

Metal Atom Synthesis of Metallaboron Clusters. 4.¹ Direct Synthesis of (η^6 -Arene)ferracarborane Clusters from Alkynes and Boranes. Structural Characterization of the Four-Carbon (η^6 -Arene)metallacarboranes

1- $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe-4,5,7,8-(CH}_3)_4\text{C}_4\text{B}_3\text{H}_3$ and 2- $[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{Fe-6,7,9,10-(CH}_3)_4\text{C}_4\text{B}_5\text{H}_5$

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Received February 23, 1984

The reaction of thermally generated iron atoms with pentaborane(9), toluene, and 2-butyne was found to yield as the major product the (π -arene)ferracarborane sandwich complex 1- $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe-2,3-(CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$, I, along with smaller amounts of the four-carbon metallacarborane complexes 1- $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe-4,5,7,8-(CH}_3)_4\text{C}_4\text{B}_3\text{H}_3$, II, 1- $[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{Fe-4,5,7,8-(CH}_3)_4\text{C}_4\text{B}_3\text{H}_3$, III, and 2- $[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{Fe-6,7,9,10-(CH}_3)_4\text{C}_4\text{B}_5\text{H}_5$, IV. Reactions carried out in the absence of toluene also yielded I and II but in reduced yields. The structures of II and IV were determined by single-crystal determinations. Compound II was shown to have an arachno-type cage geometry derived from a bicapped-square antiprism missing two vertices, with the iron atom occupying the five-coordinate 1-position in the cage and the four carbons occupying positions on the open face of the cage. An unusually short carbon-carbon bond distance of 1.367 (4) Å was observed for the non-metal-bonded carbons in the cage and is thought to result from localized multiple bond character between these carbons. Crystal data for II: space group $P2_1/c$, $Z = 4$, $a = 8.753$ (3) Å, $b = 10.190$ (2) Å, $c = 22.118$ (3) Å, $\beta = 95.08$ (2)°, $V = 1965$ Å³. The structure was refined by full-matrix least squares to a final R of 0.060 and $R_w = 0.066$ for the 2597 unique reflections which had $F_o^2 > 3\sigma(F_o^2)$. Compound IV was shown to be an analogue of decaborane(14) in which the iron atom occupies the five-coordinate 2-position in the cage and the carbon atoms occupy the 6,7- and 9,10-positions on the open face. Crystal data for IV: space group $P\bar{1}$, $Z = 2$, $a = 9.368$ (5) Å, $b = 11.399$ (4) Å, $c = 8.708$ (4) Å, $\alpha = 90.84$ (4)°, $\beta = 116.51$ (5)°, $\gamma = 94.03$ (4)°, $V = 829$ Å³. The structure was refined by full-matrix least squares to a final R of 0.074 and $R_w = 0.065$ for the 760 unique reflections which had $F_o^2 > 3\sigma(F_o^2)$. The iron to arene bonding in both II and IV appears normal and is consistent with a symmetrical η^6 -coordination. Reactions of iron atoms with hexaborane(10), toluene, and 2-butyne were also found to give low yields of compounds I, II, and III.

Introduction

There have been several recent reports^{1,3-5} of the synthesis of (π -arene)metallacarborane complexes using a variety of synthetic approaches; however, the number and diversity of these complexes are still small when compared to the extensive range of (cyclopentadienyl)metallacarborane clusters. We have previously suggested¹ that metal atom reaction techniques may lead to potentially general synthetic routes for the formation of such π -arene complexes. For example, we have already demonstrated¹ that the complex 1- $(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)\text{Fe-2,3-(C}_2\text{H}_5)_2\text{C}_2\text{B}_4\text{H}_4$ can be prepared in good yield by the reaction of thermally generated iron atoms with toluene and the small carborane 2,3-(C₂H₅)₂C₂B₄H₆. Furthermore, it was also found that several of the minor products of the reaction, for which only mass spectral data could be obtained, such as $(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)\text{Fe(C}_2\text{H}_5)_4\text{C}_4\text{B}_7\text{H}_7$ and $(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)\text{Fe(C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8$, were apparently higher carbon content metallacarborane clusters. These results suggested that with use of suitable experimental conditions, metal atom

reaction techniques might allow the incorporation of additional carbon atoms into these clusters resulting in the production of new hybrid compounds with properties intermediate between those of organometallic and metallaborane complexes.

We have now expanded our studies of the use of metal atom reactions for the synthesis of (π -arene)metallaboron complexes and report here that the direct reaction of either pentaborane(9) or hexaborane(10) with iron atoms in the presence of toluene and 2-butyne results in the formation of a number of new (π -arene)ferracarborane clusters, including complexes such as 1- $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe-4,5,7,8-(CH}_3)_4\text{C}_4\text{B}_3\text{H}_3$ and 2- $[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{Fe-6,7,9,10-(CH}_3)_4\text{C}_4\text{B}_5\text{H}_5$, which have resulted from the incorporation of two 2-butyne molecules into the cage structure. Full details of the synthesis and structural properties of these unique hybrid clusters are described below.

Experimental Section

Materials and Procedure. Iron metal (lumps, random) was obtained from Alfa Products/Ventron Division. Toluene (Amend Drug and Chemical Co. or MCB Manufacturing Chemists, Inc.) was degassed under vacuum and dried over CaCl₂ (Mallinckrodt) with stirring. Pentaborane(9) was obtained from laboratory stock, while hexaborane(10) was prepared by using Shore's⁶ method. All other reagents were commercially obtained, as indicated, and used as received.

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Table I. ^{11}B NMR Data

compd ^a	δ (J, Hz)	rel areas
1- $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe-2,3-}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$ (I) ^b	9.8 (134)	1
	4.3 (141)	2
	3.7 (128)	1
1- $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe-4,5,7,8-}(\text{CH}_3)_4\text{C}_4\text{B}_3\text{H}_3$ (II) ^c	14.8 (156)	1
	-12.2 (129)	2
1- $[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{Fe-4,5,7,8-}(\text{CH}_3)_4\text{C}_4\text{B}_3\text{H}_3$ (III) ^d	16.1 (156)	1
	-12.7 (125)	2
2- $[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{Fe-6,7,9,10-}(\text{CH}_3)_4\text{C}_4\text{B}_5\text{H}_5$ (IV) ^c	14.1 (156)	1
	6.2 (141)	1
	1.6 (166)	1
	-2.2 (137)	1
	-23.8 (157)	1

^a All complexes were run in CH_2Cl_2 with internal C_6D_6 lock material. ^b ^{11}B NMR spectrum at 115.5 MHz. ^c ^{11}B NMR spectrum at 64.2 MHz. ^d ^{11}B NMR spectrum at 32.1 MHz.

