clusters of osmium.[19] Perhaps, the (dimethylamino)carbyne ligand plays a similar role in the assembly of these higher clusters of ruthenium. This is strongly suggested by the observation that the ligand can adopt the quadruply bridging bonding mode.

The formation of 4 may occur by a process that is independent of the formation of 2 and 3. The metal nuclearity suggests that it is formed by a combination of two formula equivalents of 1 that is accompanied by the appropriate loss of CO groups and the hydride ligands. The source of the carbido carbon atom in 4 has not been determined; however, it was shown that the carbido ligand in $Ru_6(C)(CO)_{17}$, obtained from the pyrolysis of $Ru_3(CO)_{12}$, was derived from a CO ligand.[20] It seems reasonable to assume that the carbido ligand in 4 was also derived from CO.

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Registry No. **1**, 59532-85-3; **2**, 112139-08-9; **3**, 112139-10-3; **4**, 112139-09-0; $Ru(CO)_5$, 16406-48-7.

Supplementary Material Available: Tables of positional parameters of the hydrogen atoms for 3 and 4 and anisotropic thermal parameters (*U* values) for all three structural analyses (7 pages); listings of structure factor amplitudes for all three structural analyses (63 pages). Ordering information is given on any current masthead page.

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Metal Atom Synthesis of Metallaboron Clusters. 10.[1] Synthesis and Structural Characterization of (η^6-Arene)thiaferraborane Clusters

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The reactions of thermally generated iron atoms with toluene and *nido*-7-$SB_{10}H_{12}$ or *nido*-6-SB_9H_{11} were found to give the first examples of (η^6-arene)thiametallaborane complexes, *closo*-2-[η^6-$C_6H_5CH_3$]-2,1-$FeSB_{10}H_{10}$ (I) and *nido*-8-[η^6-$C_6H_5CH_3$]-8,7-$FeSB_9H_{11}$ (II), in high yield. The sandwich structures of I and II were confirmed by single-crystal X-ray crystallographic studies. Crystal data for I: space group *Pbca*; $Z = 8$; $a = 16.338$ (2) Å, $b = 14.429$ (4) Å, $c = 11.760$ (2) Å; $V = 2772.4$ Å^3. The structure was refined to a final R of 0.040 and R_w of 0.048 for the 1417 reflections that had $F_o^2 > 3\sigma(F_o^2)$. Crystal data for II: space group $P2_1/n$; $Z = 4$; $a = 8.736$ (2) Å, $b = 13.919$ (1) Å, 11.807 (2) Å; $\beta = 105.76$ (2)°; $V = 1381.9$ Å^3. The structure was refined to a final R of 0.063 and R_w of 0.089 for the 2587 reflections that had $F_o^2 > 3\sigma(F_o^2)$.

Introduction

As part of our interest in the synthesis and structural characterization of new types of hybrid main group–transition metal clusters, we have explored new routes to metallathiaborane clusters. We have previously demonstrated that metal atom techniques can be used to generate a number of new metallathiaborane cage systems including $(\eta\text{-}C_5H_5)_2Co_2S_2B_5H_5$,[2] $(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$,[2] $(\eta\text{-}C_5H_5)CoS_2B_6H_8$,[2] and $(\eta\text{-}C_5H_5)_2Co_2S_2B_2H_2$.[3] These complexes were obtained from reactions involving the reactive small cage borane, pentaborane(9); however, we have recently begun to investigate the synthesis of new types of larger cage metallathiaborane clusters.

The *nido*-thiaborane clusters 7-$SB_{10}H_{12}$ and 6-SB_9H_{11} were originally reported by Muetterties[4] in 1967. Although both compounds can be obtained in reasonable yields, the chemistry of these two clusters has not been as extensively developed as their carborane analogues. For example, studies of the transition-metal chemistry of these cage systems have led to the isolation of only a limited number of different types of compounds, including bis(thiaborane) sandwich complexes[4,5] as well as complexes having either cyclopentadienyl[1,6] or phosphine[7–12] metal ligands.

One area of recent interest in polyhedral boron cluster chemistry has been the synthesis and properties of (η^6-

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arene)metallacarborane[13] and -borane[14] complexes. We report here that metal vapor reactions can be used to produce (η^6-arene)thiaborane clusters in good yields and as examples present the syntheses and structural characterizations of the first two such clusters, *closo*-2-[η^6-$C_6H_5CH_3$]-2,1-$FeSB_{10}H_{10}$ and *nido*-8-[η^6-$C_6H_5CH_3$]-8,7-$FeSB_9H_{11}$.

