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.

Scheme I

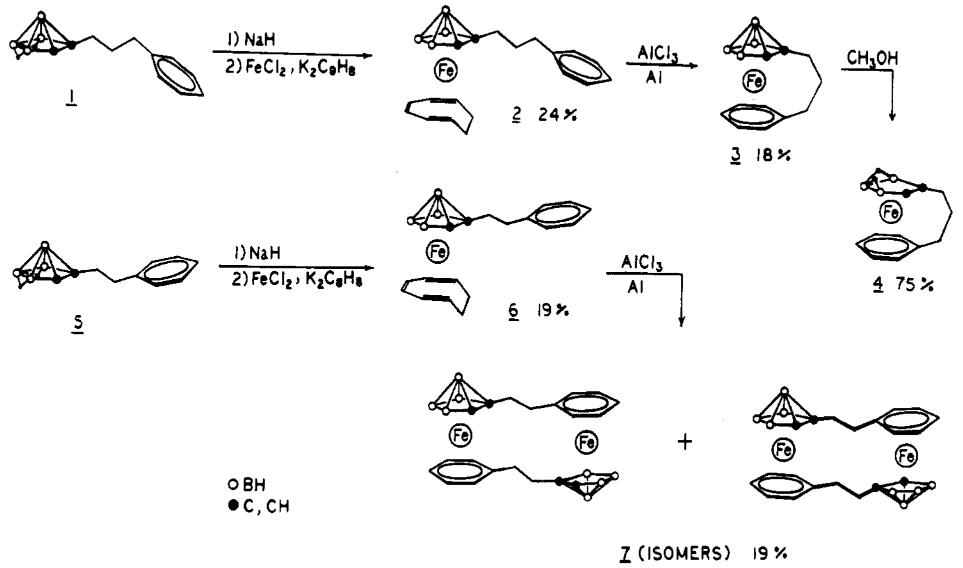

Table I. 115.8-MHz ^{11}B FT NMR Data

compound	solv[a]	δ (J_{BH}, Hz)[b]	rel area
2-Ph(CH$_2$)$_3$-2,3-C$_2$B$_4$H$_7$ (1)	H	3.42 (162), 1.08,[c] 0.40,[c] −46.85 (181)	1:1:1:1
(C$_8$H$_{10}$)Fe[Ph(CH$_2$)$_3$C$_2$B$_4$H$_5$] (2)	D	11.61 (145), 3.39,[c] 1.09[c]	1:1:2
[C$_6$H$_5$(CH$_2$)$_3$]Fe(C$_2$B$_4$H$_5$) (3)	D	7.94,[c] 6.13,[c] 2.15[c]	1:1:2
	B	10.01 (147), 7.65 (163), 2.85 (154)	1:1:2
[(C$_6$H$_5$(CH$_2$)$_3$]Fe(C$_2$B$_3$H$_6$) (4)	H	2.96 (129), −0.83 (116)	1:2
	D	2.53 (136), −2.08 (131)	1:2
2-Ph(CH$_2$)$_2$-2,3-C$_2$B$_4$H$_7$ (5)	H	2.29 (164), −0.02 (120), −0.62 (155), −48.03 (180)	1:1:1:1
(C$_8$H$_{10}$)Fe[Ph(CH$_2$)$_2$C$_2$B$_4$H$_5$] (6)	D	11.36 (141), 3.12,[c] 0.85 (150)	1:1:2
[Ph(CH$_2$)$_2$C$_2$B$_4$H$_5$]$_2$Fe$_2$ (7)	E	13.31,[c] 9.58,[c] 4.39,[c] 1.48[c]	~1:1:2:4

[a] Key: H = hexane, D = dichloromethane, B = benzene, E = C$_6$D$_6$. [b] BF$_3$·OEt$_2$ shift is zero, positive shifts downfield. [c] J not measurable.

metallic synthesis. One idea which appeared worthy of exploration was to prepare (arene)(carborane)metal sandwich complexes in which the arene and carborane ligands are linked via a hydrocarbon chain.[4] If the arene ring in such a complex can be induced to dissociate from the metal at least part of the time in some media, the metal center will be coordinatively unsaturated and hence highly reactive; at the same time, the permanent attachment of the arene to the –C$_2$B$_4$H$_5$ carborane ligand (itself firmly metal-bound[5]) ensures that the arene–metal dissociation is reversible. Such complexes are of potential value as homogeneous catalysts which would exploit both the robustness of MC$_2$B$_4$ metal–carborane clusters[6] and the propensity of arenes toward decomplexation from transition-metal centers under some conditions.[7] A somewhat similar concept has been employed in an icosahedral phosphinorhodacarborane containing a metal-chelating 4-butenyl side chain attached to the carborane ligand, which is a precursor to a particularly active catalyst for homogeneous hydrogenation.[8] As distinct from the rhodium species, whose alkenyl ligand is irreversibly converted by H$_2$ to a noncoordinating butyl group,[8] our proposed complexes would utilize arenes and first-row transition metals (e.g., iron) as well as the small carborane (C$_2$B$_4$) ligand; hence a substantially different chemistry is anticipated.