Table II. ^1H NMR Data

compd ^a	δ (rel area)	assignt
I ^b	1.92 (18)	Ph-CH ₃
	1.87 (6)	CH ₃
	3.72 (1) ^d	B-H
	3.36 (2) ^d	B-H
	1.48 (1) ^d	B-H
II ^b	2.17 (6)	CH ₃
	1.94 (18)	Ph-CH ₃
	1.85 (6)	CH ₃
	4.00 (1) ^d	B-H
	1.26 (2) ^d	B-H
III ^c	4.93 (5) ^e	C ₆ H ₅
	2.25 (6)	CH ₃
	1.94 (3)	Ph-CH ₃
	1.81 (6)	CH ₃
	4.83 (5) ^e	C ₆ H ₅
IV ^c	1.94 (3)	CH ₃
	1.84 (3)	CH ₃
	1.76 (3)	CH ₃
	1.74 (3)	CH ₃
	1.47 (3)	CH ₃
	1.81 (6)	CH ₃
	1.94 (3)	CH ₃

^a All complexes were run in C_6D_6 . ^b ^1H NMR spectrum at 250 MHz. ^c ^1H NMR spectrum at 200.1 MHz. ^d ^1H NMR spectrum at 100 MHz. ^e Center of multiplet.

Preparative thin-layer chromatography was performed on 0.5 mm (20 × 20 cm) silica gel F-254 plates (Merck). Boron-11 and proton Fourier transform NMR spectra at 32.1 and 100 MHz, respectively, were obtained on a JEOL PS-100 spectrometer equipped with the appropriate decoupling accessories. Proton NMR spectra, at 250 MHz, were obtained on a Bruker WH-250 Fourier transform spectrometer. Boron-11 and proton Fourier transform NMR spectra at 64.2 and 200.1 MHz, respectively, were obtained on an IBM WP200SY Fourier transform spectrometer. Boron-11 NMR spectra, at 115.5 MHz, were obtained on a Bruker WH-360 Fourier transform spectrometer located in the Mid-Atlantic Regional NMR Facility. All boron-11 chemical shifts were referenced to $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual benzene from the lock solvent (99.5% C_6D_6) and then referenced to Me_4Si (0.0 ppm). High- and low-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMH-2 mass spectrometer and/or a VG Micromass 7070H mass spectrometer interfaced to a Kratos DS50S data system. Infrared spectra were obtained on either a Perkin-Elmer 337 or an IBM FT-IR/97 spectrophotometer. All melting points are uncorrected.

The metal atom apparatus employed in these studies was based on a design published by Klabunde⁷ and is described elsewhere.^{8,9}

Table III. Infrared Data

compd	IR absorptions, cm^{-1}
I ^{a,c}	3001 (w), 2951 (m), 2910 (m), 2853 (w), 2533 (sh), 2501 (vs), 1448 (m), 1387 (s), 1066 (m), 1041 (vw), 1009 (m), 913 (w), 886 (sh), 878 (m), 815 (w), 795 (vw), 732 (w), 704 (w), 510 (w)
II ^{b,c}	2914 (vs), 2839 (sh), 2478 (sh), 2435 (s), 1738 (sh), 1714 (m), 1633 (w), 1446 (s), 1378 (s), 1255 (m), 1161 (vw), 1088 (m), 1066 (m), 1018 (m, br), 949 (m), 651 (w, br)
III ^{a,d}	2953 (s), 2918 (vs), 2866 (w), 2851 (m), 2449 (vs)
IV ^{a,d}	2953 (s), 2921 (vs), 2867 (sh), 2851 (s), 2547 (m), 2520 (m), 2489 (s)

^a KBr Pellet. ^b Carbon tetrachloride solution.

^c Perkin-Elmer 337. ^d IBM FT-IR/97.

Reaction of Iron Vapor with Toluene, B_5H_9 , and 2-Butyne.

Approximately 1.5 g of iron was placed in an integral tungsten alumina evaporation crucible (Sylvania Emissive Products, CS-1008), and iron vapor (~0.75 g) was generated by electrical heating (~8.0 V, ~64 A). The metal vapor was cocondensed with 25 mL of toluene, 15 mL of B_5H_9 , and 15 mL of 2-butyne (Farchan Division) over a 1.5-h period onto the walls of the reactor, which were maintained at -196 °C. Upon completion of metal deposition and ligand cocondensation, the matrix was warmed to -78 °C and stirred for 45 min. The dark slurry was then warmed to room temperature and stirred for an additional 45 min. Excess ligands were removed in vacuo, and the reactor was flushed with $\text{N}_2(\text{g})$. The dark residue was extracted with methylene chloride, filtered through a coarse frit, and then stirred with silica gel and filtered again, giving a dark brown filtrate. The filtrate was concentrated and then separated by TLC on silica gel by using a 30% benzene in hexanes solution. This preliminary separation gave a number of different colored bands. A yellow band (R_f 0.2) was further purified by TLC via successive developments in a 20% benzene in hexanes solution and was found to be I, 1- $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe-2,3-}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$ [orange; 8.2 mg; mp 220.5–222.0 °C; mass measurement calcd for $^{12}\text{C}_{16}^{1}\text{H}_{28}^{11}\text{B}_4^{56}\text{Fe}$ 320.1912, found 320.1928 (major fragment at m/e 218, $[\text{C}_6(\text{CH}_3)_6\text{Fe}^+]$); A red-purple band (R_f 0.5) was purified by successive developments in a 10% benzene in hexanes solution, giving two compounds: II, 1- $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe-4,5,7,8-}(\text{CH}_3)_4\text{C}_4\text{B}_3\text{H}_3$ [red-purple; 1.6 mg; mp 202–202.5 °C dec; mass measurement calcd for $^{12}\text{C}_{20}^{1}\text{H}_{33}^{11}\text{B}_3^{56}\text{Fe}$ 362.2211, found 362.2220 (major fragment at m/e 218, $[\text{C}_6(\text{CH}_3)_6\text{Fe}^+]$); III, 1- $[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{Fe-4,5,7,8-}(\text{CH}_3)_4\text{C}_4\text{B}_3\text{H}_3$ [orange; 0.29 mg; mass measurement calcd for $^{12}\text{C}_{15}^{1}\text{H}_{33}^{11}\text{B}_3^{56}\text{Fe}$ 292.1428, found 292.1442 (major fragment at m/e 200, $[\text{Fe}(\text{CH}_3)_4\text{C}_4\text{B}_3\text{H}_3^+]$). Several bands were also observed between R_f values of 0.1 and 0.0, and further purification by single development in a 40% benzene in hexanes solution yielded compound IV, 2- $[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{Fe-6,7,9,10-}(\text{CH}_3)_4\text{C}_4\text{B}_5\text{H}_5$ [R_f 0.7; yellow; 1.0 mg; mass measurement calcd for $^{12}\text{C}_{15}^{1}\text{H}_{26}^{11}\text{B}_5^{56}\text{Fe}$ 316.1771, found 316.1781 (major fragment at m/e 224, $[\text{Fe}(\text{CH}_3)_4\text{C}_4\text{B}_5\text{H}_5^+]$).