Experimental Section

Materials and Procedures. Iron metal (powder) was obtained from Alfa Products/Ventron Division. Toluene (Amend Drug and Chemical Co.) was degassed under vacuum and dried over $CaCl_2$ (Mallinckrodt) with stirring. 6-SB_9H_{11}[4,15] and 7-$SB_{10}H_{12}$[16] were synthesized by published procedures. All other reagents were commercially obtained, as indicated, and used as received. Flash column chromatography was performed with silica gel (230–400 mesh, EM Science).

Boron-11 NMR spectra at 160.5 MHz were obtained on a Bruker AM-500 spectrometer equipped with the appropriate decoupling accessories. Proton NMR spectra, at 250 MHz, were obtained on a Bruker WH-250 Fourier transform spectrometer. All boron-11 chemical shifts are 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). Two-dimensional ^{11}B–^{11}B NMR experiments were conducted as follows: 160.5-MHz ^{11}B shift correlated COSY experiments were performed with S-type selection parameters. The sweep width in the F_2 direction was 25 000 and in the F_1 direction was 12 500. A total of 256 increments (increment size of 0.04 ms) was collected, each slice having 512W F_2 data points for I and 1K data points for II. The data were zero filled twice for I and once for II in the F_1 directions. These data were 2-D Fourier transformed with sine-bell apodization in both domains. A total of 600 scans for I and 500 scans for II were taken for each increment with a recycling time of 100 ms.

High- and low-resolution mass spectra were obtained on Hitachi Perkin-Elmer RMH-2 and/or VG micromass 7070H mass spectrometers. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer. All melting points are uncorrected. Elemental analysis was obtained from Schwarkopf Laboratories, Woodside, NY.

The metal atom apparatus employed in these studies was based on a design by Klabunde[17] and is described elsewhere.[18]

Table I. Data Collection and Structure Refinement Information

	I	II
space group	*Pbca*	$P2_1/n$
a, Å	16.338 (2)	8.736 (2)
b, Å	14.429 (4)	13.919 (1)
c, Å	11.760 (2)	11.807 (2)
β, deg		105.76 (2)
V, Å^3	2772.4	1381.9
Z	8	4
ρ(calcd), g cm^{-3}	1.429	1.386
cryst dimens, mm	0.07 × 0.15 × 0.25	0.176 × 0.45 × 0.325
mol formula	$C_7H_{18}SB_{10}Fe$	$C_7H_{19}SB_9Fe$
mol wt	298.24	288.44
λ	Mo Kα, 0.717 03 Å	Mo Kα, 0.717 03 Å
scanning range, deg	$4° \le 2\theta \le 55°$	$4° \le 2\theta \le 55°$
scan mode	ω–2θ	ω–2θ
$\pm h,\pm k,\pm l$, collected	21,18,15	11,18,±15
no. of measd intensities	7158	3518
no. of $F_o^2 > 3\sigma(F_o^2)$	1417	2587
no. of variables	244	163
abs coeff (μ), cm^{-1}	12.01	12.03
trans coeff, %	90.0	77.0
max, min, %	92.0, 83.2	80.6, 69.7
R	0.040	0.063
R_w	0.048	0.089

