applications, it is desirable to be able to synthesize *N*-alkylporphyrin complexes of different stabilities with respect to dealkylation. We have shown that some non-N-alkylated metalloporphyrins can be made more rapidly by a two-step reaction sequence beginning with an *N*-alkylporphyrin than by the normal complexation reaction of the non-Nalkylated porphyrin. The rapid sequence has been used to make radioactive palladium-109 hematoporphyrin for selective lymphatic ablation to prevent the rejection of transplanted organs.[20,36] Synthesis of some other complexes by this method has not been possible because of the sluggishness of dealkylation of the appropriate *N*-methylporphyrin precursor. The high reactivity we have found for *N*-benzyl substituents greatly expands the possible applications of *N*-alkylporphyrins as synthetic precursors for rapid metalloporphyrins synthesis. On the other hand, *N*-arylporphyrin complexes such as the *N*-phenyl species or sterically hindered *N*-alkyl species may be of use as electrochemical catalysts where long-term stability is required.

Acknowledgment. We gratefully acknowledge support by the National Institutes of Health (Grants CA 25427 and RR 08176) and the PSC-BHE grants program of the City University of New York. We appreciate the generous gift of (*N*-phenylprotoporphinato)zinc(II) from Paul Ortiz de Montellano and Kent Kunze of the University of California, San Francisco, and we thank Robert Cavallo and A. Sudhakar for their technical assistance.

Registry No. Cu-*N*-$CH_3TPP^+CF_3SO_3^-$, 84799-60-0; Cu-*N*-$C_2H_5TPP^+CF_3SO_3^-$, 92396-64-0; Cu-*N*-*p*-$C_6H_4NO_2TPP^+CF_3SO_3^-$, 92366-26-2; Cu-*N*-$C_6H_5TPP^+CF_3SO_3^-$, 92396-66-2; di-*n*-butylamine, 111-92-2; cytochrome P-450, 9035-51-2.

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(36) Liddane, K.; Lavallee, D. K.; Srivastava, S. C.; Prach, T.; Richards, P.; Fawwaz, R. A., work in progress.

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Metal Atom Synthesis of Metallaboron Clusters. 5.[1] Synthesis of the First (η^6-Arene)metallaborane and (η^6-Arene)metallaoxaborane Clusters. Structural Characterizations of $5\text{-}[\eta^6\text{-}C_6(CH_3)_3H_3]FeB_9H_{13}$ and $2\text{-}[\eta^6\text{-}C_6(CH_3)_3H_3]Fe\text{-}6\text{-}OB_8H_{10}$

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The reaction of thermally generated iron atoms with decaborane(14) and mesitylene under rotary metal atom conditions was found to yield the first three reported examples of (η^6-arene)ferraborane complexes, $5\text{-}[\eta^6\text{-}C_6(CH_3)_3H_3]FeB_9H_{13}$ (I), $1\text{-}[\eta^6\text{-}C_6(CH_3)_3H_3]FeB_9H_9$ (II), and $1\text{-}[\eta^6\text{-}C_6(CH_3)_3H_3]FeB_{10}H_{10}$ (III). An analogous reaction employing toluene as a reactant resulted in the isolation of $5\text{-}[\eta^6\text{-}C_6H_5CH_3]FeB_9H_{13}$ (V) and $1\text{-}[\eta^6\text{-}C_6H_5CH_3]FeB_{10}H_{10}$ (VI). A single-crystal X-ray study of I demonstrated that the compound is a decaborane(14) analogue, consistent with its $2n + 4$ skeletal electron count, in which the iron atom occupies the cage 5-position on the open face. Crystal data for I: space group $P2_1/c$; $Z = 4$; $a = 9.348$ (2) Å, $b = 9.842$ (1) Å, $c = 17.335$ (2) Å, $\beta = 90.70$ (2)°; $V = 1594.7$ Å^3. The structure was refined by full-matrix least squares to a final R of 0.049 and R_w of 0.049 for the 1755 reflections that had $F_o^2 > 3\sigma(F_o^2)$. Compounds II, III, and VI are each $2n$ skeletal electron systems and would be expected according to skeletal electron counting theory to adopt distorted polyhedral structures. The spectroscopic data for II, however, support a C_{3v} closo polyhedral structure, while the data for compounds III and VI are consistent with a closo octadecahedral geometry. In addition to the three (η^6-arene)ferraborane complexes produced in the mesitylene reaction, a fourth compound was isolated in trace amounts and was identified as $2\text{-}[\eta^6\text{-}C_6(CH_3)_3H_3]Fe\text{-}6\text{-}OB_8H_{10}$ (IV) by means of a single-crystal X-ray determination. The compound was shown to have a decaborane(14) structure in which the iron atom occupies the five-coordinate 2-position while the oxygen atom is in the 6-position on the open face. Compound IV is thus the first example of a polyhedral boron cage compound containing an oxygen atom in a cage vertex position. Crystal data for IV: space group $P2_1/c$; $Z = 4$; $a = 12.647$ (3) Å, $b = 13.437$ (2) Å, $c = 9.281$ (7) Å, $\beta = 104.57$ (3)°; $V = 1526.5$ Å^3. The structure was refined to a final R of 0.059 and $R_w = 0.065$ for the 1449 reflections that had $F_o^2 > 3\sigma(F_o^2)$.

Introduction

We have previously demonstrated that metal atom techniques can provide useful synthetic routes to (η^6-arene)metallacarborane complexes,[1,3] and we have now used this method to prepare a variety of these species, including both two-carbon and four-carbon complexes, such as $1\text{-}[\eta^6\text{-}CH_3C_6H_5]Fe\text{-}2,3\text{-}(C_2H_5)_2C_2B_4H_4$,[3] $1\text{-}[\eta^6\text{-}C_6(CH_3)_6]Fe\text{-}4,5,7,8\text{-}(CH_3)_4C_4B_3H_3$,[1] and $2\text{-}[\eta^6\text{-}CH_3C_6H_5]Fe\text{-}6,7,9,10\text{-}(CH_3)_4C_4B_5H_5$.[1] Others have also recently reported[4] the synthesis of (η^6-arene)metallacarboranes using different synthetic approaches.

Given the rapidly increasing number of (η^6-arene)metallacarborane complexes, it is indeed surprising that there has been heretofore no report of the synthesis of an (η^6-arene)metallaborane cluster. However, we have now found that metal atom reactions can be used to prepare these complexes, and we report here the synthesis of three different types of (η^6-arene)ferraborane cage systems, $1\text{-}(\eta^6\text{-arene})FeB_{10}H_{10}$, 1-

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[1] For part 4 see: Micciche, R. P.; Briguglio, J. J.; Sneddon, L. G. *Organometallics* **1984**, *3*, 1396-1402.

[2] Alfred P. Sloan Fellow.

[3] Micciche, R. P.; Sneddon, L. G. *Organometallics* **1983**, *2*, 674-678.

[4] (a) Garcia, M. P.; Green, M.; Stone, F. G. A.; Sommerville, R. G.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 871-872. (b) Hanusa, T. P.; Huffman, J. C.; Todd, L. J. *Polyhedron* **1982**, *1*, 77-82. (c) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* **1983**, *2*, 506-514.