In addition to the above compounds, small amounts of several alkyl- and alkenyl-substituted (η^6 -arene)ferracarboranes were isolated. Mass spectral data, along with ^{11}B NMR for several of the compounds, suggest the following as possible structural formulations: $[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{Fe}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_3[\text{C}_2(\text{CH}_3)_2\text{H}]$ [R_f 0.5 (40% hexanes in benzene); yellow; mass measurement calcd for $^{12}\text{C}_{15}^{1}\text{H}_{24}^{11}\text{B}_5^{56}\text{Fe}$ 304.1599, found 304.1606 (major fragments at m/e 250, $(\text{CH}_3\text{C}_6\text{H}_5)\text{Fe}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4^+$, and m/e 212, $[\text{Fe}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_3[\text{C}_2(\text{CH}_3)_2\text{H}]^+]$]; two isomers of $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_3[\text{C}_2(\text{CH}_3)_2\text{H}]$ [A [R_f 0.5 (40% hexanes in benzene); yellow; mass measurement calcd for $^{12}\text{C}_{20}^{1}\text{H}_{33}^{11}\text{B}_4^{56}\text{Fe}$ 374.2382, found 374.2397 (major fragments at m/e 320, $[\text{C}_6(\text{CH}_3)_6]\text{Fe}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4^+$, and m/e 218, $[\text{C}_6(\text{CH}_3)_6\text{Fe}^+]$]; and B [R_f 0.3 (30% benzene in hexanes); yellow; parent m/e 374 (major fragment at m/e 218, $[\text{C}_6(\text{CH}_3)_6\text{Fe}^+]$]; two isomers of $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_3[\text{C}_2(\text{CH}_3)_2\text{H}_3]$ [A [R_f 0.36 (30% benzene in hexanes); yellow; parent m/e 376 (major fragment at m/e 218, $[\text{C}_6(\text{CH}_3)_6]\text{Fe}^+]$; ^{11}B NMR (ppm, C_6D_6 , 64.2 MHz) 10.82 (s), 8.54 (D,

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Table IV. Data Collection and Structure Refinement Information

	1- $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe-4,5,7,8-}$ (CH_3) ₄ C ₄ B ₃ H ₃	2- $[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{Fe-6,7,9,10-}$ (CH_3) ₄ C ₄ B ₅ H ₅
space group	$P2_1/c$	$P\bar{1}$
<i>a</i> , Å	8.753 (3)	9.368 (5)
<i>b</i> , Å	10.190 (2)	11.399 (4)
<i>c</i> , Å	22.118 (3)	8.708 (4)
α , deg		90.84 (4)
β , deg	95.08 (2)	116.51 (5)
γ , deg		94.03 (4)
<i>V</i> , Å ³	1965	829
<i>Z</i>	4	2
ρ (calcd), g cm ⁻³	1.222	1.263
cryst dimens, mm	0.450 × 0.200 × 0.088	0.175 × 0.075 × 0.050
mol formula	FeC ₂₀ B ₃ H ₃₃	FeC ₁₅ B ₅ H ₂₅
mol wt	361.77	315.27
λ (Mo K α), Å	0.710 73	0.710 73
scanning range, deg	0 < 2 θ < 55	0 < 2 θ < 50
scan mode	ω -2 θ	ω -2 θ
$\pm h, \pm k, \pm l$	+28, +13, ± 1	$\pm 11, \pm 13, +10$
no. of measd intensities	4509	2915
unique reflectns $F_o^2 > 3\sigma(F_o^2)$	2597	760
no. of variables	226	190
abs coeff μ , cm ⁻¹	7.63	8.94
transmissn coeff, %		
max	94.71	
min	85.33	
<i>R</i>	0.060	0.074
<i>R</i> _w	0.066	0.065

$J_{\text{BH}} = 195$ Hz), 3.82 (D, 2, $J_{\text{BH}} = 144$ Hz)]; B [R_f 0.31 (30% benzene in hexanes); yellow; mass measurement calcd for ¹²C₂₀¹H₃₆¹¹B₄⁵⁶Fe 376.2538, found 376.2541 (major fragment at *m/e* 218, [$\text{C}_6\text{-(CH}_3)_6\text{]Fe}^+$); ¹¹B NMR (ppm, C₆D₆, 64.2 MHz) 14.16 (s), 8.99 (D, $J_{\text{BH}} = 140$ Hz), 4.28 (D, 2, $J_{\text{BH}} = 146$ Hz)].

A 0.8-mg sample of II was heated at 240 °C in an evacuated Pyrex tube for 8.5 h. Analysis of the resultant sample by TLC gave no evidence of either isomerization or decomposition.

Reaction of Iron Vapor with B₅H₉ and 2-Butyne. Iron vapor (~0.75 g) was cocondensed with 15 mL of B₅H₉ and 30 mL of 2-butyne (Chemicals Procurement Labs, Inc., 98%, purified by fractionation through -78 °C trap) over a 1-h period at -196 °C. After metal deposition was complete, the reactor was warmed to -26 °C and stirred for 0.5 h. The dark slurry was then warmed to room temperature and stirred for an additional 45 min. The reaction was worked up in the manner described above to give a material that was separated by TLC on silica gel using a 20% benzene in hexanes solution. The resulting separation gave several compounds that were shown, by both mass spectral evidence and direct comparison, to be identical with those above: I (6.9 mg) and II (0.3 mg). In addition, small amounts of three alkyl- and alkenyl-substituted (η^6 -hexamethylbenzene)ferracarboranes were isolated: [$\eta^6\text{-C}_6(\text{CH}_3)_6\text{]Fe}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_9[\text{C}_2(\text{CH}_3)_2\text{H}]$ and two isomers of [$\eta^6\text{-C}_6(\text{CH}_3)_6\text{]Fe}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_9[\text{C}_2(\text{CH}_3)_2\text{H}_3]$.