Reaction of Iron Vapor with Toluene and 7-$SB_{10}H_{12}$. Approximately 1.5 g of iron powder was added to the integral tungsten alumina evaporation crucible (Sylvania Emissive Products, CS-1008) in the reactor. Sublimed 7-$SB_{10}H_{12}$ (1.0 g, 6.5 mmol) was placed in the bottom of the reactor that was then evacuated. The iron vapor (~0.75 g), generated by electrical heating (~8.0 V, 50 A), was cocondensed with 25 mL of toluene over a 2-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 with the 7-$SB_{10}H_{12}$ for 40 min. The dark slurry was then warmed to room temperature and stirred for an additional 90 min. Excess ligands were removed in vacuo, and the reactor was flushed with N_2(g). The dark residue was extracted with methylene chloride and filtered through a coarse frit. The orange filtrate was then evaporated to dryness in vacuo. The solid was sublimed at 60 °C and unreacted 7-$SB_{10}H_{12}$ (~0.56 g) recovered. The unsublimed material was then separated by flash column chromatography with a hexane/benzene mixture (50:50) under nitrogen pressure. An orange-colored band was collected and recrystallized from methylene chloride and cold pentane to give *closo*-2-[η^6-$C_6H_5CH_3$]-2,1-$FeSB_{10}H_{10}$ (I): R_f 0.65 in benzene; 0.51 g (1.7 mmol, 59%); mp 215–216 °C dec; mass measurement calcd for $^{12}C_7{}^{32}S_1{}^1H_{18}{}^{11}B_{10}{}^{56}Fe$ 300.141, found 300.146; ^{11}B NMR (ppm, CD_2Cl_2, 160.5 MHz), 11.0 (d, B12, J_{BH} = 145 Hz), 9.5 (d, B7,11, J_{BH} = 142 Hz), 6.4 (d, B9, J_{BH} = 142 Hz), −1.7 (d, B3,6, J_{BH} = 160 Hz), −8.1 (d, B8,10, J_{BH} = 144 Hz), −18.1 (d, B4,5, J_{BH} = 164 Hz); ^1H NMR (δ, CD_2Cl_2, 250 MHz), 6.19 (m, 3, C_6H_5), 5.94 (m, 2, C_6H_5), 2.44 (s, 3); IR (KBr pellet, cm^{-1}) 3080 (w), 2960 (w), 2920 (w), 2580 (s), 2540 (s), 2480 (s), 1465 (m), 1440 (m), 1380 (m), 1260 (m), 1190 (m), 1160 (m), 1075 (w), 1035 (w), 1010 (s), 930 (m), 905 (m), 890 (m), 880 (m), 840 (m), 810 (br, w), 785 (w), 755 (m), 720 (m), 685 (w), 645 (w), 620 (m), 565 (w), 535 (m), 490 (m), 430 (m), 410 (s), 370 (m), 330 (w).

Reaction of Iron Vapor with Toluene and 6-SB_9H_{11}. A reaction analogous to that described above was carried out by using 1.2 g (8.45 mmol) of SB_9H_{11}. Sublimation of the reaction mixture at 40 °C yielded ~0.8 g (~5.6 mmol) of unreacted 6-SB_9H_{11}. The material remaining in the sublimator was recrystallized from a methylene chloride/pentane solvent mixture to give a red product that was identified as *nido*-8-[η-$C_6H_5CH_3$]-8,7-$FeSB_9H_{11}$ (II); R_f 0.49 in benzene; 0.53 g (1.83 mmol, 65%); mp 128–129 °C dec; mass measurement calcd for $^{12}C_7{}^{32}S_1{}^1H_{19}{}^{11}B_9{}^{56}Fe$ 290.139, found 290.135; ^{11}B NMR (ppm, CD_2Cl_2, 160.5 MHz) 12.5 (d, B5, J_{BH} = 140 Hz), 0.6 (d, B3, J_{BH} = 155 Hz), −4.1 (d, B9, J_{BH} = 149 Hz),

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Table II. Atomic Positional Parameters and Their Estimated Standard Deviations for *closo*-2-[η^6-$C_6H_5CH_3$]-2,1-$FeSB_{10}H_{10}$ (I)[a]