Table I. ^{11}B NMR Data

compd[a]	δ (*J*, Hz)	rel areas
5-[η^6-$C_6(CH_3)_3H_3$]FeB_9H_{13} (I)[b]	30.1 (114)	1
	22.5 (126)	1
	12.6 (136)	1
	4.3 (133)	2
	0.1 (155)	1
	−3.0 (133)	1
	−18.6 (150)	1
	−37.8 (162)	1
1-[η^6-$C_6(CH_3)_3H_3$]FeB_9H_9 (II)[c]	106.5 (178)	3
	27.7 (144)	3
	−11.4 (148)	3
1-[η^6-$C_6(CH_3)_3H_3$]$FeB_{10}H_{10}$ (III)[b]	130.2 (167)	2
	18.3 (143)	6
	17.1 (164)	2
5-[η^6-$C_6H_5CH_3$]FeB_9H_{13} (V)[c]	29.5 (137)	1
	22.5 (118)	1
	13.4 (137)	1
	6.2 (137)	2
	0.6 (164)	1
	−3.5 (141)	1
	−18.5 (146)	1
	−37.1 (169)	1
1-[η^6-$C_6H_5CH_3$]$FeB_{10}H_{10}$ (VI)[d]	129.6 (188)	2
	18.1 (157)	8

[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	δ (rel area)	assignt	compd	δ (rel area)	assignt
I[a,d]	4.73 (3)	C_6H_3	III[a,c]	4.39 (3)	C_6H_3
	1.83 (9)	Ph-CH_3		1.31 (9)	Ph-CH_3
	4.83[e]	B-H		12.06 (2)[b,e]	B-H
	4.04[e]	B-H		4.45 (2)[b,e]	B-H
	3.70[e]	B-H		2.73 (2)[b,e]	B-H
	3.47[e]	B-H		1.23 (4)[b,e]	B-H
	1.50[e]	B-H	V[a,c]	4.85 (5)[f]	C_6H_5
	1.13[e]	B-H		1.64 (3)	Ph-CH_3
	−2.98 (2)[e]	B-H-B		4.08[e]	B-H
	−3.67 (1)[e]	B-H-B		3.81[e]	B-H
	−23.39 (1)[e]	B-H-Fe		3.50[e]	B-H
II[a,c]	4.57 (3)	C_6H_3		1.19[e]	B-H
	1.38 (9)	Ph-CH_3		−2.93 (2)[e]	B-H-B
	10.05 (3)[b,e]	B-H		−3.59 (1)[e]	B-H-B
	3.80 (3)[b,e]	B-H		−22.81 (1)[e]	B-H-Fe
	0.38 (3)[b,e]	B-H	VI[a,c]	4.69 (5)[f]	C_6H_5
				0.98 (3)	Ph-CH_3

[a] Complex was run in C_6D_6. [b] Complex was run in C_6D_6/$DCCl_3$ solution. [c] ^1H NMR spectrum at 250 MHz. [d] ^1H NMR spectrum at 200.1 MHz. [e] ^{11}B spin-decoupled ^1H NMR spectrum at 100 MHz. [f] Center of multiplet.

Table III. Infrared Data

compd[a]	IR absorptions, cm^{-1}
I[b]	3036 (w), 2985 (w), 2964 (w), 2926 (m), 2848 (w), 2583 (m), 2548 (s), 2533 (s), 2516 (s), 2503 (s), 2481 (m), 1542 (sh), 1537 (m), 1461 (sh), 1451 (m), 1439 (m), 1382 (m), 1321 (w), 1306 (w), 1279 (vw), 1266 (w), 1094 (w), 1053 (m), 1028 (m), 1020 (w), 1002 (m), 951 (w), 939 (w), 926 (vw), 917 (vw), 891 (m), 846 (m), 838 (sh), 799 (m), 776 (m), 709 (m), 682 (w), 646 (w), 615 (w), 597 (vw)
II[c]	3027 (w), 2982 (sh), 2957 (w), 2911 (w), 2837 (sh), 2521 (vs), 2460 (s), 2337 (br, sh), 1727 (w), 1660 (w), 1557 (m), 1539 (sh), 1489 (vw), 1447 (m), 1437 (sh), 1372 (s), 1307 (m), 1250 (w), 1160 (w), 1030 (m), 1015 (sh), 971 (s), 960 (sh), 906 (sh), 890 (m), 862 (m), 851 (sh), 830 (s), 772 (w), 753 (m), 726 (w), 619 (w), 500 (m)
III[c]	3030 (vw), 2911 (w), 2568 (m), 2505 (sh), 2466 (vs), 2315 (br, sh), 1602 (w), 1550 (w), 1450 (m), 1375 (m), 1301 (w), 1257 (w), 1029 (m), 1007 (s), 929 (w), 896 (w), 848 (m), 825 (sh), 803 (w), 745 (w)
V[c]	3076 (w), 2961 (sh), 2916 (w), 2836 (br, sh), 2546 (s), 2511 (s), 2336 (br, sh), 1736 (w), 1636 (w), 1534 (w), 1466 (m), 1461 (sh), 1443 (sh), 1411 (sh), 1385 (w), 1324 (w), 1152 (w), 1092 (w), 1048 (m), 1037 (sh), 1016 (sh), 1003 (sh), 998 (m), 939 (w), 895 (w), 864 (sh), 841 (m), 806 (m), 780 (m), 715 (w)

[a] KBr pellet. [b] IBM FT-IR/97. [c] Perkin-Elmer 337.

(η^6-arene)FeB_9H_9, and 5-(η^6-arene)FeB_9H_{13}, as products of the reactions of iron atoms with decaborane(14) in the presence of either toluene or mesitylene. In addition, we have also been able to isolate and structurally characterize a minor product from the mesitylene reaction, which proved to be the first example of a boron cage compound in which an oxygen atom has been inserted into a cage position: 2-[η^6-$C_6(CH_3)_3H_3$]-Fe-6-OB_8H_{10}.[5]

Experimental Section

Materials and Procedure. Iron metal (lumps, random) was obtained from Alfa Products/Ventron Division. Mesitylene (J. T. Baker Chemical Co.) and toluene (MCB Manufacturing Chemists, Inc.) were both degassed under vacuum and dried over $CaCl_2$ (Mallinckrodt) with stirring. Decaborane(14) was obtained from Callery Chemical Co. and recrystallized from heptane (MCB) before use. All other reagents were commercially obtained, as indicated, and used as received.

Preparative thin-layer chromatography was performed on 0.5-mm (20 × 20 cm) silica gel F-254 plates (Merck). Boron-11 (Table I) and proton Fourier transform (Table II) 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 transfer 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 $BF_3{\cdot}O(C_2H_5)_2$ (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 (0.00 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 (Table III) were obtained on either a Perkin-Elmer 337 or an IBM FT-IR/97 spectrophotometer. All melting points are uncorrected.

The rotary metal atom apparatus used was purchased from Kontes/Martin (Model No. K-927550) and modified according to a design published by Ittel and Tolman.[6]

Reaction of Iron Vapor with Mesitylene and $B_{10}H_{14}$. A solution of 2 g of $B_{10}H_{14}$ in 250 mL of mesitylene was placed in the rotary metal atom reactor. After degassing, the solution was warmed to −40

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(5) 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. By the use of this system these compounds would have the following names and numbering: I, 5-(η^6-mesitylene)-(2,4-μH),(2,5-μH),(3,6-μH),(3,7-μH)-5-ferra-1-debor[C_{2v}-($1v^62v^44v^52v^52v^5$)-Δ^{18}-*closo*]undecaborane(13); II, 1-(η^6-mesitylene)-1-ferra[C_{3v}-($1v^63v^43v^53v^5$)-Δ^{16}-*closo*]decaborane(9); III, 1-(η^6-mesitylene)-1-ferra[C_{2v}-($1v^62v^44v^52v^52v^5$)-Δ^{18}-*closo*]undecaborane(10); IV, 8-(η^6-mesitylene)-(3,6-μH),(3,7-μH)-2-oxa-8-ferra-1-debor[C_{2v}-($1v^62v^44v^52v^52v^5$)-Δ^{18}-*closo*]undecaborane(10); V, 5-(η^6-toluene)-(2,4-μH),(2,5-μH),(3,6-μH),(3,7-μH)-5-ferra-1-debor[C_{2v}-($1v^62v^44v^52v^52v^5$)-Δ^{18}-*closo*]undecaborane(13); VI, 1-(η^6-toluene)-1-ferra[C_{2v}-($1v^62v^44v^52v^52v^5$)-Δ^{18}-*closo*]undecaborane(10). See: Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1983**, *22*, 2228–2235, 2236–2245.

