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Organotransition-Metal Metallacarboranes. 7.[1] Complexes of Polycyclic Arenes: Preparation and Structures of (η^6-Arene)ferracarborane Sandwiches of Naphthalene and Phenanthrene

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The reaction of a (cyclooctatriene)ferracarborane complex, (η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$) (1), with naphthalene at 200 °C or with phenanthrene at 175 °C, both in the absence of solvent, gave respectively red (η^6-naphthalene)Fe($Et_2C_2B_4H_4$) (3) and (η^6-phenanthrene)Fe($Et_2C_2B_4H_4$), the latter as red (4) and yellow (5) isomers. Compounds 3–5 were obtained as air-stable crystals. The reaction of 1 with naphthalene over Al/$AlCl_3$ followed by treatment with CH_3OH gave a mixture of (arene)Fe($Et_2C_2B_4H_4$) products in which the arene ligands are proposed to be dihydronaphthalene and tetrahydronaphthalene, respectively. The structures of 3, 4, and 5 were determined via high-resolution ^{11}B and ^1H NMR, IR, and mass spectra and X-ray diffraction studies on 3 and 4. In 3 the iron atom is η^6-coordinated in nearly symmetrical fashion to one ring of naphthalene, the Fe–C(9) and Fe–C(10) distances being slightly longer than the other Fe–C bonds; the naphthalene ligand is essentially planar and is almost parallel to the carborane bonding face (dihedral angle 3.54°). In 4, the metal is η^6-coordinated to an end ring of phenanthrene and is nearly centered over that ring; the phenanthrene is tilted slightly (5.30°) with respect to the carborane ring plane. The phenanthrene ligand is not quite planar, the three ring planes exhibiting small dihedral angles (≤4°) with respect to each other. The structures of 3 and 4 are comparable to those of (η^6-arene)$Cr(CO)_3$ (arene = naphthalene and phenanthrene); however, the metal–arene distance (~1.50 Å) in 3 and 4 is much shorter than in the chromium complexes. Crystal data for 3: $M_r = 309$, space group $P2_1/c$, $Z = 4$, $a = 8.588$ (3) Å, $b = 14.798$ (5) Å, $c = 13.397$ (5) Å, $\beta = 103.52$ (2)°, $V = 1655$ Å^3, $R = 0.058$ for 1876 reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for 4: $M_r = 364$, space group $P2_1/c$, $Z = 4$, $a = 11.817$ (3) Å, $b = 10.231$ (4) Å, $c = 16.362$ (4) Å, $\beta = 108.56$ (2)°, $V = 1875$ Å^3, $R = 0.078$ for 1550 reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Complexes of metal atoms and ions with arenes have been widely studied, owing in part to their demonstrated utility in synthesis[3] and also to interest in their electronic structures, especially with respect to the effect of the metal center on the arene ligand.[3,4] A particularly interesting subclass consists of complexes having polycyclic arene ligands such as naphthalene, phenanthrene, and coronene.[5] In such systems the extent of electron delocalization is expected to be large, and there are intriguing possibilities for "molecular engineering" leading to novel types of electrically conducting polymers in which individual polycyclic hydrocarbon molecules are linked by metals.[6] As precursors to such materials, complexes containing more than one metal η^6-coordinated to a given arene ligand (via the same or different rings) are obvious candidates; however, relatively few such species have been structurally well characterized, particularly electrically neutral ones. Many (arene)metal complexes are cations or contain metals in low oxidation states, making them difficult to isolate and/or susceptible to air oxidation. This is particularly true of iron–arene species[7] such as (η^6-C_6H_6)$_2$Fe, which decomposes explosively above −50 °C.

The readily accessible *nido*-$R_2C_2B_4H_4^{2-}$ carborane ligand offers an attractive means of stabilizing neutral metal–arene complexes, containing formal +2 metals, and has given rise to a family of electrically neutral, air-stable metallacarborane sandwich complexes containing η^6-arene, η^6-cyclooctatriene, or η^8-$C_8H_8^{2-}$ ligands.[8,9] An added advantage lies in the fact that, in most such complexes, the pyramidal $R_2C_2B_4H_4^{2-}$ unit can be converted to a cyclic planar $R_2C_2B_3H_5^{2-}$ ligand[1,8b,9,10] which itself is capable of binding to additional metals. The systematic development of this transition-metal–arene chemistry in our laboratory has been reported in a series of papers,[1,8,9] and we here describe its extension to complexes of polyaromatic hydrocarbons.

Results and Discussion

Reaction of (η^8-C_8H_{10})Fe($Et_2C_2B_4H_4$) (1) with Naphthalene over Al/$AlCl_3$. Our initial attempts to prepare a (naphthalene)ferracarborane complex utilized the displacement of the cyclooctatriene ligand in 1 over aluminum and aluminum chloride, a procedure we had employed earlier to prepare various (η^6-arene)ferracarboranes.[1,8] However, we found that the analogous naphthalene complex could not be obtained by this method, the product instead consisting of combined (tetrahydronaphthalene)- and (dihydronaphthalene)-

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[1] Part 6: second of three papers in this issue.

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

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

compound	solv^{a}	δ (J_{BH}, Hz)^{b}	rel area
$(C_{10}H_{12})Fe(Et_2C_2B_4H_4)$ (**2**)	H	9.65 (143), 5.50 (160), 2.35 (151)	1:1:2
	D	9.18 (125), 6.17,^{c} 3.97 (153)	1:1:2
$(C_{10}H_8)Fe(Et_2C_2B_4H_4)$ (**3**)	B	7.18 (157), 4.44 (149), 0.36 (140)	1:1:2
$(C_{14}H_{10})Fe(Et_2C_2B_4H_4)$, red (unsymmetrical) isomer (**4**)	B	8.05 (137), 4.72 (150), 0.47 (122)	1:1:2
$(C_{14}H_{10})Fe(Et_2C_2B_4H_4)$, yellow (symmetrical) isomer (**5**)	B	6.81 (140), 5.57 (157), 0.84 (150)	1:1:2

^{a} Key: H = hexane, D = dichloromethane, B = benzene. ^{b} $BF_3 \cdot OEt_2$ shift is zero, positive shifts downfield. ^{c} *J* not measurable.