atom	x	y	z	B, Å^2
Fe	0.69544 (4)	0.40345 (4)	0.56693 (5)	2.75 (1)
SB1	0.7771 (1)	0.3565 (1)	0.4290 (1)	3.71 (3)
B3	0.7672 (3)	0.2776 (3)	0.5696 (5)	3.1 (1)
B4	0.8693 (4)	0.2871 (4)	0.4944 (5)	3.9 (1)
B5	0.8881 (4)	0.4067 (4)	0.4541 (5)	4.0 (1)
BS6	0.7958 (3)	0.4836 (2)	0.4965 (3)	4.48 (9)
B7	0.7764 (3)	0.3500 (4)	0.6944 (5)	3.4 (1)
B8	0.8627 (4)	0.2841 (4)	0.6436 (5)	4.0 (1)
B9	0.9326 (4)	0.3590 (4)	0.5760 (5)	4.1 (1)
B10	0.8910 (4)	0.4731 (4)	0.5798 (6)	4.3 (1)
B11	0.7937 (3)	0.4700 (4)	0.6549 (5)	3.4 (1)
B12	0.8784 (4)	0.3967 (4)	0.6970 (5)	4.0 (1)
C13	0.5876 (3)	0.3372 (3)	0.6298 (4)	4.1 (1)
C14	0.5855 (3)	0.3409 (4)	0.5101 (4)	4.4 (1)
C15	0.5969 (3)	0.4244 (4)	0.4520 (4)	4.6 (1)
C16	0.6118 (3)	0.5059 (4)	0.5121 (5)	5.1 (1)
C17	0.6143 (3)	0.5039 (4)	0.6308 (5)	4.7 (1)
C18	0.6027 (3)	0.4200 (3)	0.6893 (4)	4.2 (1)
C19	0.5767 (4)	0.2476 (4)	0.6915 (5)	5.7 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2\mathrm{B}(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Atomic Positional Parameters and Their Estimated Standard Deviations for *nido*-8-[η^6-$C_6H_5CH_3$]-8,7-$FeSB_9H_{11}$ (II)[a]

atom	x	y	z	B, Å^2
Fe	0.05726 (6)	0.13561 (4)	0.28010 (4)	2.77 (1)
SB7	0.0563 (2)	0.2941 (1)	0.2453 (1)	3.75 (3)
BS9	−0.1383 (2)	0.1452 (1)	0.3675 (2)	3.99 (4)
B1	0.1102 (6)	0.2855 (3)	0.5118 (4)	3.8 (1)
B2	0.0941 (6)	0.3622 (3)	0.3924 (4)	3.6 (1)
B3	0.1896 (5)	0.2442 (3)	0.3967 (4)	3.42 (9)
B4	0.0832 (6)	0.1628 (3)	0.4631 (4)	3.40 (9)
B5	−0.0764 (6)	0.2310 (4)	0.4983 (4)	4.0 (1)
B6	−0.0694 (6)	0.3523 (3)	0.4521 (4)	3.57 (9)
B10	−0.2160 (6)	0.2743 (4)	0.3683 (5)	4.2 (1)
B11	−0.1092 (6)	0.3578 (3)	0.2980 (4)	3.6 (1)
C12	0.2682 (5)	0.0714 (4)	0.2655 (6)	9.0 (1)
C13	0.1730 (6)	0.0036 (3)	0.3200 (4)	5.6 (1)
C14	0.0221 (6)	−0.0132 (3)	0.2606 (5)	5.2 (1)
C15	−0.0517 (7)	0.0238 (4)	0.1625 (5)	5.9 (1)
C16	0.0183 (7)	0.0826 (4)	0.1092 (4)	5.7 (1)
C17	0.1681 (6)	0.1094 (4)	0.1493 (4)	7.5 (1)
C18	0.4352 (8)	0.0834 (7)	0.335 (1)	23.7 (4)

[a] Anistropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a{\cdot}2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

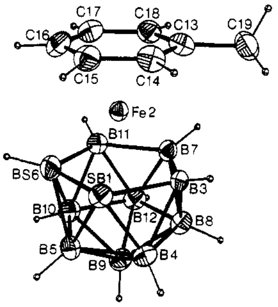

Figure 1. ORTEP drawing of the molecular structure of *closo*-2-[η^6-$C_6H_5CH_3$]-2,1-$FeSB_{10}H_{10}$ (I).

−5.3 (d, B4, J_{BH} = 154 Hz), −11.4 (d, B11, J_{BH} = 166 Hz), −13.1 (d, B2, J_{BH} = 179 Hz), −16.6 (d, B6, $J_{BH} \approx$ 135 Hz), −17.0 (d, B1, $J_{BH} \approx$ 125 Hz), −19.2 (d, B10, J_{BH} = 148 Hz); ^{1}H NMR (δ, CD_2Cl_2, 250 MHz), 6.18 (m, 2, C_6H_5), 6.00 (m, 1, C_6H_5), 5.89 (m, 2, C_6H_5), 2.41 (s, 3, CH_3Ph), −5.28 (s, 1, BHB), −16.57 (q, 1, FeHB, $J_{BH} \approx$ 70 Hz); IR (KBr pellet, cm^{-1}) 3070 (w), 2920 (w), 2580 (sh, m), 2540 (s), 2500 (s), 1460 (m), 1435 (m), 1360 (m), 1260 (w), 1210 (w), 1160 (w), 1075 (w), 1030 (w), 1005 (s), 980 (w), 950 (w), 930 (w), 905 (w), 865 (w), 845 (m), 820 (w), 780 (w), 750 (w), 720 (m), 705 (w), 630 (m), 575 (w), 520 (w), 475 (w), 455 (w), 410 (m), 395 (m), 360 (w), 340 (w). Anal. Calcd for $C_7SH_{19}B_9Fe$: C, 29.15; H, 6.64. Found: C, 31.32; H, 6.96.