(6) Ittel, S. D.; Tolman, C. A. *Organometallics* **1982**, *1*, 1432–1436.

°C and maintained at that temperature for the entire reaction. Iron vapor (~0.75 g) was condensed into the rotating solution over a 1-h period. Upon completion of metal deposition, the dark slurry was warmed to room temperature and rotated for an additional 20 min. Excess mesitylene was removed in vacuo, and the reactor was flushed with $N_2(g)$. The remaining black residue was extracted with methylene chloride, the resulting mixture filtered through a coarse frit, and the filtrate concentrated. Excess $B_{10}H_{14}$ was removed by vacuum sublimation, and the subsequent residue was separated by TLC on silica gel by using a 40% hexanes in benzene solution. The resulting separation yielded several new (η^6-arene)ferraboranes: I, 5-[η^6-$C_6(CH_3)_3H_3$]FeB_9H_{13},[5,7] [R_f 0.4; reddish purple; 2.0 mg; mp 175 °C dec; mass measurement calcd for $^{12}C_9{}^1H_{25}{}^{11}B_9{}^{56}Fe$ 288.2136, found 288.2163 (major fragments at *m/e* 176, [$C_6(CH_3)_3H_3$]Fe^+, *m/e* 120, $C_6(CH_3)_3H_3^+$, and *m/e* 105, $C_6(CH_3)_2H_3^+$)]; II, 1-[η^6-$C_6(CH_3)_3H_3$]FeB_9H_9[5] [R_f 0.13; reddish brown; 1.4 mg; mp 236–237.5 °C dec; mass measurement calcd for $^{12}C_9{}^1H_{21}{}^{11}B_9{}^{56}Fe$ 284.1830, found 284.1844 (major fragments at *m/e* 176 [$C_6(CH_3)_3H_3$]Fe^+, *m/e* 120, $C_6(CH_3)_3H_3^+$, and *m/e* 105, $C_6(CH_3)_2H_3^+$)]; III, 1-[η^6-$C_6(CH_3)_3H_3$]$FeB_{10}H_{10}$[5] [R_f 0.06; yellow; 2.2 mg; air sensitive; mass measurement calcd for $^{12}C_9{}^1H_{22}{}^{11}B_{10}{}^{56}Fe$ 296.2002, found 296.2023 (major fragments at *m/e* 120, $C_6(CH_3)_3H_3^+$, and *m/e* 105, $C_6(CH_3)_2H_3^+$)]. The yields of compounds I–III based on vaporized metal are each less than 1%.

In addition, small amounts of a fourth compound were obtained. Mass spectral evidence was consistent with the formula [η^6-$C_6(CH_3)_3H_3$]$FeOB_8H_{10}$ (IV) [R_f 0.6; yellow; mass measurement calcd for $^{12}C_9{}^1H_{22}{}^{11}B_8{}^{16}O{}^{56}Fe$ 290.1764, found 290.1775 (major fragments at *m/e* 260, [$C_6(CH_3)_3H_3$]$FeB_7H_7^+$, *m/e* 176, [$C_6(CH_3)_3H_3$]Fe^+, *m/e* 120, $C_6(CH_3)_3H_3^+$, and *m/e* 105, $C_6(CH_3)_2H_3^+$)]. The compound was subsequently identified by means of a single-crystal X-ray study, discussed below, as 2-[η^6-$C_6(CH_3)_3H_3$]Fe-6-OB_8H_{10}.

A 0.6-mg sample of I was heated at ~180 °C in an evacuated Pyrex tube for 19 h. Analysis of the resultant product by TLC indicated that extensive decomposition had occurred and that the closo complex, 1-[η^6-$C_6(CH_3)_3H_3$]FeB_9H_9 (II), was formed in low yield.

Reaction of Iron Vapor with Toluene and $B_{10}H_{14}$. A solution of 2 g of $B_{10}H_{14}$ in 250 mL of toluene was placed in the rotary metal atom reactor. After degassing, the solution was warmed to −78 °C and maintained at that temperature for the entire reaction. Iron vapor (~0.75 g) was condensed into the rotating solution over a 45-min period. Upon completion of metal deposition, the black slurry was warmed to room temperature and rotated for an additional 30 min. Excess toluene was removed in vacuo, and the reactor was flushed with $N_2(g)$. The remaining black residue was extracted with methylene chloride, filtered through a coarse frit, the filtrate mixed with silica gel and then filtered again, and the resulting filtrate concentrated to give a rose-colored solution. Excess $B_{10}H_{14}$ was removed by vacuum sublimation. The remaining residue formed a wine red solution in methylene chloride, which was separated by TLC on silica gel by using a 30% hexanes in benzene solution. The resulting separation gave two new (η^6-arene)ferraboranes: V, 5-[η^6-$C_6H_5CH_3$]FeB_9H_{13}[5] [R_f 0.4; pinkish purple; 2 mg; mp 131–140 °C dec; mass measurement calcd for $^{12}C_7{}^1H_{21}{}^{11}B_9{}^{56}Fe$ 260.1830, found 260.1835 (major fragment at *m/e* 148, ($C_6H_5CH_3$)Fe^+)]; VI, 1-[η^6-$C_6H_5CH_3$]$FeB_{10}H_{10}$[5] [R_f 0.1; yellow; 1 mg; air sensitive; parent *m/e* 268].

Crystallographic Data for 5-[η^6-$C_6(CH_3)_3H_3$]FeB_9H_{13} (I) and 2-[η^6-$C_6(CH_3)_3H_3$]Fe-6-OB_8H_{10} (IV). Single crystals of I and IV were grown in 1 day by vapor diffusion of pentane into a methylene chloride solution and by slow evaporation in air of a heptane/methylene chloride solution, respectively. In each case, a crystal of suitable size was mounted on a glass fiber and transferred to the diffractometer. The Enraf-Nonius program SEARCH was used to obtain 25 reflections for both I and IV, which 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 25 accurately centered reflections. On the basis of several θ 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 Kα 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.

Table IV. Data Collection and Structure Refinement Information

	5-[η^6-$C_6(CH_3)_3H_3$]-FeB_9H_{13} (I)	2-[η^6-$C_6(CH_3)_3H_3$]-Fe-6-OB_8H_{10} (IV)
space group	$P2_1/c$	$P2_1/c$
a, Å	9.348 (2)	12.647 (3)
b, Å	9.842 (1)	13.437 (2)
c, Å	17.335 (2)	9.281 (7)
β, deg	90.70 (2)	104.57 (3)
V, Å^3	1594.7	1526.5
Z	4	4
ρ(calcd), g cm^{-3}	1.193	1.252
cryst dimens, mm	0.30 × 0.20 × 0.10	0.50 × 0.05 × 0.05
mol formula	$B_9C_9H_{25}Fe$	$B_8C_9H_{22}OFe$
mol wt	286.45	288.61
λ(Mo Kα), Å	0.710 73	0.710 73
scanning range	$0° < 2\theta < 50°$	$0° < 2\theta < 50°$
scan mode	ω–2θ	ω–2θ
$\pm h, \pm k, \pm l$ collcd	±11,−11,+20	±15,−16,+11
no. of measd intens	2800	2391
no. of unique reflcns ($F_o^2 > 3\sigma(F_o^2)$)	1755	1449
no. of variables	247	211
abs coeff (μ), cm^{-1}	9.20	9.64
transmission coeff, %: max, min	91.17, 81.18	99.52, 93.81
R	0.049	0.059
R_w	0.049	0.065

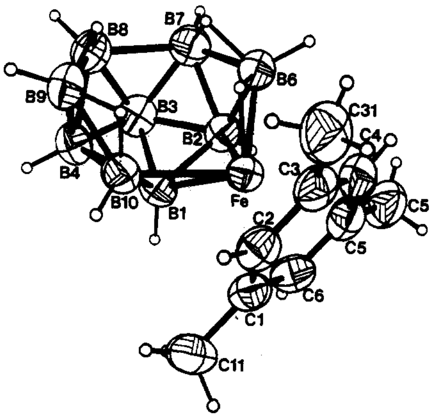

Figure 1. ORTEP drawing of 5-[η^6-$C_6(CH_3)_3H_3$]FeB_9H_{13} (I). Nonhydrogen atoms are shown as 50% thermal ellipsoids.