Reaction of Iron Vapor with Toluene, B₆H₁₀, and 2-Butyne. Iron vapor (~0.75 g) was cocondensed with 25 mL of toluene, 5 mL of B₆H₁₀, and 15 mL of 2-butyne (CPL) over a 2-h period at -196 °C. Upon completion of metal deposition and ligand cocondensation, the matrix was warmed to -78 °C and stirred for 45 min. The dark slurry was then warmed to room temperature and stirred for an additional 1 h. The reaction was worked up in a manner similar to that already described, giving small amounts of I, II, and III. An additional compound was also isolated but in yields too low to allow complete characterization; however, a possible structural formulation for this compound, as indicated by mass spectral analysis, is the following: [$\eta^6\text{-C}_6\text{-(CH}_3)_6\text{]Fe}(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_6$ [R_f 0.2 (30% CCl₄ in hexanes solution); red; mass measurement calcd for ¹²C₂₀¹H₃₆¹¹B₆⁵⁶Fe 398.2745, found 398.2754 (major fragments at *m/e* 236, Fe(CH₃)₄C₄B₆H₆⁺, and *m/e* 218, [$\text{C}_6(\text{CH}_3)_6\text{]Fe}^+$)].

Crystallographic Data for 1- $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe-4,5,7,8-}$ (CH_3)₄C₄B₃H₃ (II) and 2- $[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{Fe-6,7,9,10-}$ (CH_3)₄C₄B₅H₅ (IV). Single crystals of II and IV were grown overnight by slow evaporation in air of benzene and heptane solutions, respectively. In each case, one of the crystals was cut to a suitable size, mounted on a glass fiber, and transferred to the diffractometer. The

Enraf-Nonius program SEARCH was used to obtain suitable reflections that were then used in the program INDEX to obtain an orientation matrix for data collection. Refined cell dimensions and their standard deviations were obtained from the least-squares refinement of these accurately centered reflections. On the basis of several theta scans the mosaicity of each crystal was judged acceptable. See Table IV for crystal data.

Collection and Reduction of the Data. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP 8/A computer, employing Mo K α radiation from a highly oriented graphite-crystal monochromator. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius program START.

Solution and Refinement of the Structure. All calculations were performed on a PDP 11/60 computer using the Enraf-Nonius structure package.¹⁰ The full-matrix least-squares refinement was based on *F*, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights (*w*) were taken as $(4F_o/\sigma(F_o))^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for non-hydrogen atoms were taken from Cromer and Waber^{11a} and those for hydrogen from Stewart.^{11b} The effects of anomalous dispersion for iron were included in *F_c* by using Cromer and Ibers' values¹² for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$.

A three-dimensional Patterson synthesis gave the coordinates of the iron atom for each molecule. Subsequent Fourier maps led to the location of the remaining heavy atoms of each complex. Anisotropic least-squares refinement of these atoms followed by a difference Fourier synthesis resulted in the location of the three hydrogen atoms bonded to the boron atoms in compound II. The positions of the remaining 30 hydrogen atoms in II and all hydrogen atoms in compound IV were calculated and included (but not refined) in the structure factor calculations. Final refinement of II included an absorption correction along with anisotropic thermal parameters for non-hydrogen atoms and fixed isotropic thermal parameters (5.00) for the hydrogen atoms. For IV, final refinement included anisotropic thermal parameters for non-

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Table V. Positional Parameters and Their Estimated Standard Deviations for $1-[\eta^6-C_6(CH_3)_6]Fe-4,5,7,8-(CH_3)_4C_4B_3H_3$

atom	x	y	z
Fe	0.19290 (8)	0.27401 (7)	0.36930 (3)
C7	0.1455 (6)	0.0996 (5)	0.4110 (2)
C8	0.2692 (6)	0.0822 (5)	0.3764 (2)
B3	0.4107 (7)	0.1703 (7)	0.3953 (3)
B2	0.3413 (7)	0.3008 (6)	0.4449 (3)
B6	0.1723 (7)	0.2038 (6)	0.4621 (3)
C5	0.3326 (6)	0.1850 (5)	0.5009 (2)
C4	0.4542 (6)	0.1689 (5)	0.4669 (2)
C7A	0.0032 (6)	0.0149 (6)	0.4048 (3)
C8A	0.2708 (7)	-0.0199 (6)	0.3275 (3)
C5A	0.3438 (7)	0.1990 (6)	0.5695 (3)
C4A	0.6202 (6)	0.1649 (6)	0.4925 (3)
C9	-0.0057 (6)	0.3903 (5)	0.3568 (2)
C10	-0.0107 (6)	0.2986 (5)	0.3094 (2)
C11	0.1118 (7)	0.2866 (5)	0.2745 (2)
C12	0.2460 (6)	0.3617 (5)	0.2877 (2)
C13	0.2487 (6)	0.4585 (5)	0.3341 (2)
C14	0.1231 (6)	0.4713 (5)	0.3687 (2)
C9A	-0.1407 (8)	0.4042 (8)	0.3942 (3)
C10A	-0.1532 (8)	0.2184 (7)	0.2932 (3)
C11A	0.107 (1)	0.1935 (7)	0.2216 (3)
C12A	0.3833 (8)	0.3445 (8)	0.2511 (3)
C13A	0.3857 (8)	0.5449 (7)	0.3468 (3)
C14A	0.1239 (9)	0.5721 (7)	0.4179 (3)
HB3	0.503 (5)	0.183 (4)	0.361 (2)
HB2	0.384 (5)	0.407 (4)	0.457 (2)
HB6	0.071 (5)	0.244 (4)	0.486 (2)

Table VI. Intramolecular Bond Distances (Å) for $1-[\eta^6-C_6(CH_3)_6]Fe-4,5,7,8-(CH_3)_4C_4B_3H_3$

Fe-C7	2.062 (3)	B2-C4	1.714 (5)
Fe-C8	2.067 (3)	B6-C5	1.591 (5)
Fe-B3	2.211 (4)	C5-C4A	1.367 (4)
Fe-B2	2.043 (4)	C5-C5A	1.519 (5)
Fe-B6	2.196 (4)	C4-C4A	1.513 (5)
Fe-C9	2.103 (3)	B3-HB3	1.17 (3)
Fe-C10	2.140 (3)	B2-HB2	1.16 (3)
Fe-C11	2.158 (3)	B6-HB6	1.14 (3)
Fe-C12	2.103 (3)	C9-C10	1.402 (5)
Fe-C13	2.109 (3)	C9-C14	1.404 (5)
Fe-C14	2.101 (3)	C9-C9A	1.509 (5)
C7-C8	1.392 (4)	C10-C11	1.382 (5)
C7-B6	1.553 (5)	C10-C10A	1.509 (5)
C7-C7A	1.512 (4)	C11-C12	1.411 (5)
C8-B3	1.558 (5)	C11-C11A	1.503 (5)
C8-C8A	1.502 (4)	C12-C13	1.422 (5)
B3-B2	1.860 (6)	C12-C12A	1.517 (5)
B3-C4	1.597 (5)	C13-C14	1.400 (5)
B2-B6	1.848 (6)	C13-C13A	1.495 (5)
B2-C5	1.718 (5)	C14-C14A	1.496 (5)