Crystallographic Data for *closo*-2-[η^6-$C_6H_5CH_3$]-2,1-$FeSB_{10}H_{10}$ (I) and *nido*-8-[η^6-$C_6H_5CH_3$]-8,7-$FeSB_9H_{11}$ (II). Single crystals of I and II were grown by slow evaporation in air of dichloroethane/heptane solutions. In each case, a suitably sized crystal was mounted and transferred to the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 20–25 accurately centered reflections.

Collection and Reduction of the Data. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer employing Mo Kα radiation from a highly oriented graphite-crystal monochromator. The intensities of three standard reflections measured at intervals of 100 reflections showed no systemic change during data collection. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius program BEGIN.

Solution and Refinement of the Structure. All calculations were performed on a VAX 11/750 computer using the Enraf-Nonius structure package.[19] 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 $4F_o^2/(\sigma(F_o^2))^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The neutral-atom scattering factors and complex anomalous dispersion corrections were taken from ref 20 and 21. The ratios of the sulfur–boron scattering factors for disordered atoms were adjusted during isotropic refinement to equalize thermal parameters on all the disordered atoms. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. Three-dimensional Patterson syntheses gave the coordinates of the metal atoms. Subsequent Fourier maps led to the location of the remaining heavy atoms. Anisotropic refinements followed by difference Fourier syntheses resulted in the location of all hydrogens in both I and II; however, the hydrogen positions in II were not refined.

Results and Discussion

The reaction of iron vapor with toluene and 7-$SB_{10}H_{12}$ was found to give a single product (I) in 59% yield (based on consumed $SB_{10}H_{12}$) which was obtained as an air-stable, orange crystalline material. Exact mass measurements on the parent ion support the formulation of the compound as $(C_6H_5CH_3)FeSB_{10}H_{10}$, suggesting that a ($\eta^6$-$C_6H_5Me$)Fe unit has been inserted into the open face of the thiaborane cage, with the corresponding loss of the two bridging hydrogens. The ^{11}B NMR spectrum indicates the presence of a mirror plane, showing six doublet resonances in a 1:2:1:2:2:2 ratio. The ^{1}H NMR spectrum shows the resonances expected for a η^6-toluene unit.

The structure of I was confirmed by a single-crystal X-ray study, as shown in the ORTEP drawing in Figure 1. In agreement with its closo 26-skeletal-electron count, the cage structure is composed of a 12-vertex icosahedron, with the iron and sulfur atoms occupying adjacent positions. Although several isoelectronic metalla heteroatom boranes containing a group VI element, including complexes such as (η^5-C_5H_5)Co-$EB_{10}H_{10}$ (E = S,[4] Se,[22] Te[22]), have previ-

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[19] B. A. Frenz and Assoc. Inc., College Station, TX 77840, and Enraf-Nonius, Delft, Holland.

[20] (a) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–87.

[21] *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

[22] Little, J. L.; Friesen, G. D.; Todd, L. J. *Inorg. Chem.* **1977**, *16*, 869–872.