Solution and Refinement of the Structure. All calculations were performed on a PDP 11/60 computer using the Enraf-Nonius structure package.[8] 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 $(4F_o/\sigma(F_o)^2)^2$, 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,[9] and those for hydrogen, from Stewart.[10] The effects of anomalous dispersion were included in F_c by using Cromer and Ibers' values[11] 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. Anisotropic refinement followed by a difference Fourier synthesis resulted in the location of all 25 hydrogen atoms in I. The location of all hydrogen atoms bonded

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(7) 5-[η^6-$C_6(CH_3)_3H_3$]FeB_9H_{13} was orginally isolated as a minor product in the reaction of iron vapor with mesitylene, B_5H_9, and carbonyl sulfide in methylcyclohexane. Reported at the 186th National Meeting of the American Chemical Society, Washington, DC, Aug 1983.

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Table V. Positional Parameters and Their Estimated Standard Deviations for 5-[η^6-$C_6(CH_3)_3H_3$]FeB_9H_{13}

atom	x	y	z	atom	x	y	z
Fe	0.27877 (7)	0.46847 (7)	0.33924 (4)	HB4	0.325 (4)	0.537 (4)	0.092 (2)
C1	0.5013 (4)	0.4709 (5)	0.3705 (3)	HB6	−0.015 (4)	0.498 (4)	0.373 (2)
C11	0.6330 (5)	0.4872 (6)	0.3233 (3)	HB7	−0.095 (4)	0.618 (4)	0.229 (2)
C2	0.4439 (5)	0.3420 (5)	0.3831 (3)	HB8	0.016 (4)	0.484 (4)	0.089 (2)
C3	0.3218 (5)	0.3216 (5)	0.4274 (3)	HB9	0.215 (4)	0.257 (4)	0.111 (2)
C31	0.2609 (6)	0.1859 (6)	0.4375 (3)	HB10	0.433 (4)	0.353 (4)	0.214 (2)
C4	0.2583 (5)	0.4391 (5)	0.4583 (3)	H56	0.139 (4)	0.387 (4)	0.324 (2)
C5	0.3085 (5)	0.5689 (5)	0.4461 (3)	H67	−0.009 (4)	0.455 (4)	0.262 (2)
C51	0.2352 (6)	0.6923 (7)	0.4781 (3)	H89	0.073 (4)	0.360 (4)	0.165 (2)
C6	0.4315 (5)	0.5838 (5)	0.4010 (3)	H910	0.242 (4)	0.316 (4)	0.219 (2)
B1	0.3108 (6)	0.5765 (6)	0.2352 (3)	HC2	0.485 (4)	0.263 (4)	0.361 (2)
B2	0.1580 (6)	0.6290 (6)	0.2861 (3)	HC4	0.177 (4)	0.425 (4)	0.485 (2)
B3	0.1532 (6)	0.6250 (6)	0.1835 (3)	HC6	0.463 (4)	0.665 (4)	0.386 (2)
B4	0.2671 (6)	0.5044 (6)	0.1429 (3)	H11A	0.717 (4)	0.505 (4)	0.355 (2)
B6	0.0601 (6)	0.4971 (6)	0.3240 (3)	H11B	0.648 (4)	0.421 (4)	0.286 (2)
B7	0.0053 (6)	0.5664 (6)	0.2346 (4)	H11C	0.626 (4)	0.557 (4)	0.288 (2)
B8	0.0813 (6)	0.4814 (6)	0.1403 (3)	H31A	0.167 (4)	0.179 (4)	0.446 (2)
B9	0.2033 (6)	0.3441 (6)	0.1524 (3)	H31B	0.291 (4)	0.141 (4)	0.478 (2)
B10	0.3362 (6)	0.4031 (6)	0.2197 (3)	H31C	0.272 (4)	0.127 (4)	0.393 (2)
HB1	0.403 (4)	0.644 (4)	0.235 (2)	H51A	0.268 (4)	0.711 (4)	0.525 (2)
HB2	0.157 (4)	0.727 (4)	0.312 (2)	H51B	0.272 (4)	0.781 (4)	0.446 (2)
HB3	0.130 (4)	0.720 (4)	0.156 (2)	H51C	0.147 (4)	0.680 (4)	0.483 (2)

Table VI. Bond Distances (Å) for 5-[η^6-$C_6(CH_3)_3H_3$]FeB_9H_{13}

atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
Fe	C1	2.144 (3)	C31	H31B	0.87 (3)	B3	HB3	1.07 (3)
Fe	C2	2.117 (4)	C31	H31C	0.97 (3)	B4	B8	1.751 (6)
Fe	C3	2.138 (4)	C4	C5	1.378 (6)	B4	B9	1.695 (6)
Fe	C4	2.095 (4)	C4	HC4	0.90 (3)	B4	B10	1.779 (6)
Fe	C5	2.114 (4)	C5	C51	1.504 (6)	B4	HB4	1.09 (3)
Fe	C6	2.106 (4)	C5	C6	1.406 (5)	B6	B7	1.764 (7)
Fe	B1	2.118 (4)	C51	H51A	0.88 (3)	B6	HB6	1.11 (3)
Fe	B2	2.143 (4)	C51	H51B	1.10 (3)	B6	H56	1.31 (3)
Fe	B6	2.077 (5)	C51	H51C	0.83 (3)	B6	H67	1.31 (3)
Fe	B10	2.241 (5)	C6	HC6	0.89 (3)	B7	B8	1.977 (6)
Fe	H56	1.55 (3)	B1	B2	1.765 (6)	B7	HB7	1.07 (3)
C1	C11	1.495 (5)	B1	B3	1.780 (6)	B7	H67	1.20 (3)
C1	C2	1.395 (5)	B1	B4	1.794 (6)	B8	B9	1.778 (7)
C1	C6	1.396 (5)	B1	B10	1.744 (7)	B8	HB8	1.08 (3)
C11	H11A	0.97 (3)	B1	HB1	1.09 (3)	B8	H89	1.27 (3)
C11	H11B	0.93 (3)	B2	B3	1.778 (6)	B9	B10	1.791 (7)
C11	H11C	0.93 (3)	B2	B6	1.723 (7)	B9	HB9	1.13 (3)
C2	C3	1.398 (5)	B2	B7	1.784 (6)	B9	H89	1.25 (3)
C2	HC2	0.95 (3)	B2	HB2	1.06 (3)	B9	H910	1.23 (3)
C3	C31	1.463 (6)	B3	B4	1.749 (6)	B10	HB10	1.04 (3)
C3	C4	1.409 (5)	B3	B7	1.749 (7)	B10	H910	1.23 (3)
C31	H31A	0.89 (3)	B3	B8	1.732 (7)			

to the boron atoms and the three phenyl hydrogen atoms on the mesitylene ring in IV were found in a similar manner. The positions of the remaining nine methyl hydrogen atoms in IV were calculated and included (but not refined) in the structure factor calculations. Final refinement for both I and IV included an absorption correction along with anisotropic thermal parameters for non-hydrogen atoms and fixed isotropic thermal parameters (4.00) for the hydrogen atoms.