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

compd	$\delta^{a,b}$	rel areas
2 ($CDCl_3$)	5.21 s,^{c} 5.09 s,^{c} 3.75 t,^{e} 3.02 m,^{d} 2.63,^{f} 2.57 m,^{d} 2.36,^{f} 2.21 m,^{d} 1.68 m,^{d} 1.22 t^{g}	1:1:1:1:1:1:1:1:1:3
3 (C_6D_6)	6.90 s,^{h} 6.88 s,^{h} 5.65 s,^{i} 5.33 s,^{i} 1.76 m,^{f} 1.65 m,^{f} 1.16 t^{g}	1:1:1:1:1:1:3
4 (acetone-e_6)	8.67 d (H5),^{j} 7.98 s (H8),^{j} 7.89 d (H10),^{k} 7.79 s (H6, H7),^{j} 7.53 d (H9),^{k} 7.08 s (H4),^{m} 6.33 d (H1),^{m} 5.89 s (H2, H3),^{m} 1.72 m,^{f} 1.65 m,^{f} 1.00 t,^{g} 0.79 t^{g}	1:1:1:2:1:1:1:2:2:2:3:3
5 (acetone-d_6)	5.66 s,^{j} 5.55 s,^{j,n} 2.74 m,^{f} 2.38 m,^{f} 1.25 t^{g}	2:3:1:1:3

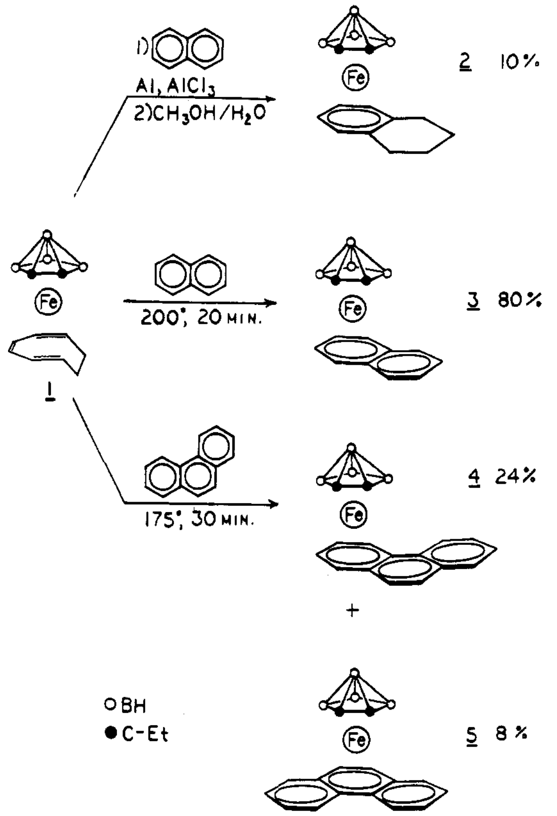
^{a} Legend: m = multiplet, d = doublet, t = triplet. ^{b} Ppm relative to $Si(CH_3)_4$. ^{c} $C_{10}H_{12}$, coordinated ring. ^{d} $C_{10}H_{12}$, saturated ring. ^{e} Impurity. ^{f} Ethyl CH_2. ^{g} Ethyl CH_3. ^{h} Naphthalene, uncoordinated ring. ^{i} Naphthalene, coordinated ring. ^{j} Phenanthrene, uncoordinated end ring. ^{k} Phenanthrene, uncoordinated center ring. ^{m} Phenanthrene, coordinated end ring. ^{n} Phenanthrene, coordinated center ring.

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

2	3070 w, 3050 w, 2940 s, 2920 s, 2850 s, 2500 vs, 1735 w, 1722 w, 1628 w, 1490 m, 1450 s, 1440 s, 1420 s, 1368 m, 1350 w, 1340 w, 1270 w, 1240 w, 1215 w, 1140 w, 1090 m, 1055 m, 1010 m, 952 m, 930 m, 890 w, 870 s, 832 s, 800 s, 720 s, 660 m, 595 m, 440 m, 400 m, 375 m
3	2960 s, 2930 s, 2890 m, 2510 vs, 1475 s, 1450 s, 1380 s, 1255 m, 1205 w, 1170 w, 1150 w, 1100 w, 1065 w, 990 w, 965 w, 935 w, 880 s, 850 s, 815 m, 795 w, 750 s, 730 w, 675 w, 630 w, 605 w, 540 w, 470 m, 410 m
4	2950 s, 2920 s, 2850 m, 2510 vs, 2470 vs, 1530 w, 1450 m, 1425 m, 1375 m, 1325 w, 1270 m, 1225 m, 1205 w, 1150 w, 1120 w, 1080 w, 1040 w, 1020 w, 1000 w, 985 w, 960 w, 865 s, 825 s, 800 s, 765 s, 745 s, 720 m, 705 m, 690 m, 665 m, 615 m, 600 w, 570 w, br, 480 m, 440 m, 415 w
5	2970 s, 2930 s, 2870 m, 2515 vs, 1630 w, br, 1445 vs, 1380 s, 1200 w, br, 1170 w, 980 w, 960 w, 890 sh, 875 m, 810 m, 730 m, 680 w, 610 w, 490 m, 420 m

^{a} KBr pellets.