Table IV. Interatomic Distances (Å) for I

Fe2–SB1	2.207 (2)	B8–B9	1.762 (8)
Fe2–B3	2.161 (5)	B8–B12	1.762 (8)
Fe2–BS6	2.171 (4)	B9–B10	1.782 (8)
Fe2–B7	2.142 (5)	B9–B12	1.763 (8)
Fe2–B11	2.138 (5)	B10–B11	1.818 (8)
SB1–B3	2.014 (6)	B10–B12	1.777 (8)
SB1–B4	1.965 (6)	B11–B12	1.809 (8)
SB1–B5	1.974 (6)	Fe2–C13	2.136 (5)
SB1–BS6	2.021 (4)	Fe2–C14	2.119 (5)
B3–B4	1.894 (8)	Fe2–C15	2.124 (5)
B3–B7	1.807 (7)	Fe2–C16	2.114 (6)
B3–B8	1.789 (8)	Fe2–C17	2.103 (5)
B4–B5	1.815 (8)	Fe2–C18	2.104 (5)
B4–B8	1.759 (8)	C13–C14	1.409 (7)
B4–B9	1.751 (8)	C13–C18	1.406 (7)
B5–BS6	1.937 (7)	C13–C19	1.494 (8)
B5–B9	1.748 (8)	C14–C15	1.399 (8)
B5–B10	1.762 (8)	C15–C16	1.393 (8)
BS6–B10	1.844 (7)	C16–C17	1.396 (8)
BS6–B11	1.873 (7)	C17–C18	1.405 (7)
B7–B8	1.802 (8)		
B7–B11	1.814 (7)		
B7–B12	1.797 (8)		

ously been reported, I is the first such compound to be structurally characterized.

The sulfur atom was found to be disordered between positions SB1 and BS6, and this disorder was treated by using mixed boron/sulfur scattering factors for the two atoms (SB1, 80:20 sulfur/boron; BS6, 20:80 boron/sulfur). This treatment causes a bond distance shortening around the SB1 atom and a bond distance lengthening around BS6. The remaining boron–boron distances in the cage appear normal.

The distance between the iron and the centroid of the toluene ring is 1.586 Å which is similar to that which has been observed in (η^6-arene)metallacarboranes, such as (η^6-$C_6H_3Me_3$)$FeC_2B_9H_{11}$,[13b] suggesting that the $SB_{10}H_{10}^{2-}$ and $C_2B_9H_{11}^{2-}$ ligands exert similar electronic effects. The distance (1.433 Å) between the iron and the centroid of the thiaborane bonding face (SB1, B3, B7, B11, and BS6) is likewise siimilar to that observed in (η^6-$C_6H_3Me_3$)-$FeC_2B_9H_{11}$.[13b]

A more detailed investigation of the ^{11}B NMR spectrum of I using two-dimensional NMR techniques,[23a–d] in conjunction with the results from the X-ray structural study, has led to the complete assignment of the spectrum as given in Figure 2. With two exceptions, all expected cross peaks were observed between the adjacent borons in the structure in Figure 1. No cross peaks were observed between adjacent borons B3 and B4 and between B5 and BS6. It should be noted that in both cases the two borons are bridged by the sulfur atom, and, indeed, we have now observed that cross peaks are generally not found between adjacent borons in either thiaboranes or metallathiaboranes that are bridged by a sulfur atom. The reason(s) for the absence of these peaks is not yet clear; however, one possibility is that there is a reduced bonding interaction resulting in weaker scalar coupling between the two borons. Consistent with this suggestion is the fact that the observed distances between B3–B4 (1.894 (8) Å) and B5–BS6 (1.937 (7) Å) are the longest boron–boron distances in the cage; however, given the disorder found in the structure of I these values must be considered with caution.