Final positional parameters for both I and IV are given in Tables V and VIII, respectively. Intramolecular bond distances and selected bond angles are presented in Tables VI and VII, respectively, for I and in Tables IX and X, respectively, for IV. Figures 1 and 2 show views of I and IV, respectively.

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

Results and Discussion

The reaction of thermally generated iron atoms with decaborane(14) and either toluene or mesitylene under rotary metal atom reaction conditions was found to yield the first reported examples of (η^6-arene)metallaborane clusters.

The compounds 5-[η^6-$C_6(CH_3)_3H_3$]FeB_9H_{13} (I) and 5-[η^6-$C_6H_5CH_3$]FeB_9H_{13} (V) were each isolated as reddish purple, air-stable, crystalline solids. The proposed composition of each compound is supported by exact mass measurements on the parent ions, and the parent envelopes of both compounds show evidence of extensive hydrogen fragmentation consistent with the presence of bridge hydrogens. I and V also exhibit major ions at m/e 176, [$C_6(CH_3)_3H_3$]Fe^+, and m/e 148, [$C_6H_5CH_3$]Fe^+, respectively, in agreement with their proposed (η^6-arene)Fe compositions. The ^{11}B NMR spectra of I and V each show eight doublets in a 1:1:1:2:1:1:1:1 ratio, while their ^1H NMR spectra show, in addition to the peaks attributable to the η^6-arenes, resonances indicative of boron–boron bridging [I, −2.98 (2), −3.67 (1) ppm; V, −2.93 (2), −3.59 (1) ppm] and

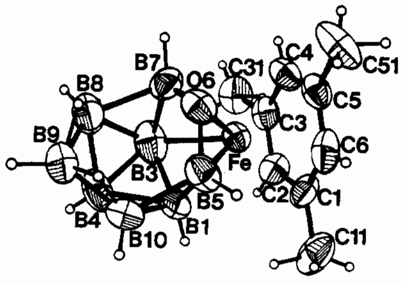

Figure 2. ORTEP drawing of 2-[η^6-$C_6(CH_3)_3H_3$]Fe-6-OB_8H_{10} (IV). Non-hydrogen atoms are shown as 50% thermal ellipsoids.

Table VII. Selected Bond Angles (deg) for $5\text{-}[\eta^6\text{-}C_6(CH_3)_3H_3]FeB_9H_{13}$

B1–Fe–B2	48.9 (2)	B1–B4–B10	58.4 (3)
B1–Fe–B10	47.1 (2)	B3–B4–B8	59.3 (3)
B2–Fe–B6	48.2 (2)	B3–B4–B9	112.1 (4)
B6–Fe–B10	99.7 (2)	B8–B4–B9	62.1 (3)
C11–C1–C2	120.3 (4)	B9–B4–B10	62.0 (3)
C11–C1–C6	120.9 (4)	Fe–B6–B2	67.9 (2)
C2–C1–C6	118.8 (3)	Fe–B6–B7	116.0 (3)
C1–C2–C3	122.3 (4)	B2–B6–B7	61.5 (3)
C2–C3–C31	121.2 (5)	B2–B7–B3	60.4 (3)
C2–C3–C4	116.2 (4)	B2–B7–B6	58.1 (3)
C31–C3–C4	122.5 (4)	B3–B7–B8	55.0 (3)
C3–C4–C5	123.8 (4)	B6–B7–B8	117.4 (3)
C4–C5–C51	122.3 (4)	B3–B8–B4	60.3 (3)
C4–C5–C6	117.7 (4)	B3–B8–B7	55.8 (3)
C51–C5–C6	120.0 (4)	B4–B8–B9	57.4 (3)
C1–C6–C5	121.1 (4)	B7–B8–B9	117.4 (3)
Fe–B1–B2	66.3 (2)	B4–B9–B8	60.5 (3)
Fe–B1–B10	70.2 (2)	B4–B9–B10	61.3 (3)
B2–B1–B3	60.2 (2)	B8–B9–B10	105.6 (3)
B2–B1–B10	118.4 (3)	Fe–B10–B1	62.8 (2)
B3–B1–B4	58.6 (3)	Fe–B10–B9	121.5 (3)
B4–B1–B10	60.4 (3)	B1–B10–B4	61.2 (3)
Fe–B2–B1	64.8 (2)	B4–B10–B9	56.7 (3)
Fe–B2–B6	63.9 (2)	B6–Fe–H56	39 (1)
B1–B2–B3	60.3 (3)	Fe–B6–H56	48 (1)
B1–B2–B6	114.0 (3)	Fe–H56–B6	93 (2)
B3–B2–B7	58.8 (3)	B7–B6–H67	43 (1)
B6–B2–B7	60.4 (3)	B6–B7–H67	48 (2)
B1–B3–B2	59.5 (2)	B6–H67–B7	89 (2)
B1–B3–B4	61.1 (3)	B9–B8–H89	45 (1)
B2–B3–B7	60.8 (3)	B8–B9–H89	46 (2)
B4–B3–B7	118.0 (4)	B8–H89–B9	90 (2)
B4–B3–B8	60.4 (3)	B10–B9–H910	43 (2)
B7–B3–B8	69.2 (3)	B9–B10–H910	43 (1)
B1–B4–B3	60.3 (3)	B9–H910–B10	93 (2)

boron–iron bridging [I, −23.39 (1) ppm; V, −22.81 (1) ppm] hydrogens. Both the ^{11}B and ^1H NMR spectra are similar to those that have been reported for $5\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$,[12] suggesting a close structural relationship. This conclusion was confirmed by a single-crystal X-ray study of I.

The molecular structure of I is given in Figure 1, and important bond distances and angles are given in Tables VI and VII. The ferraborane cage geometry is based on an octadecahedron missing one vertex and is consistent with the $2n + 4$ skeletal electron count (10 cage atoms, 24 skeletal electrons) of the cluster.[13] The structure can be envisioned as being derived from a decaborane(14)[14] structure in which an (η^6-mesitylene)Fe unit occupies the cage vertex 5-position. The cage structure is thus analogous to that of the isoelectronic complex $5\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$.[12]

The intracage boron–boron distances are normal and remarkably similar to those found in both $5\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$[12] and $B_{10}H_{14}$.[14] The iron atom is bound to borons B6, B2, B1, and B10, with an average iron–boron distance of 2.145 (5) Å, compared to an average cobalt–boron distance of 2.107 (6) Å in $5\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$. The four borons bound to the iron are approximately planar, and this plane is nearly parallel (dihedral angle 3.5°) to the plane of the mesitylene ring.

The bonding of the iron to the mesitylene appears normal with iron to ring-carbon distances (average 2.114 (4) Å) similar to those reported for (η^6-arene)ferracarboranes.[1,3,4] The distance from the iron to the plane of the mesitylene ring, 1.593 (1) Å, is significantly greater than the distance from iron to the plane of the four-boron unit, 1.378 (1) Å.

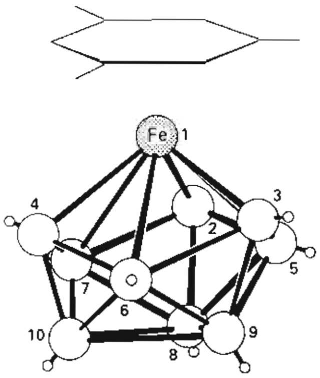

Figure 3. Proposed structure for $1\text{-}[\eta^6\text{-}C_6(CH_3)_3H_3]FeB_9H_9$ (II).