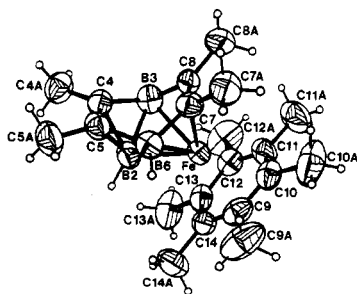


Figure 1. ORTEP drawing of $1-[\eta^6-C_6(CH_3)_6]Fe-4,5,7,8-(CH_3)_4C_4B_3H_3$, II.¹³ Non-hydrogen atoms are shown as 50% thermal ellipsoids.

hydrogen atoms and fixed isotropic thermal parameters (5.00) for the hydrogen atoms; however, no absorption corrections were applied due to the small size and irregular nature of the crystal. The final difference Fourier maps for II and IV were featureless, with the largest peaks being 0.56 and 0.32 e/Å³, respectively, with both peaks in the region of the irons.

Table VII. Selected Bond Angles (deg) for $1-[\eta^6-C_6(CH_3)_6]Fe-4,5,7,8-(CH_3)_4C_4B_3H_3$

C7-Fe-C8	39.4 (1)	B2-C5-B6	67.8 (2)
C7-Fe-B6	42.6 (1)	B2-C5-C4	66.4 (2)
C8-Fe-B3	42.5 (1)	B2-C5-C5A	130.8 (3)
B3-Fe-B2	51.7 (2)	B6-C5-C4	114.3 (3)
B2-Fe-B6	51.5 (2)	B6-C5-C5A	120.2 (3)
Fe-C7-C8	70.5 (2)	C4-C5-C5A	125.2 (3)
Fe-C7-B6	73.3 (2)	B3-C4-B2	68.3 (3)
Fe-C7-C7A	130.4 (2)	B3-C4-C5	114.5 (3)
C8-C7-B6	114.4 (3)	B3-C4-C4A	120.6 (3)
C8-C7-C7A	123.5 (3)	B2-C4-C5	66.7 (3)
B6-C7-C7A	121.8 (3)	B2-C4-C4A	129.6 (3)
Fe-C8-C7	70.1 (2)	C5-C4-C4A	124.6 (3)
Fe-C8-B3	73.7 (2)	C10-C9-C14	120.2 (3)
Fe-C8-C8A	128.6 (2)	C10-C9-C9A	119.9 (4)
C7-C8-B3	114.7 (3)	C14-C9-C9A	119.9 (4)
C7-C8-C8A	122.8 (3)	C9-C10-C11	120.2 (3)
B3-C8-C8A	122.3 (3)	C9-C10-C10A	120.6 (4)
Fe-B3-C8	63.8 (2)	C11-C10-C10A	119.1 (4)
Fe-B3-B2	59.5 (2)	C10-C11-C12	120.7 (3)
C8-B3-C4	112.0 (3)	C10-C11-C11A	121.3 (4)
B2-B3-C4	58.9 (2)	C12-C11-C11A	118.1 (4)
Fe-B2-B3	68.8 (2)	C11-C12-C13	119.0 (3)
Fe-B2-B6	68.5 (2)	C11-C12-C12A	120.8 (4)
B3-B2-C4	52.9 (2)	C13-C12-C12A	120.1 (4)
B6-B2-C5	52.8 (2)	C12-C13-C14	119.7 (3)
C5-B2-C4	46.9 (2)	C12-C13-C13A	120.3 (4)
Fe-B6-C7	64.1 (2)	C14-C13-C13A	119.9 (4)
Fe-B6-B2	60.0 (2)	C9-C14-C13	120.0 (3)
C7-B6-C5	112.3 (3)	C9-C14-C14A	119.4 (4)
B2-B6-C5	59.4 (2)	C13-C14-C14A	120.6 (4)

Table VIII. Positional Parameters and Their Estimated Standard Deviations for $2-[\eta^6-CH_3C_6H_5]Fe-6,7,9,10-(CH_3)_4C_4B_3H_5$

atom	x	y	z
Fe	0.2117 (3)	0.1812 (2)	0.3432 (3)
C16	0.280 (1)	0.033 (1)	0.482 (2)
C15	0.263 (2)	0.008 (1)	0.319 (2)
C14	0.337 (2)	0.075 (1)	0.263 (2)
C13	0.435 (1)	0.176 (1)	0.341 (2)
C12	0.447 (1)	0.202 (1)	0.502 (2)
C11	0.380 (2)	0.140 (1)	0.586 (2)
C11A	0.391 (2)	0.162 (2)	0.754 (2)
C6	0.165 (1)	0.347 (1)	0.281 (2)
C6A	0.279 (2)	0.441 (1)	0.276 (2)
C7	0.076 (1)	0.269 (1)	0.131 (2)
C7A	0.106 (2)	0.270 (2)	-0.021 (2)
B5	0.123 (2)	0.325 (1)	0.423 (2)
B1	0.009 (2)	0.185 (1)	0.377 (2)
B3	-0.029 (2)	0.153 (1)	0.156 (2)
B8	-0.133 (2)	0.282 (2)	0.056 (2)
B4	-0.183 (2)	0.201 (2)	0.203 (2)
C9	-0.175 (1)	0.342 (1)	0.180 (2)
C9A	-0.314 (2)	0.417 (1)	0.130 (2)
C10	-0.082 (1)	0.307 (1)	0.354 (2)
C10A	-0.130 (2)	0.337 (1)	0.488 (2)

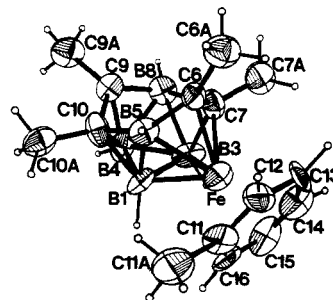


Figure 2. ORTEP drawing of $2-[\eta^6-CH_3C_6H_5]Fe-6,7,9,10-(CH_3)_4C_4B_3H_5$, IV.¹³ Non-hydrogen atoms are shown as 30% thermal ellipsoids.

