In contrast to dithiocarbamate complexes, the possible involvement of the "central" carbon atom in bonding to the metal center in phosphinomethanide complexes promotes dynamic behavior in solution, which adds flexibility and more reaction pathways for these types of complexes.

Registry No. 2, 70355-43-0; **4a,** 104911-10-6; **4b,** 104911-15-1; **5a,** 70377-69-4; **5b,** 102493-28-7; **6a,** 104946-37-4; **6b,** 104946-38-5; **7a,** 99900-56-8; **7b,** 99900-57-9; **8,** 104911-12-8; **9,** 104911-14-0; Me_2AlCl, 1184-58-3; $AlMe_3$, 75-24-1; $AlCl_3$, 7446-70-0.

Supplementary Material Available: Additional crystal structure data and complete tables of atomic positional and thermal parameters (5 pages); a listing of observed and calculated structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

Organotransition-Metal Metallacarboranes. 8. Mono-, Di-, and Triiron Polyarene Sandwich Complexes of $Et_2C_2B_4H_4^{2-}$ Containing Fluorene, 9,10-Dihydroanthracene, or [2.2]Paracyclophane Ligands[1]

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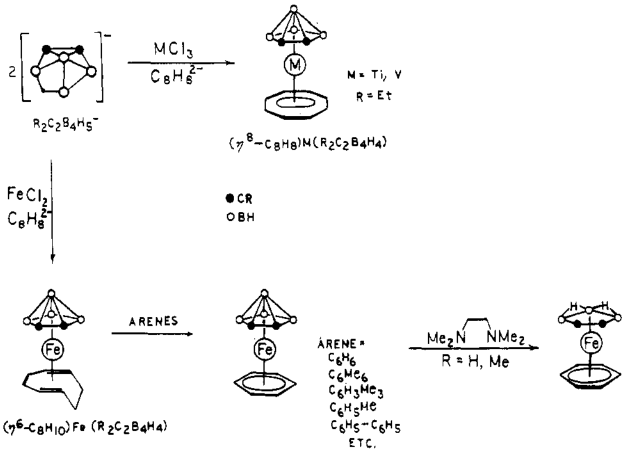
This paper describes the synthesis of mixed-ligand carborane–iron–polycyclic arene complexes from *nido*-2,3-$Et_2C_2B_4H_6$ together with structural characterization of the products via ^{11}B and ^1H NMR, infrared, and mass spectroscopic data. All products reported were isolated as air-stable crystalline solids. The main preparative route utilized displacement of the neutral ligand (L) from $(\eta^6\text{-L})Fe(Et_2C_2B_4H_4)$ (L = C_8H_{10} or $C_{16}H_{18}$) by arenes. In an alternative approach, the previously known naphthalene species $(\eta^6\text{-}C_{10}H_8)$-$Fe(Et_2C_2B_4H_4)$ was obtained directly from the $Et_2C_2B_4H_5^-$ ion, $FeCl_2$, and the naphthaleneide dianion. A monoiron fluorene complex $(\eta^6\text{-}C_{13}H_{10})Fe(Et_2C_2B_4H_4)$ (6) was prepared via both routes, employing displacement of C_8H_{10} from $(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)$ (2) as well as direct treatment of $Et_2C_2B_4H_5^-$ with $C_{13}H_{10}^-$ and $FeCl_2$. The thermal reaction of 6 with 2 gave a staggered triple-decker diiron species $(\eta^6,\eta^6\text{-}C_{13}H_{10})Fe_2(Et_2C_2B_4H_4)_2$ (7) and a staggered quadruple-decker triiron complex $Fe[(C_{13}H_{10})Fe(Et_2C_2B_4H_4)]_2$ (8), whose proposed structures are supported by spectroscopic evidence and by X-ray crystallographic data on 6 and 7. "Decapitation" (apex BH removal) of 6 was achieved by treatment with tetramethylethylenediamine giving *nido*-$(\eta^6\text{-}C_{13}H_{10})Fe(Et_2C_2B_3H_5)$.

Introduction

Small *nido*-carboranes of the $R_2C_2B_4H_6$ class (R = alkyl) are emerging as remarkably versatile reagents for the systematic construction of stable transition-metal–organometallic sandwich complexes, including those containing arenes[2] or higher cyclic polyenes[3] coordinated to the metal. Scheme I depicts the main synthetic approaches that have been developed in our laboratory in recent years.[2d-h] Among the compounds that have been prepared by these routes are the first crystallographically defined iron η^6-complexes of naphthalene and phenanthrene,[2h] as well as novel air-stable η^8-C_8H_8 complexes of vanadium and titanium (X-ray structure determinations have been conducted on the latter two species as well[3b]). These compounds, and most of the others reported thus far from our laboratory, utilize the *C,C′*-diethylcarborane ligand $Et_2C_2B_4H_4^{2-}$. The $R_2C_2B_4H_4^{2-}$ group is formally analogous to $C_5H_5^-$ but evidently forms much stronger, more covalent η^5-bonds to transition metals than do either $C_5H_5^-$ or arenes.[4a] The metal–hydrocarbon bonding in many of these species is clearly stabilized by the presence of the carborane unit, as supported by experimental evidence[2,3] and, indi-

Scheme I



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[1] (a) For part 7 see ref 2h. (b) Presented in part at the 189th National Meeting of the American Chemical Society, Miami, FL, April 1985, paper INOR-295.