This paper reports the preparation and characterization of several polymethylene-bridged (arene)ferracarboranes including an apparent "head-to-tail" dimer, a class novel to carborane chemistry.

Results and Discussion

Synthesis of Trimethylene-Linked (Arene)-ferracarborane Complexes. The synthetic route employed in this work is outlined in Scheme I. The carborane derivative 1, containing a 3-phenylpropyl unit attached to a cage carbon atom, was prepared from B$_5$H$_9$ and 5-phenyl-1-pentyne via a previously described general method[9] for the synthesis of *nido*-RR′C$_2$B$_4$H$_6$ carboranes. The characterization of 1, an air-stable liquid, was based on its 115.8-MHz ^{11}B and 360-MHz ^{1}H FT NMR (Tables I and II), IR spectrum (Table III), and mass spectrum, all of which are consistent with the proposed structure (Scheme I). Bridge-deprotonation of 1 to yield the anion 1$^-$ followed by reaction with FeCl$_2$ and C$_8$H$_8$$^{2-}$ ion in tetrahydrofuran (THF) gave the cyclooctatriene complex (η^6-C$_8$H$_{10}$)Fe[C$_6$H$_5$(CH$_2$)$_3$C$_2$B$_4$H$_5$] (2) as an orange oil. Since (η^6-C$_8$H$_{10}$)Fe(R$_2$C$_2$B$_4$H$_4$) homologues reported earlier

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[4] We are indebted to Professor Kenneth Wade for suggesting this approach.

[5] Maynard, R. B.; Grimes, R. N. *J. Am. Chem. Soc.* **1982**, *104*, 5983.

[6] Grimes, R. N. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, Chapter 5.5, pp 459–542.

[7] (a) Jaouen, G. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1978; Vol. II, Chapter 2, pp 65–120. (b) Davies, S. G. "Organotransition Metal Chemistry: Applications to Organic Synthesis"; Pergamon Press: Oxford, 1982.

[8] Delaney, M. S.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1981**, *20*, 1341.

[9] (a) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 3294. (b) Maynard, R. B.; Borodinsky, L.; Grimes, R. N. *Inorg. Synth.* **1983**, *22*, 211.

Table II. 360-MHz ^{1}H FT NMR Data

compd	δ [rel to $Si(CH_3)_4$]^a	rel areas
1^b	7.30 m (C_6H_5), 6.29 s, br (cage C–H), 2.75 t (CH_2), 2.56 m (CH_2), 1.99 t (CH_2), –1.99 s, br (B–H–B)	5:1:2:2:2:2
2^b	6.46 m (C_6H_5), 5.46 t (C_8H_{10}), 4.90 m (C_8H_{10}), 4.55 t (C_8H_{10}), 4.39 t (C_8H_{10}), 3.81 d (C_8H_{10}), 1.90 t (CH_2), 1.78 m (CH_2), 1.48 m (CH_2), 1.21 m (CH_2), –0.63 m (C_8H_{10}), –0.73 m (C_8H_{10})	5:2:3:1:1:1:3:1:1:1:1:1
3^c	5.71 m (C_6H_5), 5.47 m (C_6H_5), 5.43 m (C_6H_5), 5.03 m (C_6H_5), 4.70 m (cage C–H), 2.72 m (CH_2), 2.52 m (CH_2), 2.38 m (CH_2), 2.08–2.27 m (CH_2)	1:1:2:1:1:1:2:1:2
4^d	5.38 m (C_6H_5), 5.30 m (C_6H_5), 5.01 m (C_6H_5), 4.71 m (C_6H_5), 4.09 m (C_6H_5), 4.04 s (cage C–H), 3.65 s, br (B–H), 3.28 s, br (B–H), 2.90 s, br (B–B), 2.31 m (CH_2), 1.84 m (CH_2), 1.66 m (CH_2), 1.38 m (CH_2), –5.77 s, br (B–H–B)	1:1:1:1:1:1:1
5^b	7.31 (C_6H_5), 6.31 s, br (cage C–H), 2.98 t (CH_2), 2.85 m (CH_2), –1.95 s, br (B–H–B)	5:1:2:2:2
6^d	7.18 m (C_6H_5), 5.60 m,^{e} 4.75 t,^{e} 4.66 t,^{e} 4.25 s, br (cage C–H), 2.78 m (CH_2), 2.59 m (CH_2), 2.16 m (CH_2), 1.69 m (C_8H_{10}), –0.17 m (C_8H_{10}), –0.27 m (C_8H_{10})	5:1:2:1:1:1:1:2:1:2:1:1
7^d	5.55 m (C_6H_5), 5.10 m, 4.78 m, 4.70 t, (2.5–3.0),^{f} 2.12 t, 1.60 m, 1.35 d, –0.20 m, –0.33 m	1:1:1:1:6:0.5:4:1:1:1

[a] Legend: m = multiplet, d = doublet, t = triplet, q = quadruplet, br = broad. [b] Acetone-d_6 solution. [c] $CDCl_3$ solution. [d] C_6D_6 solution. [e] C_6H_5 and C_8H_{10} resonances, not distinguishable. [f] Overlapped series of multiplets.

were found to undergo displacement of the C_8H_{10} ligand by arenes over $AlCl_3$,[3b] similar treatment of **2** was anticipated to give a trimethylene-bridged complex $(\eta^6\text{-}C_6H_5\text{-}(CH_2)_3]Fe(C_2B_4H_5)$ (**3**), and this was in fact observed. Conversion of **2** to **3** was also achieved thermally by heating at 180 °C for 1 h.