All hydrogens were located by difference Fourier methods, and the complex was shown to have, as in both $B_{10}H_{14}$ and $5\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$, four bridging hydrogens on the open face of the cage. Three of these hydrogens are boron–boron bridging, B6–B7, B8–B9, and B9–B10, while the fourth is boron–iron bridging, B6–Fe.

The complex $1\text{-}[\eta^6\text{-}C_6(CH_3)_3H_3]FeB_9H_9$ (II) was isolated as an air-stable red-brown solid as a product of the reaction employing mesitylene. The parent envelope in the mass spectrum of II shows a characteristic nine-boron distribution with little evidence of hydrogen fragmentation, and exact mass measurements on the parent ion support the proposed composition.

If it is assumed (as was the case for I and V above) that an (η^6-arene)Fe unit donates two electrons and three orbitals to the cage for bonding, then II would be a $2n$ skeletal electron system (10 cage atoms, 20 skeletal electrons).[13] According to simple skeletal electron counting theory, such a system would leave one of the cage-bonding molecular orbitals empty and would therefore be expected to adopt a structure that is distorted from a regular polyhedral geometry. Typical types of distortions that have been observed for other $2n$ skeletal electron clusters involve the formation of capped polyhedra.[15] If II were to adopt such a capped structure, this would require that the compound have relatively low symmetry; however, the spectroscopic data indicate that the complex has a 3-fold axis strongly supporting the closo C_{3v} structure shown in Figure 3. Thus, the ^{11}B NMR spectrum shows three doublets of equal intensity with two of the doublets shifted to low field. (It should also be noted that the spectrum does not change down to −70 °C, suggesting that II is not fluxional.) The doublet at very low field, −106.5 ppm, is highly indicative of low-coordinate boron atoms directly bonded to a metal and may be, therefore, assigned to the four-coordinate B2, B3, and B4 borons. The doublet at 27.7 ppm may then be assigned to borons B5, B6, and B7, which are also bonded to the metal but which are in five-coordinate positions. The boron-decoupled ^1H NMR spectrum likewise shows, in addition to the η^6-mesitylene resonances, three equal B–H resonances with one of these shifted to low field, 10.05 ppm. Thus, the NMR data support a symmetric closo C_{3v} structure rather than a distorted geometry based on a capped polyhedron. It should be noted, however, that the structure shown in Figure 3 is not the normal structure adopted by $2n + 2$, 10-vertex closo systems. For example, compounds such as $B_{10}H_{10}^{2-}$,[16] 1,6-

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Table VIII. Positional Parameters and Their Estimated Standard Deviations for 2-[η^6-$C_6(CH_3)_3H_3$]Fe-6-OB_8H_{10}

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Fe	0.24032 (8)	0.45110 (8)	0.3366 (1)	B8	0.2008 (9)	0.4882 (8)	0.684 (1)
C1	0.3346 (5)	0.4746 (6)	0.1801 (8)	B9	0.1679 (8)	0.6136 (8)	0.683 (1)
C2	0.3866 (5)	0.4073 (6)	0.2882 (8)	B10	0.2135 (7)	0.6600 (7)	0.534 (1)
C3	0.3338 (5)	0.3229 (6)	0.3204 (8)	H89	0.108 (4)	0.530 (4)	0.654 (6)
C4	0.2239 (6)	0.3075 (6)	0.2444 (9)	H910	0.134 (4)	0.650 (4)	0.560 (6)
C5	0.1699 (5)	0.3735 (6)	0.1383 (8)	HB1	0.364 (4)	0.611 (4)	0.457 (6)
C6	0.2255 (6)	0.4559 (7)	0.1066 (9)	HB3	0.346 (4)	0.421 (4)	0.582 (6)
C11	0.3920 (6)	0.5653 (7)	0.143 (1)	HB4	0.354 (4)	0.597 (4)	0.753 (6)
C31	0.3919 (7)	0.2507 (6)	0.439 (1)	HB5	0.129 (4)	0.634 (4)	0.256 (6)
C51	0.0517 (6)	0.3591 (7)	0.062 (1)	HB7	0.108 (4)	0.369 (4)	0.499 (6)
B1	0.2973 (7)	0.5738 (7)	0.471 (1)	HB8	0.196 (4)	0.454 (4)	0.762 (6)
B3	0.2867 (7)	0.4644 (9)	0.566 (1)	HB9	0.143 (4)	0.648 (4)	0.775 (6)
B4	0.2915 (7)	0.5806 (8)	0.663 (1)	HB10	0.235 (4)	0.726 (4)	0.525 (6)
B5	0.1646 (8)	0.5836 (7)	0.357 (1)	HC2	0.452 (4)	0.424 (4)	0.347 (6)
O6	0.1043 (3)	0.4971 (4)	0.3741 (5)	HC4	0.191 (4)	0.257 (4)	0.268 (6)
B7	0.1521 (7)	0.4301 (7)	0.492 (1)	HC6	0.196 (4)	0.496 (4)	0.072 (6)

Table IX. Bond Distances (Å) for 2-[η^6-$C_6(CH_3)_3H_3$]Fe-6-OB_8H_{10}

Fe–C1	2.123 (5)	B3–B8	1.75 (1)
Fe–C2	2.097 (5)	B4–B8	1.74 (1)
Fe–C3	2.117 (5)	B4–B9	1.68 (1)
Fe–C4	2.102 (6)	B4–B10	1.72 (1)
Fe–C5	2.110 (5)	B5–O6	1.423 (7)
Fe–C6	2.098 (7)	B5–B10	1.91 (1)
Fe–B1	2.086 (6)	O6–B7	1.428 (8)
Fe–B3	2.072 (8)	B7–B8	1.90 (1)
Fe–B5	2.054 (6)	B8–B9	1.74 (1)
Fe–O6	1.942 (3)	B9–B10	1.74 (1)
Fe–B7	2.053 (7)	B1–HB1	1.02 (4)
C1–C2	1.389 (7)	B3–HB3	0.93 (4)
C1–C6	1.402 (8)	B4–HB4	1.02 (4)
C1–C11	1.503 (7)	B5–HB5	1.15 (4)
C2–C3	1.387 (7)	B7–HB7	1.01 (4)
C3–C4	1.409 (7)	B8–HB8	0.88 (4)
C3–C31	1.512 (7)	B8–H89	1.27 (4)
C4–C5	1.374 (7)	B9–HB9	1.08 (4)
C5–C6	1.384 (9)	B9–H89	1.34 (4)
C5–C51	1.499 (7)	B9–H910	1.21 (5)
B1–B3	1.74 (1)	B10–HB10	0.94 (4)
B1–B4	1.80 (1)	B10–H910	1.10 (4)
B1–B5	1.753 (9)	C2–HC2	0.90 (4)
B1–B10	1.77 (1)	C4–HC4	0.86 (4)
B3–B4	1.79 (1)	C6–HC6	0.68 (5)
B3–B7	1.73 (1)		