Final positional parameters for both II and IV are given in Tables V and VIII, respectively. Intramolecular bond distances and selected bond angles are presented in Tables VI and VII,

Table IX. Intramolecular Bond Distances (Å) for 2- $[\eta^6\text{-C}_6\text{H}_5]_2\text{Fe-6,7,9,10-(CH}_3)_4\text{C}_4\text{B}_5\text{H}_5$

Fe-C16	2.063 (12)	B1-B3	1.822 (19)
Fe-C15	2.089 (17)	B1-B4	1.789 (20)
Fe-C14	2.064 (19)	B1-C10	1.654 (17)
Fe-C13	2.109 (13)	B3-B8	1.829 (20)
Fe-C12	2.005 (13)	B3-B4	1.787 (20)
Fe-C11	2.079 (13)	B8-B4	1.785 (22)
Fe-C6	1.998 (12)	B8-C9	1.475 (18)
Fe-C7	2.044 (13)	B4-C9	1.615 (19)
Fe-B5	2.129 (15)	B4-C10	1.662 (18)
Fe-B1	2.052 (15)	C9-C9A	1.514 (15)
Fe-B3	2.110 (14)	C9-C10	1.452 (17)
C6-C6A	1.474 (15)	C10-C10A	1.470 (14)
C6-C7	1.437 (15)	C11-C11A	1.438 (17)
C6-B5	1.474 (17)	C11-C12	1.331 (17)
C7-C7A	1.474 (14)	C11-C16	1.498 (18)
C7-B3	1.672 (17)	C12-C13	1.386 (18)
C7-B8	1.782 (18)	C13-C14	1.386 (22)
B5-B1	1.793 (18)	C14-C15	1.241 (22)
B5-C10	1.734 (17)	C15-C16	1.377 (19)

Table X. Selected Bond Angles (deg) for 2- $[\eta^6\text{-C}_6\text{H}_5]_2\text{Fe-6,7,9,10-(CH}_3)_4\text{C}_4\text{B}_5\text{H}_5$

C6-Fe-C7	41.6 (4)	B1-B3-B4	59.4 (9)
C6-Fe-B5	41.7 (5)	B8-B3-B4	59.1 (9)
C6-Fe-B1	81.7 (5)	C7-B8-B3	55.1 (8)
C7-Fe-B3	47.4 (5)	C7-B8-C9	115 (1)
B5-Fe-B1	50.8 (5)	B3-B8-B4	59.2 (9)
B1-Fe-B3	51.9 (6)	B4-B8-C9	58.5 (9)
Fe-C6-C6A	125.8 (9)	B1-B4-B3	61.3 (8)
Fe-C6-C7	70.9 (8)	B1-B4-C10	57.1 (8)
Fe-C6-B5	74.0 (8)	B3-B4-B8	61.6 (9)
C6A-C6-C7	119 (1)	B3-B4-C9	104 (1)
C6A-C6-B5	127 (1)	B8-B4-C9	51.1 (9)
C7-C6-B5	114 (1)	C9-B4-C10	52.6 (8)
Fe-C7-C6	67.5 (7)	B8-C9-B4	70 (1)
Fe-C7-C7A	121.4 (9)	B8-C9-C9A	125 (1)
Fe-C7-B3	68.4 (7)	B8-C9-C10	112 (1)
C6-C7-C7A	123 (1)	B4-C9-C9A	126 (1)
C6-C7-B8	110 (1)	B4-C9-C10	65.4 (9)
C7A-C7-B3	119 (1)	C9A-C9-C10	123 (1)
C7A-C7-B8	107 (1)	B5-C10-B1	63.9 (8)
B3-C7-B8	63.9 (9)	B5-C10-C9	113 (1)
Fe-B5-C6	64.4 (8)	B5-C10-C10A	114 (1)
Fe-B5-B1	62.4 (7)	B1-C10-B4	65.3 (9)
C6-B5-C10	113 (1)	B1-C10-C10A	116 (1)
B1-B5-C10	55.9 (7)	B4-C10-C9	62.0 (8)
Fe-B1-B5	66.9 (7)	B4-C10-C10A	122 (1)
Fe-B1-B3	65.7 (7)	C9-C10-C10A	120 (1)
Fe-B1-C10	121.0 (9)	C12-C11-C16	112 (1)
B5-B1-C10	60.2 (7)	C12-C11-C11A	130 (2)
B3-B1-B4	59.3 (8)	C16-C11-C11A	118 (2)
B4-B1-C10	57.6 (8)	C11-C12-C13	128 (2)
Fe-B3-C7	64.2 (7)	C12-C13-C14	113 (2)
Fe-B3-B1	62.4 (6)	C13-C14-C15	128 (2)
C7-B3-B8	61.0 (8)	C14-C15-C16	119 (2)
C7-B3-B4	109 (1)	C11-C16-C15	121 (2)

respectively, for II and in Tables IX and X, respectively, for IV. Figures 1 and 2 show views of II and IV, respectively.

Listings of final thermal parameters, selected molecular planes, and observed and calculated structure factors for both II and IV are available as supplementary material.

Results and Discussion

The reaction of thermally generated iron atoms with pentaborane(9), toluene, and 2-butyne was found to yield as the major product the (π -arene)ferracarborane complex 1- $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe-2,3-(CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$, I, along with smaller amounts of the four-carbon metallocarborane complexes 1- $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe-4,5,7,8-(CH}_3)_4\text{C}_4\text{B}_3\text{H}_3$, II, 1- $[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{Fe-4,5,7,8-(CH}_3)_4\text{C}_4\text{B}_3\text{H}_3$, III, and 2- $[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{Fe-6,7,9,10-(CH}_3)_4\text{C}_4\text{B}_5\text{H}_5$, IV.¹³ All four com-

plexes contain π -arene ligands, with III and IV containing η^6 -toluene ligands, and I and II containing the η^6 -hexamethylbenzene group. The formation of η^6 -hexamethylbenzene complexes is perhaps surprising but is consistent with previous work¹⁴ which has shown that iron atoms, as well as other solvated metal atoms, can effectively promote the trimerization of acetylenes, and, indeed, hexamethylbenzene was found to be a major side product in the above reaction. Thus, the metal atom reactions leading to the formation of I and II involve both the incorporation of one or two 2-butyne molecules into the ferraboron cluster system and the trimerization of 2-butyne to generate the η^6 -hexamethylbenzene ligand.