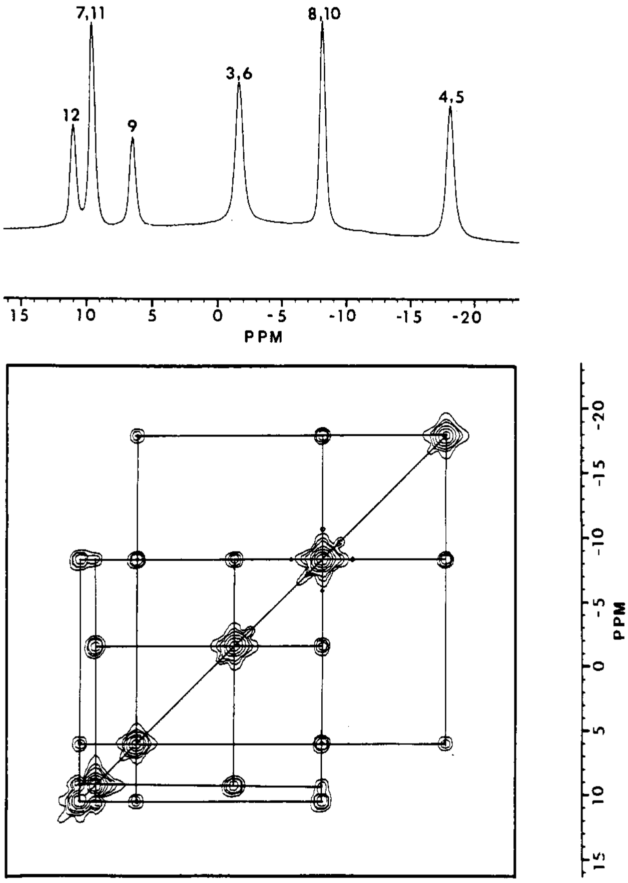

Figure 2. Two-dimensional proton spin-decoupled ^{11}B NMR spectrum (160.5 MHz) of *closo*-2-[η^6-$C_6H_5CH_3$]-2,1-$FeSB_{10}H_{10}$ (I).

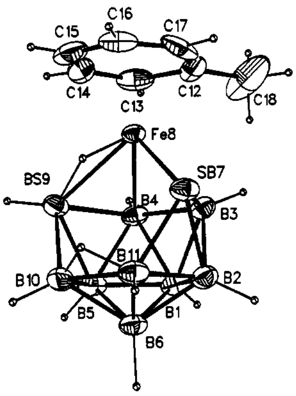

Figure 3. ORTEP drawing of the molecular structure of *nido*-8-[η^6-$C_6H_5CH_3$]-8,7-$FeSB_9H_{11}$ (II).

The reaction with *nido*-6-SB_9H_{11} also gave a single product in good yield (65% based on consumed SB_9H_{11}). Microanalysis and exact mass measurements confirm the formula ($C_6H_5CH_3$)$FeSB_9H_{11}$, indicating that the compound was formed by the direct insertion of the (η^6-C_6H_5Me)Fe group into the SB_9H_{11} cage without the loss of the two bridging hydrogens. Supporting this conclusion, the proton NMR spectrum shows, in addition to the res-

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Table V. Interatomic Distances (Å) for II

Fe8–SB7	2.243 (2)	B5–B10	1.786 (6)
Fe8–BS9	2.227 (3)	B6–B10	1.764 (6)
Fe8–B3	2.157 (4)	B6–B11	1.758 (7)
Fe8–B4	2.144 (5)	B10–B11	1.825 (8)
SB7–B2	1.928 (5)	Fe8–C12	2.097 (5)
SB7–B3	1.975 (4)	Fe8–C13	2.089 (5)
SB7–B11	1.938 (6)	Fe8–C14	2.098 (5)
BS9–B4	1.972 (5)	Fe8–C15	2.130 (5)
BS9–B5	1.910 (5)	Fe8–C16	2.088 (5)
BS9–B10	1.921 (5)	Fe8–C17	2.066 (6)
B1–B2	1.743 (7)	C12–C13	1.513 (8)
B1–B3	1.781 (8)	C12–C17	1.508 (7)
B1–B4	1.796 (7)	C12–C18	1.474 (9)
B1–B5	1.766 (8)	C13–C14	1.335 (7)
B1–B6	1.796 (7)	C14–C15	1.272 (7)
B2–B3	1.837 (7)	C15–C16	1.284 (8)
B2–B6	1.762 (8)	C16–C17	1.319 (7)
B2–B11	1.824 (7)		
B3–B4	1.777 (7)		
B4–B5	1.825 (8)		
B5–B6	1.782 (7)		

onances expected for the η^6-toluene, two separate bridge proton resonances at −5.28 and −16.57 ppm. The high-field shift and the quartet ($J \approx 70$ Hz) structure of the resonance at −16.57 ppm is highly characteristic of a metal–boron bridging hydrogen. The ^{11}B NMR spectrum shows nine separate doublet resonances indicating the absence of mirror symmetry.

The structure of II was confirmed by a single-crystal X-ray study as shown in the ORTEP drawing given in Figure 3. In agreement with its 26-skeletal-electron count, the cage adopts a structure based on a 11-vertex nido geometry, with the iron atom occupying the 8-cage position and sulfur atom the 7-position on the open face of the polyhedron. A similar structure has previously been confirmed for the isoelectronic compound $(PEt_3)_2Pt(H)(SB_9H_{10})$.[9]

As in I, the sulfur atom in II was found to be disordered between two cage positions and was treated by using mixed scattering factors for SB7 (60:40 sulfur/boron) and BS9 (40:60). Consequently, an artifically lengthened bond distance between Fe and BS9 and a shortened distance between Fe and SB7 were observed.