Complexes **2** and **3** were characterized from their ^{11}B and ^{1}H NMR, infrared (Tables I–III), and mass spectra, augmented by a ^{13}C NMR spectrum of **2** and an X-ray crystal structure analysis in the case of **3**. The ^{11}B NMR spectra of both complexes exhibit clear patterns consistent with the proposed *closo*-MC_2B_4 cage geometry having local mirror symmetry. The mass spectrum of **2** contains a strong parent grouping with a cutoff at *m/e* 355 (^{13}C peak) and a pattern of intensities closely matching that calculated for $C_{19}B_4Fe$; loss of C_8H_{10} is indicated by an even stronger grouping with local cutoff at *m/e* 249. The high-resolution ^{13}C and ^{1}H spectra of **2** confirm the presence of both cyclooctatriene and phenyl groups in the molecule, and the chemical shifts of the C_8H_{10} and C_6H_5 moieties indicate that only the former group is coordinated to iron (this is particularly evident in comparing the ^{1}H spectrum of **2** with those of the known species $(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)$[3a] and $(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_4)$[3b]). Further support for the proposed structure of **2** (Scheme I) is given by its conversion to **3** via displacement of the C_8H_{10} ligand.

The chemical ionization (CI) mass spectrum of **3** in CH_4 contains a strong parent group with a cutoff at *m/e* 250, consistent with the pattern calculated for $(C_6H_5)(CH_2)_3FeC_2B_4H_6^+$, a species indicative of protonation in the spectrometer; the presence of a less intense envelope at *m/e* 265 shows that methylation has also occurred. The NMR and IR data support the trimethylene-bridged structure shown in Scheme I, and this geometry was confirmed by an X-ray diffraction study described below.

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

1^a	3100 s, 3080 s, 3040 vs, 2940 vs, 2860 vs, 2600 vs, 1950 s, br, 1900 m, br, 1800 m, br, 1810 w, br, 1750 w, br, 1650 w, br, 1610 s, 1590 m, 1500 vs, 1460 vs, 1390 m, 1360 m, 1340 m, 1250 w, 1190 w, 1160 m, 1140 w, 1110 m, 1080 s, 1060 m, 1030 s, 970 s, 910 s, 880 m, 840 s, 790 m, 750 vs, 700 vs, 680 w, 660 s
2^b	3020 s, 2920 s, 2880 m, 2820 s, 2520 vs, 1490 m, 1450 m, 1370 w, 1340 w, 1300 w, 1110 w, 1070 m, 1060 m, 1000 s, 970 s, 690 vs, 620 m
3^a	3040 w, 2910 s, 2830 m, 2490 vs, 2470 vs, 1630 m, br, 1440 s, 1420 s, 1400 s, 1330 w, 1290 w, 1240 w, 1200 w, 1180 w, 1140 w, 1120 w, 1100 m, 1050 w, 1020 m, 1000 m, 990 m, 950 w, 930 w, 890 w, 870 s, 860 s, 840 m, 820 m, 790 m, 770 w, 750 w, 720 m, 680 m, 670 m, 620 w, 590 w, 530 br, 470 m, 390 m
4^b	3060 w, 2940 vs, 2900 vs, 2840 s, 2500 vs, 1860 s, br, 1810 w, 1700 w, 1650 w, 1600 m, br, 1530 m, 1430 s, 1410 m, 1360 m, 1330 w, 1290 w, 1230 m, 1180 w, 1140 w, 1120 w, 1090 w, 1060 m, 1050 w, 1030 w, 990 w, 950 m, 910 m, 890 w, 860 w, 820 w, 680 w, 660 m, 630 w, 550 m
5^c	3090 m, 3080 m, 3020 s, 2920 vs, 2860 s, 2580 vs, 1950 m, br, 1900 m, br, 1820 w, br, 1610 m, 1500 vs, 1460 vs, 1390 m, 1340 w, 1270 w, 1250 w, 1220 w, 1190 w, 1170 m, 1130 w, 1110 w, 1080 m, 1070 w, 1040 w, 980 m, 920 m, 850 m, 780 m, 750 s, 700 vs, 660 m
6^a	3080 w, 3060 w, 3020 m, 2920 s, 2840 m, 2520 vs, 1730 w, 1640 m, br, 1610 m, 1500 s, 1450 vs, 1440 m, 1400 m, 1380 m, 1340 m, 1330 w, 1300 m, 1280 w, 1230 w, 1220 w, 1190 w, 1160 w, 1130 m, 1080 m, 1070 s, 1030 m, 1000 w, 990 w, 970 m, 940 m, 910 w, 880 s, 870 s, 840 s, 830 s, 810 w, 750 vs, 730 s, 720 m, 700 vs, 660 w, 620 w, 580 m, 490 s, 460 s, 410 m
7^a	3100 w, 3080 w, 3040 m, 2920 vs, 2860 vs, 2540 vs, 1960 w, br, 1880 w, br, 1820 w, br, 1730 w, br, 1640 m, br, 1620 m, 1530 w, 1510 m, 1460 vs, 1430 w, 1380 w, 1350 w, 1320 w, 1270 w, 1230 w, 1200 w, 1160 w, 1120 w, 1070 w, 1040 w, 1020 w, 1010 w, 980 w, 950 w, 920 w, 880 m, 840 m, 760 m, 710 vs, 620 w, br, 560 w, br, 480 m, br