Scheme I



ferracarboranes, (η^6-$C_{10}H_n$)$Fe(Et_2C_2B_4H_4)$ (**2**, n = 10 or 12), isolated in 10% yield as orange crystals, mp 60 ± 2 °C (Scheme I). The chemical ionization (CI) mass spectrum of **2** in CH_4 exhibits a strong parent grouping with a cutoff at *m/e* 320 corresponding to the protonated ion $^{13}C^{12}C_{15}{}^{56}Fe^{11}B_4{}^{1}H_{27}{}^{+}$, and the intensity pattern is consistent with that calculated for a $C_{16}B_4Fe$ system comprised of a ~1:1 mixture of (dihydronaphthalene)- and (tetrahydronaphthalene)iron carborane complexes. The ^{11}B NMR, ^{1}H NMR, and IR spectra of **2** (Tables I–III) further support the characterization; although the 360-MHz proton NMR spectrum, which is quite complex, is consistent with the proposed composition of **2**, a detailed interpretation of this spectrum has not been attempted.

Synthesis of (η^6-Naphthalene)$Fe(Et_2C_2B_4H_4)$ (3). Since the desired (naphthalene)ferracarborane complex was not accessible by the ligand exchange route just described, evidently owing to hydrogenation of the naphthalene ligand during workup, we looked for other approaches. It was discovered that simply heating **1** with naphthalene without solvent rapidly formed (η^6-$C_{10}H_8$)$Fe(Et_2C_2B_4H_4)$ (**3**) in good yield (Scheme I). Red **3** (mp 128 ± 2 °C), an air-stable crystalline solid, was characterized via NMR, IR, and mass spectra and X-ray crystallography. The mass spectrum cointains a strong parent envelope with a cutoff at *m/e* 315 (^{13}C peak) and an intensity pattern corresponding closely to that calculated for a $C_{16}B_4Fe$ system; the spectrum is remarkably clean, there being no other intense peaks except for *m/e* 184 which is assigned to $FeC_{10}H_8{}^{+}$. Interpretation of the 360-MHz ^{1}H NMR spectrum is similarly straightforward, all types of C–H protons being clearly distinguishable (Table II).

Although the identity of **3** appeared well established, the unusual nature of this species (as evidently the first neutral (η^6-naphthalene)iron complex to be structurally charac-

Table IV. Experimental X-ray Diffraction Parameters and Crystal Data on 3 and 4

	3	4
M_r	309	364
space group	$P2_1/c$	$P2_1/c$
a, Å	8.588 (3)	11.817 (3)
b, Å	14.798 (5)	10.231 (4)
c, Å	13.397 (5)	16.362 (4)
β, deg	103.52 (2)	108.56 (2)
V, Å^3	1655	1875
μ, cm^{-1}	9.2	8.2
D(calcd), g cm^{-3}	1.24	1.29
A	0.60	0.60
B	0.35	0.35
trans coeff (max)	0.926^a	
trans coeff (min)	0.860	
2θ range, deg	1.5-60	1.5-50
reflectns obsd	2540	2564
reflectns refined	1876	1550
R	0.058	0.078
R_w	0.066	0.076
esd unit wt	1.6	2.3
Z	4	4

^{a} Crystal dimensions (mm from centroid): 100 (0.030), $\bar{1}00$ (0.030), 011 (0.008 75), $0\bar{1}\bar{1}$ (0.008 75), $01\bar{1}$ (0.530), $0\bar{1}1$ (0.013 75), $01\bar{1}$ (0.310).

terized) suggested that an X-ray diffraction study would be desirable, and this was carried out as discussed below.

Synthesis of (η^6-Phenanthrene)Fe($Et_2C_2B_4H_4$) Isomers (4 and 5). The facile replacement of the C_8H_{10} ligand in 1 by naphthalene via thermolysis, as just described, suggested that this approach may provide a general route to ferracarborane complexes of fused-ring polyaromatic hydrocarbons. Accordingly, 1 and phenanthrene were heated in an evacuated tube at 175 °C for 30 min, giving two isolable products which were separated by plate chromatography and characterized as isomers of ($C_{14}H_{10}$)Fe($Et_2C_2B_4H_4$) (Scheme I). The major product, red 4 (mp 131 ± 1 °C), exhibits a mass spectrum having an intense parent envelope with a cutoff at *m/e* 365 (^{13}C peak) and a pattern closely matching that calculated for a $C_{20}B_4Fe$ system; the only other strong peaks are at *m/e* 234 and 178 corresponding to $FeC_{14}H_{10}^+$ and $C_{14}H_{10}^+$ (phenanthrene), respectively. The ^{1}H NMR spectrum is complex and reveals that the metal is coordinated to an outer ring of phenanthrene, inasmuch as at least eight different aromatic C–H protons can be seen (Table II). This conclusion has been substantiated by an X-ray study which is reported below.

The yellow minor isomer 5, which sublimes at ~200 °C, has a more complex mass spectrum than that of 4 in that there is evidence of reaction in the spectrometer. In addition to the expected parent grouping at *m/e* 365, there is a smaller envelope with a cutoff at *m/e* 381 suggesting addition of CH_3 and H; other strong peaks are seen at *m/e* 234 and 178 ($FeC_{14}H_{10}^+$ and $C_{14}H_{10}^+$, vide supra) as well as at *m/e* 134, attributed to $FeC_6H_6^+$, and at *m/e* 250, assigned to $FeC_{15}H_{14}^+$. The ^{11}B and ^{1}H NMR spectra support the characterization of 5 as a single pure compound, and from the ^{1}H data it is evident that the iron is coordinated to the central ring of phenanthrene. Thus, the spectrum exhibits only two peaks in the aromatic C–H region, consistent with the presence of a mirror plane bisecting phananthrene and indicating superposition of some inequivalent proton resonances (Table II). Although crystals of 5 were obtained, the quality was poor and crystallographic characterization of 5 has not yet been achieved. However, assuming only two possible distinguishable isomers for an (η^6-phenanthrene)ferracarborane complex[11] and given the definitive characterization of 4 as the unsymmetrical isomer, the identity of 5 seems clearly established.