The iron is η^4-coordinated to the planar BS9, B4, B3, SB7 face of the thiaborane cage with an iron to plane-centroid distance of 1.445 Å, and this face is parallel to the η^6-toluene plane. The iron to η^6-toluene bonding appears normal with an average iron to ring-carbon distance of 2.095 Å and and iron to ring-centroid distance of 1.581 Å. The remaining intercage distances and angles are consistent with those previously reported for metallathiaborane[6,8,9] and thiaborane clusters.[24]

The two-dimensional NMR spectra of II are also consistent with the structural results and allow complete assignment of the resonances. Thus, as shown in Figure 4, cross peaks are observed between all adjacent borons except B10–B11, B11–B2, and B2–B3. B11–B2 and B2–B3 are each bridged by the sulfur atom, and as was discussed for I, no cross peaks are observed. Likewise, it has also been shown in a number of studies[23c–k] that borons connected by bridging hydrogens generally do not exhibit cross peaks; thus the cross peak between B10–B11 is not found.

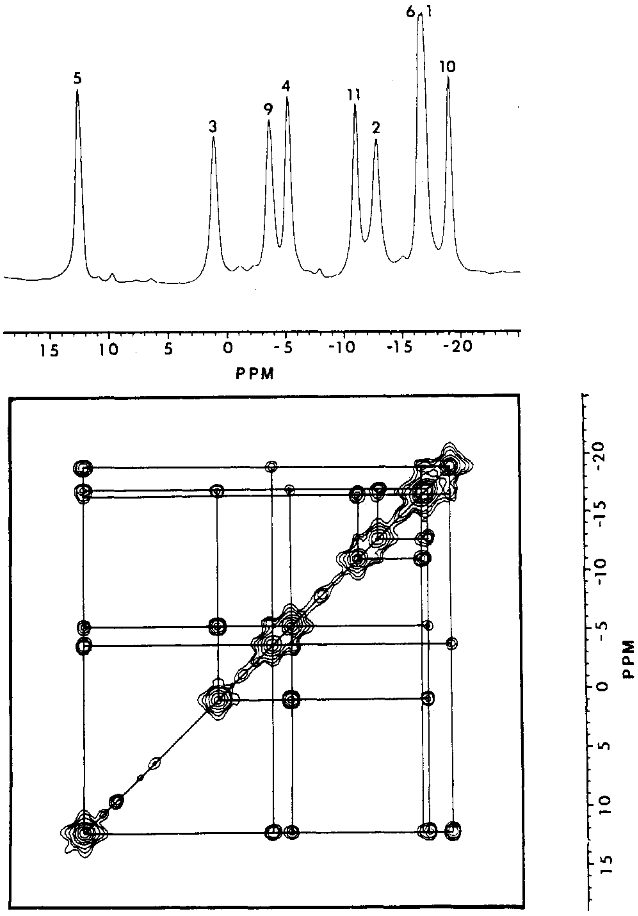

Figure 4. Two-dimensional proton spin-decoupled ^{11}B NMR spectrum (160.5 MHz) of *nido*-8-[η^6-$C_6H_5CH_3$]-8,7-$FeSB_9H_{11}$ (II).

The formation of these two (η^6-toluene)thiaferraborane complexes undoubtly both involve the reaction of the thiaboranes with solvated iron–arene reactive fragments[25] formed in the initial stages of the matrix warmup. However, the reactions with 7-$SB_{10}H_{12}$ and 6-SB_9H_{11} proceed differently to give dehydroinsertion and direct insertion products, respectively. These differences may simply reflect the special stabilities of the closo icosahedron and the 11-vertex nido geometry rather than any differences in reactivity of the two cage systems. The fact that both complexes can now be produced in excellent yields and easily isolated in pure form will allow the future development of the chemistry of these unique hybrid clusters.

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Supplementary Material Available: Tables of general temperature factors, intermolecular angles, bond distances, molecular planes, and hydrogen positions (29 pages); listings of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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