[a] KBr pellet. [b] CCl_4 solution vs. CCl_4. [c] Neat sample.

The properties of **3** have been explored to a limited extent. In an attempt to dislodge the aryl group from the metal atom, **3** was treated with an $Al/AlCl_3$ mixture in benzene, but no reaction was observed. However, **3** does undergo facile conversion to the corresponding *nido*-ferracarborane species $[\eta^6\text{-}C_6H_5(CH_2)_3]Fe(C_2B_3H_6)$ (**4**) on treatment with methanol, as depicted in Scheme I. The mass spectrum of **4** (CI in CH_4) exhibits an intense parent envelope with a cutoff at *m/e* 240 and a pattern consistent with the proposed composition; virtually no other peaks appear in the spectrum. The presence of three boron atoms is evident from the ^{11}B NMR spectrum, and an IR band at 1860 cm^{-1} is characteristic of B–H–B bridge stretching. While we have not yet examined the chemistry of **4**, it seems likely that it can be bridge-deprotonated with NaH and that the resulting anion can be complexed to

Table IV. Experimental Parameters and Crystal Data on 3

M_r	247	B	0.35
space group	$P2_1/c$	trans coeff (max)[a]	0.930
a, Å	13.942 (6)	trans coeff (min)	0.598
b, Å	6.311 (3)	2θ range, deg	1-52
c, Å	14.577 (2)	reflectns obsd	2063
β, deg	111.33	reflectns refined	1870
V, Å^3	1195	R	0.039
μ, cm^{-1}	12.5	R_w	0.049
D(calcd), g cm^{-3}	1.375	esd unit wt	1.1
A	0.60	Z	4

[a] Crystal dimensions (mm from centroid): 100 (0.050), $\bar{1}00$ (0.050), 011 (0.510), $0\bar{1}\bar{1}$ (0.510), $01\bar{1}$ (0.530), $0\bar{1}1$ (0.530), 001 (0.310), $00\bar{1}$ (0.310).

transition metal ions in a 2:1 ratio to generate multidecker species, e.g., $[C_6H_5(CH_2)_3]Fe(C_2B_3H_4)Ni(C_2B_3H_4)Fe[C_6H_5(CH_2)_3]$. Such possibilities are under investigation.

Synthesis of a Dimethylene-Linked (Arene)-ferracarborane Dimer. Since complex 3 appeared resistant to displacement of its aryl group from the metal, we sought to modify the structure of 3 to promote lability of the phenyl ring. It was felt that this might be accomplished by replacing the trimethylene-bridging chain with a dimethylene unit, thereby increasing valence angle strain in the Fe–aryl–$(CH_2)_2$–carborane linkage and hence providing thermodynamic driving force for dissociation of the phenyl group from the metal. Accordingly, the carborane 5, containing a 2-phenylethyl substituent, was prepared, deprotonated to the anion 5^-, and treated with $FeCl_2$ and $K_2C_8H_8$ to give complex 6 (Scheme I), a species analogous to 2, described above. Characterization of compounds 5 and 6 via NMR, IR, and mass spectroscopy was straightforward, the spectra exhibiting close resemblance to those of their trimethylene counterparts 1 and 2. We anticipated that treatment of 6 with $Al/AlCl_3$ would produce the desired dimethylene-bridged analogue of 3. However, no such species was detected; instead, yellow solid 7 was isolated and characterized as a dimeric complex whose proposed structure is shown (Scheme I) as a mixture of two isomers. The electron-impact (EI) mass spectrum of 7 exhibits a strong parent group with a cutoff at m/e 469 and a pattern consistent with a $C_{20}B_8Fe_2$ system, with evidence of hydrogen loss from the parent species. A strong envelope at m/e 235 with a similar intensity pattern indicates cleavage to the monomeric species in the spectrometer. From the NMR spectra it is clear that at least two (but probably only two) isomers are present; that these are inseparable on TLC plates is not surprising, given the closely similar geometries proposed in Scheme I. The suggested "head-to-tail" dimer structure has not been established; the ^1H NMR spectrum is too complex for detailed interpretation, but it does exhibit resonances in the region expected for Fe-coordinated phenyl groups ($\sim\delta$ 5.0).