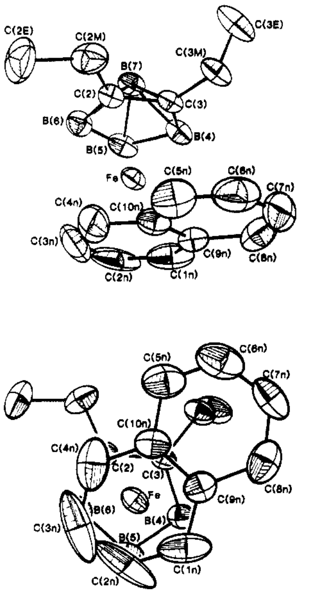


Figure 1. ORTEP views of (η^6-$C_{10}H_8$)Fe($Et_2C_2B_4H_4$), with hydrogen atoms omitted for clarity. The lower view is down the Fe–B(7) axis.

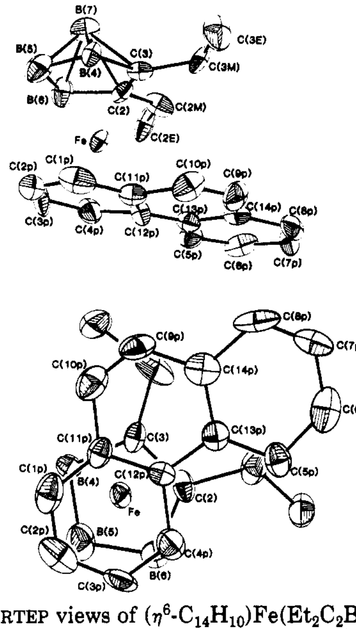


Figure 2. ORTEP views of (η^6-$C_{14}H_{10}$)Fe($Et_2C_2B_4H_4$); hydrogen atoms are omitted. The lower view is along the Fe–B(7) axis.

X-ray Structure Determination on 3 and 4. Data collection and unit cell parameters for the two compounds are given in Table IV, and atomic coordinates are listed in Tables V and VI. Bond distances and angles are compiled in Tables VII and VIII (the numbering of the hydrocarbon ligands in both species conforms to standard organic nomenclature). The molecular structures are depicted in Figures 1 and 2. Tables of calculated mean planes and stereo diagrams of the unit cell packing are available as supplementary material.

Naphthalene Complex 3. Figure 1 presents two views of the molecule, which consists of an iron atom sandwiched between η^5-$Et_2C_2B_4H_4^{2-}$ and η^6-$C_{10}H_8$ ligands, the metal

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[11] This assumption presumes free rotation of the arene relative to the carborane ligand in solution, which prevents isolation of individual rotamers.

Table V. Positional Parameters for $(C_{10}H_8)Fe(Et_2C_2B_4H_4)$ (3)

atom	x	y	z
Fe	0.1939 (1)	0.10205 (7)	0.36102 (7)
C(1n)	0.3653 (15)	0.1226 (7)	0.4951 (6)
C(2n)	0.2225 (14)	0.1070 (8)	0.5150 (6)
C(3n)	0.0869 (12)	0.1493 (9)	0.4730 (8)
C(4n)	0.1007 (11)	0.2187 (7)	0.4053 (8)
C(5n)	0.2481 (13)	0.3115 (6)	0.3160 (8)
C(6n)	0.3827 (14)	0.3334 (8)	0.2934 (7)
C(7n)	0.5246 (11)	0.2899 (7)	0.3331 (7)
C(8n)	0.5327 (11)	0.2197 (6)	0.4016 (8)
C(9n)	0.3816 (9)	0.1931 (5)	0.4306 (5)
C(10n)	0.2448 (9)	0.2424 (5)	0.3839 (5)
C(2)	0.0586 (8)	0.0825 (5)	0.2143 (5)
C(2M)	−0.0424 (12)	0.1434 (7)	0.1349 (7)
C(2E)	−0.2217 (12)	0.1523 (9)	0.1465 (10)
C(3)	0.2304 (8)	0.0735 (4)	0.2181 (5)
C(3M)	0.3122 (10)	0.1215 (5)	0.1450 (5)
C(3E)	0.3406 (12)	0.0645 (7)	0.0616 (7)
B(4)	0.310 (1)	0.0018 (6)	0.2956 (6)
B(5)	0.169 (1)	−0.0415 (6)	0.3442 (6)
B(6)	0.006 (1)	0.0166 (6)	0.2902 (7)
B(7)	0.128 (1)	−0.0297 (6)	0.2137 (7)
H(1n)	0.435 (7)	0.102 (5)	0.496 (5)
H(2n)	0.244 (8)	0.069 (5)	0.543 (5)
H(3n)	0.027 (9)	0.124 (5)	0.492 (6)
H(4n)	0.017 (7)	0.234 (4)	0.382 (5)
H(5n)	0.132 (9)	0.343 (5)	0.283 (6)
H(6n)	0.382 (9)	0.381 (6)	0.240 (6)
H(7n)	0.613 (8)	0.306 (5)	0.314 (5)
H(8n)	0.620 (8)	0.188 (5)	0.428 (5)
H(2M1)	−0.073 (9)	0.181 (6)	0.143 (6)
H(2M2)	−0.104 (8)	0.112 (5)	0.070 (5)
H(3M1)	0.255 (8)	0.167 (5)	0.121 (5)
H(3M2)	0.446 (9)	0.119 (5)	0.163 (5)
H(3E1)	0.277 (7)	0.041 (4)	0.042 (5)
H(3E2)	0.422 (8)	0.017 (5)	0.086 (5)
H(3E3)	0.369 (8)	0.096 (5)	0.006 (5)
H(4)	0.417 (8)	−0.013 (5)	0.300 (5)
H(5)	0.174 (7)	−0.097 (4)	0.399 (4)
H(6)	−0.117 (7)	0.014 (5)	0.290 (5)
H(7)	0.085 (7)	−0.071 (4)	0.144 (4)