Reactions were also performed in the absence of toluene, and while these reactions gave both compounds I and II, they were obtained in reduced yields. These observations are also consistent with previous work¹⁵ which has shown that metal atoms readily react with arenes at low temperatures to yield solvated metal-arene complexes which are highly reactive and useful reagents for organometallic synthesis. Clearly, the initial formation of the solvated iron-toluene complex, followed by displacement of a toluene, and addition of 2-butyne and pentaborane(9) molecules to the iron atom are likely (although unproven) steps in the formation of the compounds described herein.¹⁶

The spectroscopic data for I are consistent with its formulation as a sandwich complex in which an iron atom is bound in an η^6 -fashion to a hexamethylbenzene ring and also to the open pentagonal face of a 2,3-(CH_3)₂C₂B₄H₄ carborane cage. Similar complexes, including the ethyl analogue 1- $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe-2,3-(C}_2\text{H}_5)_2\text{C}_2\text{B}_4\text{H}_4$, have recently been synthesized by Grimes⁵ via the reaction of the cyclooctatriene complex 1-(η^6 -1,3,5-C₈H₁₀)Fe-2,3-(C₂H₅)₂C₂B₄H₄ with arenes over AlCl₃. Similarly, we have shown¹ that 1-(η^6 -arene)Fe-2,3-(C₂H₅)₂C₂B₄H₄ complexes may also be prepared by the direct reaction of iron atoms with 2,3-(C₂H₅)₂C₂B₄H₆ and arenes.

Compounds II and III are the (η^6 -arene)metalla analogues of the eight-vertex four-carbon carborane (CH₃)₄C₄B₄H₄ in which an (η^6 -arene)Fe unit replaces a cage boron atom. These complexes are 2n + 4 skeletal electron systems (8 framework atoms, 20 skeletal electrons), and electron-counting rules¹⁷ would therefore predict an

(13) The compounds reported herein have been numbered by using conventional procedures to allow direct comparisons with previously reported compounds; however, Casey et al. have recently proposed a new nomenclature system for polyhedral cage molecules. Using this system these compounds would have the following names and numbering: I, 1-(η^6 -hexamethylbenzene)-2,3-dimethyl-2,3-dicarba-1-ferra[*D*_{5h}-(1 ν^5 5 ν^4 1 ν^5)- Δ^{10} -closo]heptaborane(6); II, 8-(η^6 -hexamethylbenzene)-2,3,4,5-tetramethyl-2,3,4,5-tetracarba-8-ferra-1-debor[C_{2v}-(1 ν^6 4 ν^4 2 ν^6 2 ν^6)- Δ^{14} -closo]nonaborane(7); III, 8-(η^6 -toluene)-2,3,4,5-tetramethyl-2,3,4,5-tetracarba-8-ferra-1-debor[C_{2v}-(1 ν^6 4 ν^4 2 ν^6 2 ν^6)- Δ^{14} -closo]undecaborane(9). See: Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* 1983, 22, 2228-2235, 2236-2245.

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(16) We had previously proposed (ref 1) a similar mechanism to be involved in the formation of 1-(η^6 -CH₃C₆H₅)Fe-2,3-(C₂H₅)₂C₂B₄H₄.

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open-cage nido structure based on a tricapped trigonal prism missing one vertex. However, of the known eight-vertex, $2n + 4$ boron cluster systems only the cobalt-thiaborane complex $2,3,6-(\eta\text{-C}_5\text{H}_5)_2\text{Co}_2\text{SB}_5\text{H}_7$ has been shown¹⁸ to adopt a structure in agreement with these predictions, although NMR data¹⁹ for the compound $(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_4(\text{CH}_3)_4$ is also consistent with a nido structure. A close structure, based on a dodecahedral geometry, has been confirmed²⁰ for $(\eta\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_4\text{H}_4$ and, on the basis of NMR data, proposed²⁰ for $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$. Arachno structures derived from a bicapped square antiprism missing two vertices have been confirmed for B_8H_{12} ²¹ and $1,4,5,7,8-(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{C}_6\text{H}_5)_4\text{C}_4\text{B}_3\text{H}_3$ ²² are consistent with the NMR data for $\text{C}_2\text{B}_6\text{H}_{10}$ ²³ and $(\text{CH}_3)_4\text{C}_4\text{B}_4\text{H}_4$ ²⁴.

The NMR data for II and III and for $1,4,5,7,8-(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{C}_6\text{H}_5)_4\text{C}_4\text{B}_3\text{H}_3$ ²² are similar, suggesting a close structural relationship. Thus, all three compounds show two resonances in a ratio of 2:1 in their ¹¹B NMR spectra. Likewise, the boron-decoupled proton NMR spectra of II shows two B-H resonances in a ratio of 2:1 and the spectra of both II and III each show two resonances of area 6 attributable to two sets of nonequivalent cage methyl groups. These data are clearly consistent with the arachno-type structure observed for $1,4,5,7,8-(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{C}_6\text{H}_5)_4\text{C}_4\text{B}_3\text{H}_3$ for both II and III. This conclusion was confirmed by means of a single-crystal X-ray investigation of II, the results of which are depicted in the ORTEP drawing in Figure 1.

In both II and $1,4,5,7,8-(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{C}_6\text{H}_5)_4\text{C}_4\text{B}_3\text{H}_3$ the metal atom occupies the five-coordinate 1-position in an arachno-type cage and is bound to borons B2, B3, and B6 and to carbons C7 and C8. The iron atom is nearly symmetrically located in the open face with average Fe-B and Fe-C distances of 2.150 and 2.065 Å, respectively, and a Fe-ring distance of 1.584 (1) Å, which can be compared with the average Co-B and Co-C distances of 2.081 and 2.026 Å, respectively, observed in $1,4,5,7,8-(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{C}_6\text{H}_5)_4\text{C}_4\text{B}_3\text{H}_3$. The iron atom is also bound in a symmetrical fashion to the η^6 -hexamethylbenzene ring with an average Fe-ring carbon distance of 2.119 Å and an Fe-ring distance of 1.587 (1) Å, the plane of the η^6 -hexamethylbenzene ring is parallel (dihedral angle = 5.9°) to that of the pentagonal bonding face of the carborane. The remaining boron-boron and boron-carbon distances in the cage appear normal, although it should be noted that they are generally somewhat shorter (~ 0.02 Å) than in the cobalt complex.

One of the most significant aspects of the structure of II concerns the carbon-carbon bond lengths and the possible presence of localized multiple-bond character between cage carbon atoms. We had previously²² noted in the structure of $1,4,5,7,8-(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{C}_6\text{H}_5)_4\text{C}_4\text{B}_3\text{H}_3$ that while the C7-C8 bond distance (1.419 (5) Å) was in the normal range for carbon-carbon distances for small cage metallacarboranes, the C4-C5 distance was considerably

shortened (1.379 (5) Å). We also noted that similar bonding features were observed²⁵ in another four-carbon metallacarborane, $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_6\text{OC}_2\text{H}_5$, in which the two carbons not directly bonded to the metal were found to have a shortened bond, 1.374 (6) Å. In compound II both carbon-carbon distances are shortened: C7-C8 = 1.392 (4) Å and C4-C5 = 1.367 (4) Å. The C4-C5 distance is, in fact, the shortest carbon-carbon bond to be observed in a carborane or metallacarborane cage and again suggests localized multiple-bond character between C4 and C5, perhaps resulting from the higher carbon content of the cluster. We feel therefore that compounds such as these can be considered to be at the organic/inorganic interface, showing bonding properties intermediate between the two classes, and we expect that these types of bonding features will be common in other high carbon content boron and metallaboron clusters.