If the assigned structure is correct, this implies that the severe ring strain which would have been introduced by coordination of the phenyl ring in 6 to its own iron atom (as originally intended) is avoided by formation of the dimer 7. Interestingly, an earlier attempt[10] to prepare the analogous $(CH_2)_2$-bridged derivative of $(C_6H_6)Fe(C_5H_5)^+$ also failed, giving instead a complex containing three $C_6H_5(CH_2)_2C_5H_5^+$ units linked by two Fe^{2+} ions. As in the present study, the strain introduced by a dimethylene bridge apparently prevents formation of the intramolecular-bridged species. However, 7 itself opens new synthetic possibilities which are under investigation.

Table V. Positional Parameters for $[C_6H_5(CH_2)_3]Fe(C_2B_4H_5)$ (3)

atom	x	y	z
Fe	0.18503 (4)	0.05427 (9)	0.21825 (4)
C(2)	0.3373 (3)	0.0423 (7)	0.2865 (3)
C(3)	0.2800 (3)	−0.0771 (7)	0.3449 (3)
C(M1)	0.4190 (3)	−0.0585 (8)	0.2668 (3)
C(M2)	0.3995 (3)	−0.0316 (9)	0.1576 (3)
C(M3)	0.3056 (4)	−0.1502 (9)	0.0906 (3)
C(R1)	0.2049 (3)	−0.0847 (8)	0.0970 (3)
C(R2)	0.1469 (4)	−0.2211 (7)	0.1355 (3)
C(R3)	0.0619 (3)	−0.1496 (8)	0.1544 (3)
C(R4)	0.0202 (3)	0.0606 (9)	0.1324 (3)
C(R5)	0.8009 (3)	0.1967 (8)	0.0935 (3)
C(R6)	0.1673 (3)	0.1251 (8)	0.0748 (3)
B(4)	0.1977 (4)	0.0553 (10)	0.3684 (3)
B(5)	0.2113 (4)	0.2979 (9)	0.3292 (4)
B(6)	0.3033 (4)	0.2785 (8)	0.2825 (4)
B(7)	0.3238 (4)	0.1671 (10)	0.4012 (4)
H(M11)	0.486 (3)	−0.001 (7)	0.304 (3)
H(M12)	0.432 (3)	−0.208 (7)	0.287 (3)
H(M21)	0.466 (3)	−0.075 (7)	0.147 (3)
H(M22)	0.395 (3)	0.108 (8)	0.141 (3)
H(M31)	0.325 (3)	−0.295 (8)	0.108 (3)
H(M32)	0.312 (4)	−0.138 (9)	0.036 (4)
H(P2)	0.167 (3)	−0.354 (7)	0.154 (3)
H(R3)	0.028 (3)	−0.229 (8)	0.178 (3)
H(R4)	−0.030 (3)	0.106 (7)	0.141 (3)
H(R5)	0.056 (3)	0.341 (8)	0.075 (3)
H(R6)	0.202 (3)	0.209 (7)	0.055 (3)
H(3)	0.303 (3)	−0.219 (7)	0.364 (3)
H(4)	0.148 (3)	−0.000 (9)	0.402 (3)
H(5)	0.179 (3)	0.444 (8)	0.331 (3)
H(6)	0.347 (3)	0.398 (8)	0.254 (3)
H(7)	0.401 (3)	0.188 (8)	0.473 (3)

Table VI. Bond Distances (Å) in 3

Fe-C(2)	2.013 (1)	C(3)-B(7)	1.748 (3)
Fe-C(3)	2.018 (2)	B(4)-B(5)	1.669 (3)
Fe-B(4)	2.132 (2)	B(4)-B(7)	1.791 (3)
Fe-B(5)	2.164 (2)	B(5)-B(6)	1.661 (3)
Fe-B(6)	2.116 (2)	B(5)-B(7)	1.746 (3)
Fe-C(R1)	2.077 (2)	B(6)-B(7)	1.792 (3)
Fe-C(R2)	2.072 (2)	C(M1)-C(M2)	1.522 (3)
Fe-C(R3)	2.076 (2)	C(M2)-C(M3)	1.516 (3)
Fe-C(R4)	2.088 (2)	C(M3)-C(R1)	1.505 (2)
Fe-C(R5)	2.074 (2)	C(R1)-C(R2)	1.425 (2)
Fe-C(R6)	2.063 (2)	C(R1)-C(R6)	1.416 (3)
C(2)-C(3)	1.454 (2)	C(R2)-C(R3)	1.386 (3)
C(2)-B(6)	1.555 (2)	C(R3)-C(R4)	1.405 (3)
C(2)-B(7)	1.787 (2)	C(R4)-C(R5)	1.379 (3)
C(2)-C(M1)	1.509 (2)	C(R5)-C(R6)	1.403 (2)
C(3)-B(4)	1.555 (3)	⟨C-H⟩	0.92
		⟨B-H⟩	1.11