Table VI. Positional Parameters for $(C_{14}H_{10})Fe(Et_2C_2B_4H_4)$ (4)

atom	x	y	z
Fe	−0.1676 (1)	−0.2360 (2)	−0.17103 (8)
C(2)	−0.3519 (8)	−0.260 (1)	−0.2016 (6)
C(2M)	−0.4500 (10)	−0.184 (2)	−0.2705 (7)
C(2E)	−0.4994 (12)	−0.229 (1)	−0.3521 (8)
C(3)	−0.2970 (8)	−0.202 (1)	−0.1166 (5)
C(3M)	−0.3425 (14)	−0.072 (1)	−0.0958 (9)
C(3E)	−0.2754 (15)	−0.029 (2)	−0.0021 (8)
C(1p)	0.0061 (10)	−0.212 (2)	−0.1178 (7)
C(2p)	0.0016 (11)	−0.322 (1)	−0.1625 (9)
C(3p)	−0.0807 (12)	−0.333 (1)	−0.2467 (8)
C(4p)	−0.1420 (10)	−0.228 (1)	−0.2889 (6)
C(5p)	−0.2660 (11)	0.014 (1)	−0.3745 (7)
C(6p)	−0.3269 (12)	0.142 (2)	−0.4049 (9)
C(7p)	−0.3146 (10)	0.263 (2)	−0.3553 (8)
C(8p)	−0.2511 (10)	0.262 (1)	−0.2752 (7)
C(9p)	−0.1104 (12)	0.125 (1)	−0.1441 (8)
C(10p)	−0.0522 (12)	0.027 (1)	−0.1098 (8)
C(11p)	−0.0534 (9)	−0.098 (1)	−0.1576 (6)
C(12p)	−0.1249 (9)	−0.092 (1)	−0.2441 (7)
C(13p)	−0.1959 (9)	0.014 (1)	−0.2869 (7)
C(14p)	−0.1853 (10)	0.130 (1)	−0.2351 (8)
B(4)	−0.208 (1)	−0.297 (1)	−0.0559 (8)
B(5)	−0.214 (2)	−0.429 (2)	−0.1120 (10)
B(6)	−0.307 (1)	−0.404 (2)	−0.2065 (10)
B(7)	−0.343 (1)	−0.375 (1)	−0.1053 (10)
H(4)	−0.170 (7)	−0.285 (9)	0.015 (5)
H(5)	−0.163 (7)	−0.528 (9)	−0.078 (5)
H(7)	−0.415 (13)	−0.378 (16)	−0.083 (9)
H(M21)	−0.388 (10)	−0.054 (13)	−0.275 (7)
H(M22)	−0.488 (6)	−0.188 (7)	−0.257 (5)
H(E21)	−0.435 (13)	−0.214 (22)	−0.381 (9)
H(E22)	−0.534 (13)	−0.166 (15)	−0.384 (9)
H(E23)	−0.543 (8)	−0.274 (14)	−0.364 (6)
H(M31)	−0.327 (6)	−0.015 (8)	−0.114 (4)
H(M32)	−0.426 (12)	−0.075 (15)	−0.089 (8)
H(1p)	0.057 (10)	−0.184 (12)	−0.048 (7)
H(2p)	0.033 (12)	−0.415 (15)	−0.119 (9)
H(3p)	−0.093 (7)	−0.329 (8)	−0.281 (5)
H(4p)	−0.223 (8)	−0.209 (10)	−0.357 (6)
H(5p)	−0.281 (10)	−0.063 (12)	−0.439 (7)
H(6p)	−0.353 (11)	0.125 (13)	−0.456 (7)
H(7p)	−0.340 (21)	0.454 (27)	−0.469 (15)
H(8p)	−0.237 (9)	0.338 (11)	−0.227 (6)
H(9p)	−0.127 (9)	0.222 (14)	−0.122 (6)
H(10p)	−0.024 (10)	0.012 (12)	−0.056 (7)

being 1.606 Å from the plane of the carborane bonding face [C(2)–C(3)–B(4)–B(5)–B(6)] and 1.559 Å from the plane of the naphthalene ligand. These planes are nearly parallel, with a dihedral angle of 3.52°, and the iron atom is approximately centered over each bonding face; however, iron is slightly further from the two carbon atoms located at the junction of the naphthalene rings [C(9n) and C(10n)] than from the other four coordinated carbons. This effect has also been noted in structure determinations on $(\eta^6$-naphthalene$)Cr(CO)_3$[12] and $(\eta^6$-phenanthrene$)Cr(CO)_3$ isomers[13] and probably reflects the higher coordination (to non-hydrogen atoms) of the "junction" carbons.[13a] The naphthalene ligand exhibits good planarity, the sum of internal C–C–C angles in each ring equaling the ideal value of 720°. There is no significant difference between the average C–C distances in the coordinated and uncoordinated rings; although some variation is noted in individual distances, which range from 1.303 (6) to 1.492 (5) Å, there appears to be no particular pattern to these values. The essential uniformity in mean carbon–carbon bond lengths of the two rings is consistent with structures of other transition-metal η^6-complexes of fused-ring hydrocarbons,[12,13] although the relatively large thermal motions of the ring carbons preclude detailed comparison. We note, however, that the structure of the (biphenyl)ferracarborane complex reported in a companion paper[9] reveals distinct differences between the metal-coordinated and uncoordinated rings, which in that case are separate π-electron systems.