Compounds II and III are also two additional examples of eight-vertex nido skeletal electron count clusters that adopt an arachno-type cage geometry. We had previously suggested²² that the reason $1,4,5,7,8-(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{C}_6\text{H}_5)_4\text{C}_4\text{B}_3\text{H}_3$ adopts the more open arachno cage structure rather than the nido geometry observed for $2,4,6-(\eta\text{-C}_5\text{H}_5)_2\text{Co}_2\text{SB}_5\text{H}_7$ ¹⁸ may be because this structure minimizes steric repulsions between the phenyl groups attached to the cage carbons. In compounds II and III the cage carbons are methyl substituted and as a result would be expected to have diminished steric repulsions. However, these complexes also adopt an arachno structure, leading to the conclusion that although the energy differences between the various eight-vertex geometries may be small, the arachno-type structure is generally favored for open-cage systems. In fact, Mingos has reported²⁶ extended Hückel molecular orbital calculations for eight-vertex nido and arachno clusters which indicate that an arachno structure is more stable than the predicted nido structure for $2n + 4$ electron systems such as $\text{B}_8\text{H}_8^{4-}$. Mingos also concluded that while the interconversion of the nido and arachno polyhedral forms is an allowed process for the $\text{B}_8\text{H}_8^{2-}$ ion, it is a forbidden process for $\text{B}_8\text{H}_8^{4-}$. This may account for the fact that neither II nor $2,3,6-(\eta\text{-C}_5\text{H}_5)_2\text{Co}_2\text{SB}_5\text{H}_7$ (nido structure)¹⁷ isomerize upon heating at moderate temperatures.

On the basis of the above observations, it would be expected that other types of $2n + 4$, eight-vertex open-cage clusters should also adopt arachno type structures. In this regard, the recent structural characterization²⁷ of the organometallic cluster $(\eta\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{C}_6\text{Me}_6$ is of interest. The complex, which was formed by the reaction of $(\eta\text{-C}_5\text{H}_5)\text{-Fe}(\text{cod})$ with 2-butyne, is also an eight-vertex, 20 skeletal electron cluster system and was shown, in fact, to have an arachno structure remarkably similar to II in which the iron atoms are in the five-coordinate 1,2-positions in the cage while the carbon atoms occupy the remaining positions on the open face. The close similarity of II and $(\eta\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{C}_6\text{Me}_6$ further illustrates the bridging role that metallacarborane complexes play between the boron hydride and organometallic areas.

Compound IV, $2-[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{Fe-6,7,9,10-(CH}_3)_4\text{C}_4\text{B}_5\text{H}_5$, was isolated in low yield as a yellow crystalline solid. The compound is a $2n + 4$ skeletal electron system (10 cage atoms, 24 skeletal electrons) and would be expected to

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adopt a 10-vertex nido cage geometry based on an octadecahedron missing one vertex. A number of different isomers, involving different arrangements of the iron and carbon atoms in the cage, are possible; however, both the ^1H NMR data, which shows four nonequivalent cage methyl resonances, and the ^{11}B NMR spectrum, which contains five separate boron resonances, indicate that the molecule cannot contain a plane of symmetry. These conclusions were confirmed by a single-crystal X-ray study of IV which established the $2-[\eta^6\text{-CH}_3\text{C}_6\text{H}_5]\text{-6,7,9,10-(CH}_3)_4\text{C}_4\text{B}_5\text{H}_5$ structure shown in Figure 2.

As can be seen in the figure, IV can be considered a decaborane(14) analogue in which the iron atom occupies the 2-position in the cage, while the carbon atoms from the two incorporated 2-butyne molecules are in the 6,7- and 9,10-positions on the open face of the cage. The iron atom is bound to the planar-pentagonal face, composed of borons B3, B1, and B5 and carbons C6 and C7. The average Fe-B distance, 2.097 Å, Fe-C distance, 2.021 Å, and Fe-ring distance, 1.525 (3) Å, are similar to those found for II.

In contrast to the results obtained for II, discussed above, the intracage carbon-carbon distances found for IV were found to be equal (C6-C7 = 1.437 (15) Å; C9-C10 = 1.452 (17) Å) and lie in the normal range observed in metallocarboranes. For example, a similar carbon-carbon bond distance of 1.452 (5) Å has been found in the isostructural cage complex $8,6,7-(\eta\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_7\text{H}_{11}$.²⁸ This lack of apparent localized multiple-bond character in IV may be due to the higher boron to carbon ratio in this cluster resulting in a more delocalized bonding. Clearly, additional examples of high carbon content carboranes and metallocarboranes will need to be synthesized and structurally characterized before general bonding patterns can be established.²⁹

Compound IV is the only compound isolated in the reactions involving pentaborane(9) that retained the original five-boron unit. Compounds I (four borons) and II and III (three borons) must have resulted from cage fragmentations during the course of the metal atom reaction. Likewise, analogous reactions involving hexaborane(10) gave extensive cage degradation resulting in the production of compounds I, II, and III and only trace amounts of a six-boron complex, which the mass spectral data indicated could be $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe}(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_6$. Such cage fragmentation reactions are, of course, consistent with the extremely reactive nature of both pentaborane(9) and hexaborane(10). It may well be that the use of these techniques for the synthesis of (η^6 -arene)metallaborane and (η^6 -arene)metallocarborane clusters derived from the more stable larger boron cage systems will result in higher yield, more specific reactions.

In summary, the results described above illustrate the potential utility of metal atom reactions both for the synthesis of (η^6 -arene)metallaborane clusters and for the synthesis of hybrid cluster systems bridging the boron hydride and organometallic areas. Further work is currently underway in this laboratory concerned with the application of these techniques to the synthesis of other new types of η^6 -arene-cluster systems.

Acknowledgment. We thank the National Science Foundation and the Army Research Office for the support of this work.

Registry No. I, 90990-67-3; II, 91032-15-4; III, 91002-35-6; IV, 91002-36-7; Fe, 7439-89-6; B_5H_9 , 19624-22-7; 2-butyne, 503-17-3.

Supplementary Material Available: Tables of temperature factors, positional parameters, molecular planes and angles, and structure factors (33 pages). Ordering information is given on any current masthead page.

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