X-ray Diffraction Study of $[\eta^6\text{-}C_6H_5(CH_2)_3]Fe(C_2B_4H_5)$ (3). Tables IV–VII present unit cell and data collection parameters, atomic coordinates, and bond distances and angles, and two views of the molecule are shown in Figure 1. As anticipated, the complex consists of an iron atom sandwiched between C_6H_5 and $C_2B_4H_5$ ligands which are linked by a trimethylene chain. Not surprisingly, the hydrocarbon linkage places constraints on the geometry of the metal-to-ligand binding, causing the planes of the phenyl and carborane rings to be mutually tilted by 7.5°; however, the distances from iron to the phenyl and carboranyl planes (1.53 and 1.60 Å, respectively) are comparable to those in other (η^6-arene)(carborane)iron complexes.[3b] Moreover, as is the case in previously determined structures of 7-vertex MC_2B_4 *closo*-metallacarboranes, the metal atom is essentially equidistant from the six phenyl carbons, and the bond lengths within the carborane cage and the C_6H_5 group are normal. The phenyl ring is significantly distorted at the point of attachment of the

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[10] Astruc, D.; Dabard, R. *J. Organomet. Chem.* **1975**, *96*, 283.

Table VII. Bond Angles (deg) in 3

Fe-C(2)-B(7)	92.9 (1)	C(3)-B(4)-B(5)	103.4 (2)	C(M3)-C(R1)-C(R2)	122.3 (2)
Fe-C(2)-C(M1)	127.6 (1)	Fe-B(5)-B(7)	89.1 (1)	C(M3)-C(R1)-C(R6)	121.1 (2)
C(3)-C(2)-B(6)	111.4 (1)	B(4)-B(5)-B(6)	105.9 (2)	C(R2)-C(R1)-C(R6)	116.3 (2)
C(3)-C(2)-C(M1)	122.1 (2)	Fe-B(6)-B(7)	89.4 (1)	C(R1)-C(R2)-C(R3)	121.8 (2)
B(6)-C(2)-C(M1)	126.5 (2)	C(2)-B(6)-B(5)	105.1 (2)	C(R2)-C(R3)-C(R4)	120.0 (2)
B(7)-C(2)-C(M1)	139.4 (1)	C(2)-C(M1)-C(M2)	112.5 (1)	C(R3)-C(R4)-C(R5)	119.9 (2)
Fe-C(3)-B(7)	93.9 (1)	C(M1)-C(M2)-C(M3)	114.1 (2)	C(R4)-C(R5)-C(R6)	120.2 (2)
C(2)-C(3)-B(4)	114.1 (2)	C(M2)-C(M3)-C(R1)	115.7 (2)	C(R1)-C(R6)-C(R5)	121.7 (2)
Fe-B(4)-B(7)	88.9 (1)	Fe-C(R1)-C(M3)	125.8 (1)		

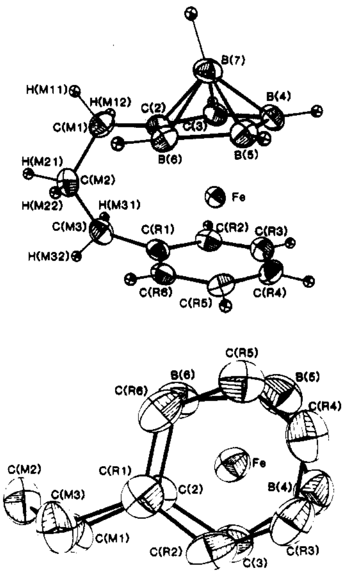

Figure 1. Two views of the molecular structure of 3. The bottom drawing is projected down the Fe–B(7) axis (B(7) is not shown).

$(CH_2)_3$ chain, as seen in the small C(R2)–C(R1)–C(R6) angle of 116.3°; the same effect is seen in the structures of $(C_6H_5C_6H_5)Fe(Et_2C_2B_4H_4)$[1] and $(C_6Me_3H_3)Fe(Et_2C_2B_4H_4)$,[3b] which also exhibit decreased internal C–C–C angles at ring carbon atoms having attached substituents. Both the phenyl ring and the carborane face bonded to iron are planar, with a maximum deviation from planarity of 0.013 Å (a table of mean planes is available as supplementary material).

In the five-carbon chain C(R1)–C(M3)–C(M2)–C(M1)–C(2), the two central C–C distances, which connect the methylene carbons, are about 0.1 Å longer than those at the ends [C(R1)–C(M3) and C(2)–C(M1)]. This probably reflects greater s character at the "end" carbons (approximately sp^2) in comparison to the three methylene carbon atoms where sp^3 hybridization is assumed. With respect to the $(CH_2)_3$ chain, it is notable that although there are apparently two possible conformations, i.e., with C(M2), bent either toward the cage carbon C(3) or away from it, only the latter is seen; no evidence for the alternate species (which would be a distinguishable isomer, not an enantiomer) has been detected. We have no satisfactory explanation for this finding at present.

It is of interest to compare the structure of 3 with those of ferrocenophanes[11] and of the $1,1'-(CH_2)_3(\eta^6-C_6H_5)Fe(\eta^5-C_5H_4)^+$ cation (8).[12] In [3]ferrocenophanes (ferrocene derivatives in which the cyclopentadienyl rings are linked by three-membered chains), those in which all three bridging atoms are carbon have tilt angles of 8.8–11° between the rings.[13] In 8, an electronic and structural analogue of 3, the corresponding tilt is 7°. Bond distances and angles involving the metal and hydrocarbon moieties are generally comparable in the two molecules, although the structure of 8 was found to have disorder vis-a-vis the C_5 and C_6 rings and was less accurately defined than that of 3.