Table X. Selected Bond Angles (deg) for 2-[η^6-$C_6(CH_3)_3H_3$]Fe-6-OB_8H_{10}

B1–Fe–B3	49.4 (3)	B1–B4–B10	60.3 (4)
B1–Fe–B5	50.1 (3)	B3–B4–B8	59.5 (4)
B3–Fe–O6	79.8 (2)	B8–B4–B9	61.0 (4)
B3–Fe–B7	49.7 (3)	B9–B4–B10	61.6 (5)
B5–Fe–O6	41.6 (2)	Fe–B5–B1	65.9 (3)
O6–Fe–B7	41.8 (2)	Fe–B5–O6	65.0 (3)
C2–C1–C6	117.8 (6)	B1–B5–B10	57.5 (4)
C2–C1–C11	121.7 (5)	O6–B5–B10	114.1 (5)
C6–C1–C11	120.6 (6)	Fe–O6–B5	73.4 (3)
C1–C2–C3	121.5 (5)	Fe–O6–B7	73.3 (3)
C2–C3–C4	118.8 (5)	B5–O6–B7	117.8 (4)
C2–C3–C31	120.6 (5)	Fe–B7–B3	65.7 (3)
C4–C3–C31	120.6 (6)	Fe–B7–O6	65.0 (3)
C3–C4–C5	121.0 (6)	B3–B7–B8	57.4 (4)
C4–C5–C6	118.8 (5)	O6–B7–B8	115.7 (5)
C4–C5–C51	120.9 (6)	B3–B8–B4	61.9 (5)
C6–C5–C51	120.3 (6)	B3–B8–B7	56.5 (4)
C1–C6–C5	122.1 (6)	B4–B8–B9	58.0 (4)
Fe–B1–B3	64.9 (3)	B7–B8–B9	112.0 (6)
Fe–B1–B5	64.0 (3)	B4–B9–B8	61.0 (5)
B3–B1–B4	60.9 (4)	B4–B9–B10	60.1 (4)
B4–B1–B5	108.9 (5)	B8–B9–B10	102.9 (6)
B4–B1–B10	57.5 (4)	B1–B10–B4	62.2 (4)
B5–B1–B10	65.7 (4)	B1–B10–B5	56.8 (4)
Fe–B3–B1	65.7 (3)	B4–B10–B9	58.3 (4)
Fe–B3–B7	64.6 (3)	B5–B10–B9	113.0 (5)
Fe–B3–B8	126.6 (5)	B9–B8–H89	50 (2)
B1–B3–B4	61.3 (5)	B8–B9–H89	46 (2)
B4–B3–B8	58.6 (4)	B8–H89–B9	83 (3)
B7–B3–B8	66.1 (4)	B10–B9–H910	39 (2)
B1–B4–B3	57.8 (4)	B9–B10–H910	44 (3)
B1–B4–B9	113.2 (5)	B9–H910–B10	97 (3)

$(CH_3)_2C_2B_8H_8$,[17] 2,6,1,10-(η-C_5H_5)$_2$$Co_2C_2B_6H_8$,[18] 2,3,10-($\eta$-$C_5H_5$)$_2$NiCoC$B_7H_8$,[19] 2,1,4-$(CO)_3Fe(CH_3)_2C_2B_7H_7$[20] and 1-($\eta$-$C_5H_5$)Ni$B_9H_9^-$,[21] which have closo skeletal electron counts, have been shown to have structures based on a bicapped square antiprism (D_{4d}) rather than the C_{3v} polyhedron shown in Figure 3. At least three other 10-vertex, 2*n* electron clusters have been previously characterized, 1,6,2,3-(η-C_5H_5)$_2$$Fe_2C_2B_6H_8$,[22a] 2,3-$(CH_3)_2$-6-($CH_2$=CH-$CH_2C_6H_4Ph_2P$)-6,2,3-Ru$C_2B_7H_7$,[22b] and [1,1,1-H($PPh_3$)($Ph_2P$-*o*-$C_6H_4$)-iso-*closo*-(1-Ir$B_9H_8$-2-)],[23] and each of these compounds have structures based on a C_{3v} rather than a D_{4d} polyhedron. Thus, it may be that 2*n*, 10-vertex systems do not show capped polyhedral distortions as a result of their electron count but rather form the "hyper-closo"[22b] or "iso-closo"[23] C_{3v} structure instead. Clearly any general statements regarding these geometries will have to await the synthesis and characterization of a wider range of such complexes.

Greenwood has previously shown that the compound [1,1,1-H(PPh_3)(Ph_2P-*o*-C_6H_4)-iso-*closo*-(1-IrB_9H_8-2-)] (isoelectronic with II) can be obtained in good yield by the thermolysis of the corresponding nido compound [H-$(PPh_3)_2$(IrB_9H_{13})].[23] These results suggest that compound I (5-[η^6-$C_6(CH_3)_3H_3$]FeB_9H_{13}) might be the precursor to II (1-[η^6-$C_6(CH_3)_3H_3$]FeB_9H_9), and indeed, it was found that thermolysis of I gave II in low yield. Thus dehydrogenation of I (perhaps metal promoted) during the metal atom reaction is the likely source of II.

Compounds III (1-[η^6-$C_6(CH_3)_3H_3$]Fe$B_{10}H_{10}$) and VI (1-[η^6-$C_6H_5CH_3$]Fe$B_{10}H_{10}$) were isolated as air-sensitive, yellow solids. The mass spectral data for both compounds

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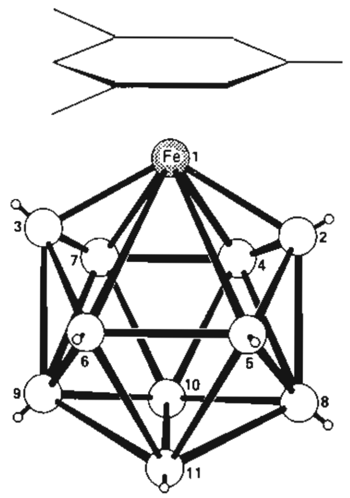

Figure 4. Proposed structure for 1-[η^6-$C_6(CH_3)_3H_3$]$FeB_{10}H_{10}$ (III).

show a parent envelope with a characteristic 10-boron pattern, and exact mass measurements on their parent ions support the proposed compositions. These compounds are, like II discussed above, 2*n* skeletal electron systems (11 cage atoms, 22 skeletal electrons) and are, to our knowledge, the first such 11-vertex systems to be reported.[42] Although electron counting rules would again predict a distorted structure, the NMR data strongly support a symmetrical closo geometry, such as the structure shown in Figure 4, rather than a capped polyhedral configuration. On the basis of the octadecahedral structure shown in Figure 4, the ^{11}B NMR spectra of these compounds would be expected to show four doublets in a 2:4:2:2 ratio, with one of the intensity 2 doublets, arising from the four-coordinate borons, B2 and B3, which are attached to the metal, shifted considerably downfield. The ^{11}B NMR spectra at 32.1 MHz of these compounds do indeed each show a doublet of intensity 2 shifted to extremely low field (130.2 ppm, III; 129.6 ppm, VI), consistent with this structure; however, only one additional doublet of intensity 8 is observed upfield for each compound. The ^{11}B NMR spectrum of III at 115.5 MHz resolves this doublet into two doublets of intensity 6:2. The intensity 6 doublet must then arise from a coincidental overlap of the B4, B5, B6, B7 and either the B8, B9 or B10, B11 resonances. The boron-spin-decoupled ^1H NMR spectrum of III shows, in addition to the η^6-mesitylene resonances, B–H resonances in the expected 2:4:2:2 ratio, with one of the peaks (B2,3–H) shifted to low field.

