^{12}C_{17}{}^{11}B_4{}^1H_{24}{}^{56}Fe^+$ with a $C_{18}B_4Fe$ pattern; in addition to loss of C_6H_4, noted above, there are intense peaks at *m/e* 210, 154, 134, and 56, corresponding to $(C_6H_5\text{–}C_6H_5)Fe^+$, $C_6H_5\text{–}C_6H_5{}^+$, $(C_6H_6)Fe^+$, and Fe^+, respectively. The ^1H and ^{13}C NMR spectra and assignments are shown in parts a and b of Figure 5.

Preparation of $(\eta^6{:}\eta^{6'}\text{-}C_6H_5\text{–}C_6H_5)[Fe(Et_2C_2B_4H_4)]$ (6). In a 10-mL Pyrex tube fitted with a greaseless vacuum stopcock,

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(19) (a) Trotter, J. *Acta Crystallogr.* **1961**, *14*, 1135. (b) Hargreaves, A.; Rizvi, S. H. *Ibid.* **1962**, *15*, 365.

(20) Program available on request.

(21) A related complex, $(\eta^6\text{-}C_{10}H_8)Fe(Et_2C_2B_4H_4)$, has been prepared: see ref 15b.

28 mg (0.082 mmol) of **5** and 29 mg (0.10 mmol) of (η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$)[2d] were combined, and the reactor was evacuated, sealed, and immersed in an oil bath at 180 °C for 20 min. After being cooled to room temperature, the mixture was extracted with CH_2Cl_2 and developed on a TLC plate with 25% CH_2Cl_2/hexane to give 12 mg of unreacted **5**, R_f 0.15. A pale yellow band (R_f 0.06) was removed and developed on another plate to give 4 mg (0.0076 mmol) of **6**, corresponding to 16% yield based on **5** consumed. Yellow **6**, R_f 0.24 (1:1 CH_2Cl_2/hexane), melts with decomposition above 200 °C. Mass spectrum: parent grouping cuts off at *m/e* 527, corresponding to $^{13}C^{12}C_{23}{}^{11}B_8{}^{1}H_{38}{}^{56}Fe_2{}^{2+}$ with a $C_{24}B_8Fe_2$ pattern. ^1H NMR in acetone-d_6: δ 1.103 (t, CH_3); 1.127 (t, CH_3) (interpreted as overlapping triplets); 2.29 (m, CH_2); 2.58 (m, CH_2); 5.72 (t, p-CH); 5.82 (t, m-CH); 6.21 (d, o-CH).

X-ray Structure Determinations on 1,2-[(η^6-C_6H_6)Fe($Et_2C_2B_4H_3$)]$_2$CH(CH_3)CH_2 (4) and (η^6-C_6H_5–C_6H_5)Fe($Et_2C_2B_4H_4$) (5). In each case, crystals grown from solution (acetone for **4** and *n*-hexane for **5**) were mounted on glass fibers, examined by precession photography, and found acceptable. Relevant parameters for the data collections and structure determinations are found in Tables III and VII. Cell dimensions and space group data were obtained by standard methods on Enraf-Nonius and Nicolet R3 four-circle diffractometers. The θ–2θ scan technique was used as previously described[22] to record the intensities for all nonequivalent reflections within the 2θ ranges given in Tables III and VII. Scan widths were calculated as ($A + B \tan \theta$), where A is estimated from the mosaicity of the crystal and B allows for the increase in peak width due to $K\alpha_1 - K\alpha_2$ splitting.

The intensities of three standard reflections showed no greater fluctuations during data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects and absorption. Only those reflections for which $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics ($p = 0.03$),[23] were used in the final refinement of the structural parameters.