The iron atom in 3 is located much closer (by ~ 0.20–0.25 Å) to the naphthalene plane than is chromium in $(\eta^6$-naphthalene$)Cr(CO)_3$[12] and in the $(\eta^6$-phenanthrene$)Cr(CO)_3$ isomers[13] (corresponding values in these species are 1.75 and 1.80 Å, respectively[14]). While this undoubtedly reflects, in part, the difference in radii of formal Fe(II) vs. Cr(0), it may also imply stronger covalent metal–ligand bonding in 3. As there appear to be no examples of iron–naphthalene or iron–phenanthrene complexes characterized by X-ray diffraction prior to this work, more direct comparisons are not possible at present.

The FeC_2B_4 ferracarborane cage in 3 exhibits normal geometry, closely resembling the several previous examples of this genre which are reported elsewhere.[1,8,9,15] One earlier example of a (naphthalene)metallacarborane complex, $(C_{10}H_8)CoCB_{10}H_{11}$, has been prepared[16] but has not

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Table VII. Bond Distances (Å) and Selected Bond Angles (deg) in 3

Bond Distances

Fe-C(1n)	2.061 (4)	C(1n)-C(9n)	1.382 (5)	C(2)-B(6)	1.549 (4)
Fe-C(2n)	2.021 (4)	C(2n)-C(3n)	1.326 (10)	C(2)-B(7)	1.765 (4)
Fe-C(3n)	2.057 (5)	C(3n)-C(4n)	1.394 (9)	C(2M)-C(2E)	1.588 (5)
Fe-C(4n)	2.048 (4)	C(4n)-C(10n)	1.379 (5)	C(3)-C(3M)	1.510 (3)
Fe-C(10n)	2.130 (3)	C(5n)-C(6n)	1.303 (6)	C(3)-B(4)	1.529 (4)
Fe-C(9n)	2.140 (3)	C(5n)-C(10n)	1.373 (5)	C(3)-B(7)	1.757 (4)
Fe-C(2)	2.057 (3)	C(6n)-C(7n)	1.370 (6)	C(3M)-C(3E)	1.465 (4)
Fe-C(3)	2.055 (2)	C(7n)-C(8n)	1.377 (5)	B(4)-B(5)	1.635 (5)
Fe-B(4)	2.088 (3)	C(8n)-C(9n)	1.492 (5)	B(4)-B(7)	1.747 (5)
Fe-B(5)	2.142 (3)	C(9n)-C(10n)	1.401 (4)	B(5)-B(6)	1.654 (5)
Fe-B(6)	2.094 (4)	C(2)-C(2M)	1.505 (4)	B(5)-B(7)	1.710 (5)
C(1n)-C(2n)	1.335 (7)	C(2)-C(3)	1.471 (4)	B(6)-B(7)	1.767 (5)

Bond Angles

C(2n)-C(1n)-C(9n)	119.2 (5)	Fe-C(9n)-C(8n)	131.7 (2)	Fe-C(3)-B(7)	91.5 (2)
C(1n)-C(2n)-C(3n)	126.2 (7)	C(1n)-C(9n)-C(8n)	125.7 (4)	C(2)-C(3)-C(3M)	123.4 (2)
C(2n)-C(3n)-C(4n)	115.1 (5)	C(1n)-C(9n)-C(10n)	118.4 (3)	C(2)-C(3)-B(4)	111.7 (2)
C(3n)-C(4n)-C(10n)	122.7 (5)	C(8n)-C(9n)-C(10n)	115.8 (3)	C(3M)-C(3)-B(4)	124.5 (3)
C(6n)-C(5n)-C(10n)	119.7 (4)	Fe-C(2)-C(2M)	134.0 (2)	C(3M)-C(3)-B(7)	133.8 (2)
C(5n)-C(6n)-C(7n)	123.4 (4)	Fe-C(2)-B(7)	91.2 (2)	C(3)-C(3M)-C(3E)	114.2 (3)
C(6n)-C(7n)-C(8n)	121.0 (4)	C(2M)-C(2)-C(3)	119.1 (3)	Fe-B(4)-B(7)	90.7 (2)
C(7n)-C(8n)-C(9n)	117.5 (3)	C(2M)-C(2)-B(6)	129.2 (3)	C(3)-B(4)-B(5)	106.8 (3)
Fe-C(10n)-C(5n)	131.8 (2)	C(2M)-C(2)-B(7)	134.4 (3)	Fe-B(5)-B(7)	89.9 (2)
C(4n)-C(10n)-C(5n)	119.0 (4)	C(3)-C(2)-B(6)	111.4 (2)	B(4)-B(5)-B(6)	104.5 (2)
C(4n)-C(10n)-C(9n)	118.3 (3)	C(2)-C(2M)-C(2E)	113.1 (3)	Fe-B(6)-B(7)	89.9 (2)
C(5n)-C(10n)-C(9n)	122.7 (3)	Fe-C(3)-C(3M)	134.7 (2)	C(2)-B(6)-B(5)	105.6 (3)