On the basis of the spectral data, compounds III and VI appear to have closo rather than capped geometries. The proposed octadecahedral structure is, in fact, the normal closo structure that has been observed for 11-vertex, 2*n* + 2 skeletal electron systems, such as $B_{11}H_{11}^{2-}$,[24] $B_9C_2H_{11}$,[25] 6,9-$(CH_3)_2C_2B_9H_9$,[26] 1,2-(η-C_5H_5)$FeCB_9H_{10}^-$,[27] 1,8,2,3-(η-C_5H_5)$_2$$FeCoC_2B_7H_9$,[28] 1,2,3-($\eta$-$C_5H_5$)$CoC_2B_8H_{10}$,[29] 1,1-$(PPh_3)_2$-1-H-1,2,4-$IrC_2B_8H_{10}$.[30] That 2*n* skeletal electron systems such as III and VI should adopt regular closo geometries is perhaps surprising in light of our discussion above concerning the adoption of an iso-closo structure for II. However, Wade[31] has recently pointed out that while the symmetries of most closo borane polyhedra are such as to cause the HOMO's and LUMO's of the anions $B_nH_n^{2-}$ to be degenerate, the HOMO and LUMO in the octadecahedral anion $B_{11}H_{11}^{2-}$ are expected to be nondegenerate. As a result, adding two electrons or removing two electrons (as in III or VI) from this system will not result in generating a paramagnetic species prone to Jahn–Teller distortions.[32] Thus, an octadecahedron may be able to accomodate 22, 24, or 26 skeletal electrons without distortion. Clearly, on the basis of our observations concerning the structures of compounds II, III, and VI, it is apparent that more theoretical and experimental work will be required before an understanding of the structures of 2*n* skeletal electron systems will be achieved.

In addition to the three [η^6-$C_6(CH_3)_3H_3$] ferraborane complexes produced in the mesitylene reaction, a fourth compound, IV, was isolated in trace amounts. Reliable ^{11}B or ^1H NMR data could not be obtained, but exact mass measurements indicated the formula [η^6-$C_6(CH_3)_3H_3$]-$FeOB_8H_{10}$. The mass spectrum of IV also showed a parent envelope with a characteristic eight-boron pattern and fragmentation corresponding to the loss of an OBH_3 group (P – 30 *m*/*e*).

There are of course numerous examples of the insertion of group 6 elements such as sulfur and selenium into polyhedral boron cage systems yielding heteroborane or metallaheteroborane clusters; however, there have been no previous reports of the insertion of an oxygen atom into a polyhedral boron cage system. In fact, given the well-known instability of the B–H bonds in boron hydrides to oxidation and the large electronegativity difference between boron and oxygen ($\Delta\chi = 1.4$), it might be expected that such compounds could not be made. We have previously demonstrated how metal atom reactions can be used to prepare metallathiaborane clusters such as 6,8,7,9-(η-C_5H_5)$_2$$Co_2S_2B_5H_5$,[33] 2,3,6-($\eta$-$C_5H_5$)$_2$$Co_2B_5H_7$,[33] 7,6,8-($\eta$-$C_5H_5$)$CoS_2B_6H_8$,[33] and 4,6,3,5-($\eta$-$C_5H_5$)$_2$$Co_2S_2B_2H_2$,[34] by direct sulfur insertion during the metal atom/borane reaction. These results suggested that IV might be formed in a similar manner, by perhaps oxidation of a reactive metallaborane fragment upon opening the metal atom reactor to air, and might indeed be the first example of a metallaoxaborane cluster. The identity of this compound was confirmed by a single-crystal X-ray study, the results of which are depicted in the ORTEP drawing in Figure 2.

If the oxygen atom is a four-electron donor (like sulfur) to the cage, then IV would be a 10-vertex, 2*n* + 4 skeletal electron system and would be isoelectronic with decaborane(14) and compounds I and V. As can be seen in Figure 2, IV does indeed have a decaborane(14) structure with the oxygen stom in the 6-position on the open face. The iron is bound to the planar pentagonal face composed of borons B1, B3, B5, and B7 and the oxygen atom and is situated in the 2-position in the cage. The iron–oxygen distance, 1.942 (3) Å, is, as expected on the basis of the relative covalent radii of boron (0.90 Å) and oxygen (0.73 Å),[35] smaller than the average iron–ring boron distance, 2.066 (8) Å, and is in the normal range observed for other compounds containing iron–oxygen bonds.[36]

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The iron to oxaborane ring distance is 1.499 (1) Å, which is again smaller than the comparable iron to carborane ring distance, 1.525 (3) Å, observed in the analogous complex $2\text{-}[\eta^6\text{-}CH_3C_6H_5]Fe\text{-}6,7,9,10\text{-}(CH_3)_4C_4B_5H_5$.[1] The bonding of the iron to the η^6-mesitylene ring appears normal, with the distance from the iron to the plane of the mesitylene ring, 1.584 (1) Å, being similar to that observed for $5\text{-}[\eta^6\text{-}C_6(CH_3)_3H_3]FeB_9H_{13}$ and to that reported for (η^6-arene)-ferracarboranes.[1,3,4] The plane of the η^6-mesitylene is nearly parallel (dihedral angle 1.6°) to the plane of the oxaborane ring.

The boron–oxygen bond distances B5–O6 and B7–O6 are equal, 1.423 (7) and 1.428 (8) Å, respectively, and are typical of boron–oxygen bond lengths observed in compounds such as $3\text{-}(\eta\text{-}C_5H_5)Co\text{-}8\text{-}OCOCH_3\text{-}1,2\text{-}C_2B_9H_{10}$ (1.453 (7) Å,[37] $8\text{-}C_2H_5O\text{-}9,9\text{-}(PPh_3)_2\text{-}6,9\text{-}SPtB_8H_9$ (1.476 (24) Å),[38] and $12\text{-}C_2H_5O\text{-}1,2,3,7,8\text{-}(\eta\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6$ (1.383(6) Å),[39] which contain an exopolyhedral boron–oxygen single bond. The observed boron–oxygen distances in IV are perhaps surprising since it might be expected that if the oxygen atom was involved in multicenter bonding in the polyhedral cage, then the B–O distances would be lengthened relative to a single boron–oxygen bond. However, recent molecular orbital calculations[40] for azaboranes, such as $4\text{-}NB_8H_{13}$, $B_9H_{12}NH^-$, and $10,7,8\text{-}NC_2B_8H_{11}$, which have nitrogens in cage framework positions, have indicated that nitrogen cage atoms tend to form polarized boron–nitrogen bonds that have a localized two-center character. Therefore, in IV it is possible that the bonding of the oxygen atom to B5 and B7 is largely two-center in character, resulting in the observed distances. It might also be expected that this effect would alter the cage-bonding patterns in other parts of the molecule, and in fact, several of the boron–boron bond distances in the cage appear to be significantly shortened. In particular, the B7–B8, 1.90 (1) Å, and B5–B10, 1.91 (1) Å, distances are considerably smaller than similar distances in $B_{10}H_{14}$,[14a] 1.973 (4) and 1.973 (4) Å, or $2\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$,[41] 1.980 (6) and 1.963 (7) Å, and may be caused by the polarization of B7 and B5 by the oxygen atom. Likewise, the other distances between the boron atoms on the open face, B8–B9 and B9–B10, are also shortened, although to a lesser degree (~0.04 Å). Molecular orbital calculations will of course be required before these differences and the bonding requirements of a highly electronegative cage atom can be fully understood. The synthesis of IV suggests, however, that a wide range of metallaoxaborane clusters may be possible with bonding properties intermediate between those of localized and delocalized cage systems.

Conclusions. The results described herein describe the synthesis of the first three (η^6-arene)metallaborane complexes, as well as the first example of a metalloxaborane cluster, and further illustrate the potential of metal atom reaction techniques for the synthesis of new types of compounds unattainable by using more conventional synthetic techniques. Furthermore, on the basis of these studies it is expected that in the future a wide range of both (η^6-arene)metallaboranes and -metallaoxaborane clusters can be synthesized and that detailed structural characterization of these unique cluster systems will provide valuable insight into the relationships among cage geometries, bonding interactions, and skeletal electron configurations.

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Registry No. I, 92524-61-3; II, 92524-62-4; III, 92543-04-9; IV, 92524-63-5; V, 92575-03-6; VI, 92543-05-0; $B_{10}H_{14}$, 17702-41-9; Fe, 7439-89-6.

Supplementary Material Available: Tables of general temperature factors, molecular planes, calculated hydrogen positions, and observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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