Solution and Refinement of the Structures. Three-dimensional Patterson syntheses were used to determine the heavy-atom positions, which phased the data sufficiently well to permit location of the remaining non-hydrogen atoms from Fourier syntheses. Full-matrix least-squares refinements were carried out as previously described.[22] In **4**, one cage ethyl group was found to be positionally disordered. Anisotropic temperature factors were introduced for all non-hydrogen atoms in each structure except for the disordered ethyl group in **4**. Additional Fourier difference functions permitted location of all hydrogen atoms other than those on the disordered ethyl. For both structures, the hydrogen locations were included in four cycles of least-squares refinement and then held fixed.

The models converged to the R values given in Tables III and VII, and final difference Fourier maps were featureless. Listings of the observed and calculated structure factors are available together with thermal parameters as supplementary material.

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Registry No. **1a**, 95464-79-2; **1b**, 87862-00-8; **2**, 95464-80-5; **3**, 95552-49-1; **4**, 95482-47-6; **5**, 95482-48-7; **6**, 95464-81-6; *closo*-1,2,3-(η^6-C_6H_6)Fe($Et_2C_2B_4H_4$), 84582-99-0; *closo*-1,2,3-(η^6-C_6Me_6)Fe($Et_2C_2B_4H_4$), 84583-01-7; (η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$), 95464-66-7; biphenyl, 92-52-4; naphthalene, 91-20-3.

Supplementary Material Available: Tables of calculated and observed structure factors, thermal parameters, and mean planes (28 pages). Ordering information is given on any current masthead page.

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[22] Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447.

[23] Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

Organotransition-Metal Metallacarboranes. 6.[1] Synthesis of $(CH_2)_n$-Bridged (η^6-Arene)ferracarboranes: Ferrocenophane Analogues. Structure of [η^6-$C_6H_5(CH_2)_3$]Fe($C_2B_4H_5$)

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The ferracarborane (η^6-C_8H_{10})Fe([Ph(CH_2)$_3$]$C_2B_4H_5$) containing a 3-phenylpropyl substituent on a cage carbon atom was prepared and treated with $AlCl_3$/Al to give [η^6-$C_6H_5(CH_2)_3$]Fe($C_2B_4H_5$) (**3**), an air-stable yellow solid containing a trimethylene group bridging the carborane and benzene ligands. Reaction of **3** with CH_3OH removed the apex boron of the carborane ligand to give *nido*-[η^6-$C_6H_5(CH_2)_3$]Fe($C_2B_3H_6$) (**4**). In an attempt to prepare analogous dimethylene-bridged complexes, (η^6-C_8H_{10})Fe([Ph(CH_2)$_2$]$C_2B_4H_5$) was synthesized and treated with $AlCl_3$/Al, but species containing intramolecular bridges were not obtained; instead, the main product was a dimer, [η^6-$C_6H_5(CH_2)_2$Fe($C_2B_4H_5$)]$_2$, which is proposed to have a "head-to-tail" structure in which each iron binds to one carborane ligand and to the phenyl group attached (through a –$(CH_2)_2$– chain) to the other carborane. The structures of the new compounds were determined via high-resolution ^{11}B, ^1H, and ^{13}C NMR, IR, and mass spectra and an X-ray crystal structure analysis of **3**. Crystal data: $M_r = 247$, space group $P2_1/c$, $Z = 4$, $a = 13.942$ (6) Å, $b = 6.311$ (3) Å, $c = 14.577$ (2) Å, $\beta = 111.33$ (3)°, $V = 1195$ Å^3, $R = 0.039$ for 1870 reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The preceding articles in this series have described practical, directed syntheses of metallacarboranes containing cyclic π-systems such as $C_8H_8{}^{2-}$ or arenes coordinated to the metal atom.[1,3] As these synthetic approaches are quite general, the way is open to the construction of complexes having specific desired structural features, including those of potential value in organic or organo-

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[1] Part 5: first of three papers in this issue.

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[3] (a) Maynard, R. B.; Swisher, R. G.; Grimes, R. N. *Organometallics* **1983**, *2*, 500. (b) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Ibid.* **1983**, *2*, 506. (c) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Ibid.* **1984**, *3*, 599.