Experimental Section

Materials and Instrumentation. Except where otherwise indicated, all syntheses were conducted in vacuo or under dry nitrogen, and reagents and solvents were reagent grade and used as received. Chromatography was carried out in air on silica columns or plates. ^{11}B, ^1H, and ^{13}C FT NMR spectra at 115.8, 360, and 90 MHz, respectively, as well as IR and mass spectra, and calculations of mass spectra, were obtained as described in the preceding paper.[1] The mass spectra of all new compounds reported exhibit intense parent envelopes and intensity profiles in the parent region consistent with calculated spectra based on natural isotope distribution.

Preparation of 2-Ph$(CH_2)_3$-*nido*-2,3-$C_2B_4H_7$ (1). This synthesis employs the general method of Hosmane and Grimes[9] for preparing *nido*-$R_2C_2B_4H_6$ carboranes. A 2.880-g (20-mmol) sample of 5-phenyl-1-pentyne (Farchan) was placed in a 500-mL Pyrex reactor equipped with a Teflon vacuum stopcock, and the reactor was cooled in liquid nitrogen and evacuated. The contents were degassed by thawing and refreezing, and 20 mmol of pentaborane(9) (B_5H_9) from laboratory stock and 17 mmol of triethylamine were distilled into the reactor. The flask was placed in an ice bath and stirred magnetically; within several minutes the mixture evolved gas vigorously and became viscous. *Note: As this reaction is highly exothermic, it is recommended that it not be conducted on a larger scale than that described here. Several 20-mmol reactions may, however, be conveniently run simultaneously.* The reaction mixture was stirred overnight at 0 °C and then for 1 day at room temperature, after which unreacted B_5H_9 was distilled from the reactor and collected in a trap at liquid-nitrogen temperature. The reactor was filled with dry N_2 to 1 atm of pressure and opened to the air, and the crude product was extracted from the viscous yellow mixture with five 50-mL portions of *n*-hexane. The extract was reduced in volume by rotary evaporation and placed on a 2.5 × 45-cm silica gel column charged with *n*-hexane, and the carborane was eluted with hexane to give 210 mg (1.08 mmol) of pure 1. The IR of the pure material has a single sharp B–H stretching band at 2600 cm^{-1}; the presence of other bands in the 2200–2600 cm^{-1} region indicates impurities which can be removed by repeated chromatography. Pure 1 is an air-stable, colorless liquid with low (<0.1 mm) vapor pressure at room temperature.

Preparation of $(C_8H_{10})Fe[Ph(CH_2)_3C_2B_4H_5]$ (2). A solution of $K_2C_8H_8$ was prepared from 0.353 g (9.05 mmol) of potassium metal and 0.373 g (3.59 mmol) of cyclooctatetraene in 25 mL of dry tetrahydrofuran (THF) at –30 °C. This solution was filtered in vacuo onto 0.455 g (3.59 mmol) of $FeCl_2$ in a 100-mL round-bottom flask cooled in liquid nitrogen. A solution of $Na^+[Ph(CH_2)_3C_2B_4H_6]^-$ was prepared from 0.672 g (3.46 mmol) of 1 and 0.075 g (3.13 mmol) of NaH in 25 mL of THF and was filtered in vacuo into the reactor containing $K_2C_8H_8$ and $FeCl_2$ immersed in liquid N_2. The reactor was placed in an ice–salt water bath and stirred for 1 h and then at room temperature for 3 h. The

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(11) Deeming, A. J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, 1982; Vol. 4, Chapter 31.3, pp 377–512, and references therein.

(12) Nesmeyanov, A. N.; Tolstaya, M. V.; Rybinskaya, M. I.; Shulpin, G. B.; Bokii, N. G.; Batsanov, A. S.; Struchkov, Yu. T. *J. Organomet. Chem.* 1977, 89.

(13) Reference 11, p 490.

mixture was opened to the air and vacuum filtered through 3 cm of silica gel, after which the silica was washed with acetone until the effluent became colorless. The filtrate was reduced in volume by rotary evaporation, after which it was placed on 3 × 30 cm silica gel column charged with *n*-hexane. The column was eluted first with hexane to remove organic materials and then with 1:1 CH_2Cl_2/*n*-hexane which eluted the complex **2**. Final purification of **2** was achieved by thick-layer chromatography on silica gel with 1:3 CH_2Cl_2/hexane, R_f 0.23. The pure product was isolated as 0.268 g (0.757 mmol) of orange oil.