Table VIII. Bond Distances (Å) and Selected Bond Angles (deg) in 4

Bond Distances

Fe-C(2)	2.088 (4)	C(2)-B(7)	1.940 (10)	C(3p)-C(4p)	1.357 (12)
Fe-C(3)	2.029 (5)	C(2M)-C(2E)	1.359 (12)	C(4p)-C(12p)	1.553 (10)
Fe-B(4)	2.178 (6)	C(3)-C(3M)	1.512 (9)	C(5p)-C(6p)	1.501 (11)
Fe-B(5)	2.337 (9)	C(3)-B(4)	1.539 (7)	C(5p)-C(13p)	1.409 (7)
Fe-B(6)	2.321 (8)	C(3)-B(7)	1.872 (9)	C(6p)-C(7p)	1.456 (12)
Fe-C(1p)	1.973 (6)	C(3M)-C(3E)	1.550 (12)	C(7p)-C(8p)	1.286 (9)
Fe-C(2p)	2.147 (7)	B(4)-B(5)	1.622 (11)	C(8p)-C(14p)	1.591 (11)
Fe-C(3p)	2.095 (9)	B(4)-B(7)	1.733 (9)	C(9p)-C(10p)	1.250 (9)
Fe-C(4p)	2.047 (5)	B(5)-B(6)	1.607 (10)	C(9p)-C(14p)	1.471 (9)
Fe-C(11p)	1.920 (5)	B(5)-B(7)	1.660 (13)	C(10p)-C(11p)	1.489 (9)
Fe-C(12p)	2.056 (6)	B(6)-B(7)	1.860 (12)	C(11p)-C(12p)	1.400 (7)
C(2)-C(2M)	1.546 (9)	C(1p)-C(2p)	1.333 (10)	C(12p)-C(13p)	1.419 (7)
C(2)-C(3)	1.459 (7)	C(1p)-C(11p)	1.412 (10)	C(13p)-C(14p)	1.440 (8)
C(2)-B(6)	1.576 (10)	C(2p)-C(3p)	1.416 (14)		

Bond Angles

Fe-C(2)-C(2M)	126.8 (5)	C(3)-C(3M)-C(3E)	111.7 (6)	C(9p)-C(10p)-C(11p)	122.8 (6)
Fe-C(2)-B(7)	95.4 (3)	C(3)-B(4)-B(5)	105.2 (5)	Fe-C(11p)-C(10p)	125.3 (4)
C(2M)-C(2)-C(3)	119.6 (6)	B(4)-B(5)-B(6)	107.7 (6)	C(1p)-C(11p)-C(10p)	123.0 (6)
C(2M)-C(2)-B(6)	128.4 (6)	C(2)-B(6)-B(5)	103.8 (6)	C(1p)-C(11p)-C(12p)	123.3 (6)
C(2M)-C(2)-B(7)	137.0 (5)	C(2p)-C(1p)-C(11p)	121.2 (6)	C(10p)-C(11p)-C(12p)	113.6 (6)
C(3)-C(2)-B(6)	111.8 (5)	C(1p)-C(2p)-C(3p)	120.0 (7)	C(4p)-C(12p)-C(11p)	112.9 (5)
C(2)-C(2M)-C(2E)	122.1 (8)	C(2p)-C(3p)-C(4p)	121.2 (9)	C(4p)-C(12p)-C(13p)	119.2 (5)
Fe-C(3)-C(3M)	128.3 (5)	C(3p)-C(4p)-C(12p)	120.1 (6)	C(11p)-C(12p)-C(13p)	126.8 (5)
Fe-C(3)-B(7)	99.5 (4)	C(6p)-C(5p)-C(13p)	113.7 (6)	C(5p)-C(13p)-C(12p)	124.5 (6)
C(2)-C(3)-C(3M)	119.2 (6)	C(5p)-C(6p)-C(7p)	126.9 (7)	C(5p)-C(13p)-C(14p)	120.7 (6)
C(2)-C(3)-B(4)	111.4 (5)	C(6p)-C(7p)-C(8p)	119.2 (7)	C(12p)-C(13p)-C(14p)	114.7 (5)
C(3M)-C(3)-B(4)	128.8 (5)	C(7p)-C(8p)-C(14p)	118.2 (7)	C(8p)-C(14p)-C(9p)	120.3 (6)
C(3M)-C(3)-B(7)	132.1 (5)	C(10p)-C(9p)-C(14p)	123.4 (6)	C(8p)-C(14p)-C(13p)	121.1 (6)
				C(9p)-C(14p)-C(13p)	118.6 (6)

been crystallographically characterized.

Phenanthrene Complex 4. The molecular structure, depicted in Figure 2, consists of an essentially planar phenanthrene ligand coordinated to iron via an end ring, with the metal nearly equidistant from the six carbon atoms. Thus, the slight asymmetry noted in the iron–hydrocarbon bonding in 3 (vide supra) is not in evidence in 4, although it should be noted that the structure of 4 is less precisely defined that that of 3. The carborane and phenanthrene bonding faces are tilted slightly (dihedral angle 6.86°), and the metal is located much closer to phenanthrene than to the carborane ligand (1.47 vs. 1.73 Å), in this respect resembling the naphthalene complex 3 and suggesting strong covalent Fe–hydrocarbon linkage. The mean phenanthrene carbon–carbon bond distances in the metal-bonded ring and the central ring are the same (1.412 vs. 1.414 Å), paralleling the naphthalene species (vide supra), but the distances in the uncoordinated end ring are slightly longer (mean value 1.447 Å), perhaps indicative of an electronic effect. Again, however, there is no clear pattern in the observed variation in C–C distances throughout the ligand. The extremely short C(9p)–C(10p) and C(7p)–C(8p) lengths (<1.3 Å) are anomalous and are attributed to large thermal motions in the uncoordinated ring atoms.

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While the phenanthrene ligand is approximately planar, with the sum of internal angles in each ring very close to 720°, there is a slight deformation such that the outer uncoordinated ring is bent by 4.01° with respect to the ring attached to iron.

Distances and angles in the ferracarborane cluster are normal except for the unusually long Fe–C and Fe–B distances already noted.

Conclusions

The (arene)ferracarborane complexes described in this and the accompanying papers[1,9] are uniformly neutral, air-stable, diamagnetic compounds containing formal iron(II), in which the $Et_2C_2B_4H_4^{2-}$ or $Et_2C_2B_3H_5^{2-}$ ligand clearly exerts a stabilizing influence. The robustness and electroneutrality of these products offers distinct advantages over their non-boron analogues such as the unstable $(\eta^6\text{-}C_6H_6)_2Fe$ or the $(\eta^6\text{-}C_6H_6)Fe(\eta^5\text{-}C_5H_5)^+$ cation, which have yet to be crystallographically characterized. The X-ray structure determinations on the naphthalene and phenanthrene complexes **3** and **4** reported herein are, to our knowledge, the first π-complexes of iron with fused polyarene ligands to be examined by crystallography. Also of significance, the synthetic route by which **3** and **4** were obtained, involving thermolysis of $(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)$ and the hydrocarbon without solvent, appears to have general applicability and we are currently using this method to generate other metallacarborane–polyaromatic ring complexes to be reported later. Finally, the complexes containing the cyclic planar $R_2C_2B_3H_5^{2-}$ ligand[1,9] open numerous possibilities for generating stacked complexes, which are under investigation.

Experimental Section

Materials and Instrumentation. Experimental techniques and spectroscopic analyses were as described in the accompanying papers.[1,9] All commercial reagents were reagent grade and used as received; $(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)$ was prepared as described elsewhere.[8a]

Preparation of $(C_{10}H_{12})Fe(Et_2C_2B_4H_4)$ (2). Naphthalene (0.50 g, 3.9 mmol), aluminum powder (0.040 g, 1.48 mmol), $AlCl_3$ (0.150 g, 1.12 mmol), and 20 mL of cyclohexane were placed in a 100-mL round-bottom flask equipped with a magnetic stirrer and refluxed under N_2 for 15 min with stirring. During this time the mixture darkened. A 0.109 g (0.37 mmol) quantity of $(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)$ (1) was added, and the mixture was refluxed for 1 h under N_2 and then allowed to cool to room temperature. After removal of solvent by rotary evaporation, unreacted naphthalene was sublimed out of the reactor at room temperature and 20 mL of methanol/water (1:1) was added slowly. The crude product was extracted from the mixture with four 20-mL portions of CH_2Cl_2, and the yellow-brown extract was dried over Na_2SO_4 and concentrated by rotary evaporation. Development on silica gel TLC plates with CH_2Cl_2/hexane (1:3) produced **2** as an orange solid: R_f 0.23; yield 12 mg (0.038 mmol, 10%).

Preparation of $(C_{10}H_8)Fe(Et_2C_2B_4H_4)$ (3). Naphthalene (0.50 g) and **1** (25 mg, 0.086 mmol) were sealed into an evacuated 5-mL Pyrex tube, which was immersed in an oil bath at 200 °C for 20 min. The tube was allowed to cool to room temperature, opened, and placed in a vacuum sublimator to remove unreacted naphthalene. Development of the residue on silica gel TLC plate with CH_2Cl_2/hexane (1:1) gave two bands: orange unreacted **1**, 10 mg (0.034 mmol), and red **3**, 13 mg (0.041 mmol), R_f 0.41, and yield 80.4% based on **1** consumed.

Preparation of $(C_{14}H_{10})Fe(Et_2C_2B_4H_4)$ (4). Phenanthrene (0.210 g, 1.180 mmol) and **1** (46 mg, 0.158 mmol) were placed in a 10-mL Pyrex tube equipped with a vacuum stopcock. The reactor was evacuated, sealed, and immersed in an oil bath at 175 °C for 30 min. After the reactor was cooled to room temperature, the contents were dissolved in CH_2Cl_2, the solution was placed on a rotary evaporator, and the solvent was removed. The residue was extracted with a few milliters of ether, the volume reduced, and the ether solution was placed on a silica gel column (1.5 × 30 cm) charged with *n*-hexane. After elution with *n*-hexane to remove any unreacted phananthrene, unreacted **1** (15 mg, 0.051 mmol) was eluted with CH_2Cl_2/hexane (1:3). Elution with CH_2Cl_2 gave a red band which was collected, placed on a silica gel TLC plate, and developed with CH_2Cl_2/hexane (1:1) to give two bands. The major product was red **4**: R_f 0.38; yield 9 mg (0.025 mmol, 23.5% based on **1** consumed). The minor species was yellow **5**: R_f 0.40; yield 3 mg (0.008 mmol, 7.5%).

X-ray Structure Determinations on 3 and 4. Single crystals of **3** and **4** were grown from benzene and methylene chloride solutions, respectively, mounted on glass fibers, and found acceptable. Parameters for the data collections and structure determinations are given in Table IV. For each crystal, 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[17] to record the intensities for all nonequivalent reflections within the 2θ ranges given in Table IV. 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 (in the case of **3**) for absorption. Only those relfections for which $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics ($p = 0.03$),[18] 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.[17] Anisotropic temperature factors were introduced for all non-hydrogen atoms in each structure. Additional Fourier difference functions permitted location of all non-ethyl and several ethyl hydrogen atoms, which were included in four cycles of least-squares refinement and then held fixed.

The models converged to the R values given in Table IV, and final difference Fourier maps were featurless. Listings of the observed and calculated structure factors are available together with thermal parameters as supplementary materla.

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Registry No. 1, 84583-03-9; 2, 95464-65-6; 3, 95464-66-7; 4, 95464-67-8; 5, 95464-68-9; (η^6-dihydronaphthalene)$Fe(Et_2C_2B_4H_4)$, 95464-69-0; napthalene, 91-20-3; phenanthrene, 85-01-8.

Supplementary Material Available: Tables of calculated and observed structure factors, thermal parameters, and calculated mean planes and stereo diagrams of unit cell packing (24 pages). Ordering information is given on any current masthead page.

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