Preparation of [$C_6H_5(CH_2)_3$]Fe($C_2B_4H_5$) (3). A 0.123-g (0.347-mmol) sample of **2** was dissolved in 20 mL of dry cyclohexane in a 50-mL round-bottom flask. To this solution were added aluminum powder (0.040 g, 1.48 mmol) and $AlCl_3$ (0.200 g, 1.50 mmol) with stirring. The mixture was refluxed for 1.5 h under nitrogen and cooled to room temperature, and the solvent was removed by rotary evaporation. A solution of methanol/water (1:1) was added slowly with stirring. The crude product was extracted with four 20-mL portions of CH_2Cl_2. The yellow brown extract was dried over Na_2SO_4. After concentration, the mixture was developed on a silica gel TLC plate with 1:1 CH_2Cl_2/*n*-hexane to give 0.016 g (0.064 mmol) of yellow solid **3**: R_f 0.32; mp 140–142 °C.

Conversion of 3 to [$C_6H_5(CH_2)_3$]Fe($C_2B_3H_6$) (4). In a 50-mL round-bottom flask a 0.025-g (0.101-mmol) sample of **3** was dissolved in 20 mL of methanol, and the solution was stirred at room temperature for 4 days. The volume was reduced by rotary evaporation and the solution developed on a silica gel TLC plate with CH_2Cl_2/*n*-hexane (1:3) to give 0.018 g (0.076 mmol) of yellow solid **4**.

Preparation of 2-Ph(CH_2)$_2$-*nido*-2,3-$C_2B_4H_7$ (5). In a procedure identical with that described above for the synthesis of **1**, 2.600 g (20 mmol) of 4-phenyl-1-butyne (Farchan), 20 mmol of B_5H_9, and 17 mmol of $(C_2H_5)_3N$ were employed to give 0.176 g (0.978 mmol) of **5** as a slightly air-sensitive, colorless liquid.

Preparation of (C_8H_{10})Fe[Ph(CH_2)$_2C_2B_4H_5$] (6). A procedure identical with that described above for preparing **2** was employed, using 0.624 g (3.47 mmol) of **5**, 0.150 g (7.48 mmol) of NaH, 0.354 g (3.40 mmol) of C_8H_8, 0.337 g (8.64 mmol) of potassium metal, and 0.44 g (3.50 mmol) of $FeCl_2$. The product was obtained as a red-brown solid: mp 51–54 °C; 0.224 g (0.659 mmol); R_f 0.25 in 1:3 CH_2Cl_2/*n*-hexane.

Preparation of [Ph(CH_2)$_2C_2B_4H_5$]$_2$Fe$_2$ (7). In a 25-mL round-bottom flask 0.075 g (0.221 mmol) of **6** was dissolved in 10 mL of dry cyclohexane. To this solution were added 25 mg (0.926 mmol) of powdered aluminum metal and 150 mg (1.125 mmol) of $AlCl_3$. The mixture was refluxed with stirring under nitrogen for 30 min and then allowed to cool to room temperature. The solvent was removed by rotary evaporation, and 10 mL of aqueous methanol (1:1) was added slowly. The crude product was extracted with five 5-mL portions of CH_2Cl_2. After the methylene chloride extract was dried over Na_2SO_4, the volume was reduced and developed with CH_2Cl_2/*n*-hexane (1:1) to give 10 mg of yellow solid **7**.

X-ray Structure Determination on [η^6-$C_6H_5(CH_2)_3$]Fe($C_2B_4H_5$) (3). A crystal grown from $CDCl_3$ solution was mounted on a glass fiber, examined by precession photography, and found acceptable. Relevant parameters for the data collection and structure determination are given in Table IV. Cell dimensions and space group data were obtained by standard methods on an Enraf-Nonius four-circle CAD-4 diffractometer. The θ–2θ scan technique was used as previously described[14] to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 52°$. 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 ($\rho = 0.03$),[15] were used in the final refinement of the structural parameters after averaging for equivalent reflections.

Solution and Refinement of the Structure. A three-dimensional Patterson synthesis was 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 refinement was carried out as previously described.[14] Anisotropic temperature factors were introduced for all non-hydrogen atoms. Further Fourier difference functions permitted location of all hydrogen atoms, which were included in four cycles of least-squares refinement and then held fixed.

The model converged to the R values given in Table IV, and a final difference Fourier map was featureless. Listings of the observed and calculated structure factors are available together with thermal parameters (supplementary material).

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Registry No. **1**, 95464-77-0; **2**, 95464-72-5; **3**, 95464-73-6; **4**, 95464-74-7; **5**, 95464-78-1; **6**, 95464-70-3; **7** (isomer I), 95464-71-4; **7** (isomer II), 95530-48-6; $K_2C_8H_8$, 59391-85-4; Na^+[Ph(CH_2)$_3C_2B_4H_6$]$^-$, 95464-76-9; Na^+[Ph(CH_2)$_2C_2B_4H_6$]$^-$, 95464-75-8; B_5H_9, 19624-22-7; $FeCl_2$, 7758-94-3; cyclooctatetraene, 629-20-9; 5-phenyl-1-pentyne, 1823-14-9; 4-phenyl-1-butyne, 16520-62-0.

Supplementary Material Available: Tables of calculated and observed structure factors, thermal parameters, and mean planes and stereo drawing of unit cell packing (11 pages). Ordering information is given on any current masthead page.

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(14) Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447.

(15) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.