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[3] (a) Swisher, R. G.; Sinn, E.; Brewer, G. A.; Grimes, R. N. *J. Am. Chem. Soc.* **1983**, *105*, 2079. (b) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Ibid.* **1984**, *3*, 599.

[4] (a) Calhorda, M. J.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *229*, 229. (b) Calhorda, M. J.; Mingos, D. M. P. *Ibid.* **1982**, *228*, 309 and references therein.

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

compd[a]	δ (J_{BH}, Hz)[b]	rel areas
$Et_2C_2B_4H_6$ (**1**)	−2.26 (150.2), −5.40 (154.1), −48.42 (170.1)	1:2:1
$(C_8H_{10})Fe(Et_2C_2B_4H_4)$ (**2**)	10.65 (141.1), 6.22 (160.3), 3.10 (149.2)	1:1:2
$(C_{16}H_{18})Fe(Et_2C_2B_4H_4)$ (**3**)	12.54 (141.6), 6.56 (159.4), 3.23 (148.5)	1:1:2
$(C_{10}H_8)Fe(Et_2C_2B_4H_4)$ (**4**)	7.18 (157.1), 4.44 (149.3), 0.36 (140.7)	1:1:2
$(C_{14}H_{12})Fe(Et_2C_2B_4H_4)$ (**5**)	5.56,[c] 3.28,[c] 0.14[c]	1:1:2
$(C_{13}H_{10})Fe(Et_2C_2B_4H_4)$ (**6**)	7.07 (139.5), 4.23 (169.1), 2.09 (173.8), 1.03 (136.2)	1:1:1:1
$(C_{13}H_{10})Fe_2(Et_2C_2B_4H_4)_2$ (**7**)	8.05,[c] 5.10,[c] 1.96[c]	1:1:2
$Fe[(C_{13}H_{10})Fe(Et_2C_2B_4H_4)]_2$ (**8**)	6.94 (143.7), 4.12 (170.8), 2.04 (156.1), 0.94 (135.5)	1:1:1:1
$(C_{13}H_{10})Fe(Et_2C_2B_3H_5)$ (**9**)	2.62 (131.7), −0.56,[c] −1.06[c]	1:1:1
$(C_{16}H_{16})Fe(Et_2C_2B_4H_4)$ (**10**)	3.25 (139), −1.20 (144)	2:2

[a] CH_2Cl_2 solutions. [b] Relative to $BF_3 \cdot Et_2O$ at 0 ppm with positive shifts downfield. [c] *J* not measurable.

rectly, from theoretical calculations.[4]

This chemistry appears well-suited to the preparation of extended sandwich complexes containing polyarene ligands in combination with transition metals and pyramidal $R_2C_2B_4H_4^{2-}$ or planar $R_2C_2B_3H_5^{2-}$ units (species of the latter type are derived from the former by base-induced extraction of the apex BH). An important synthetic goal is the construction of very large multidecker arrays exhibiting substantial electron delocalization.[5] Carborane–transition-metal–polycyclic arene sandwich complexes are potentially useful as building blocks for such purposes and moreover are intrinsically interesting systems which combine electronically interacting carbacycles, carborane ligands, and metal centers. Polyarenes having two or more electronically communicating π-systems are particularly attractive candidate ligands. This paper reports a synthetic, spectroscopic, and structural investigation of stable ferracarborane complexes having one to three iron atoms and incorporating fluorene, naphthalene, 9,10-dihydroanthracene, or [2.2]paracyclophane.

Results and Discussion

Syntheses of (Polycyclic arene)Fe($Et_2C_2B_4H_4$) Complexes. A previously described route to η^6-arene ferracarborane complexes,[2e–h] depicted in Scheme I, was utilized to prepare several new (η^6-arene)iron($R_2C_2B_4H_4$) complexes as shown in Scheme II. In this method, *nido*-2,3-$Et_2C_2B_4H_6$ (**1**) is converted to the cyclooctatriene complex **2** with concomitant formation of the complex $(C_{16}H_{18})Fe(Et_2C_2B_4H_4)$ (**3**), followed by thermal displacement of the C_8H_{10} ligand in **2** by the desired arene.[2e] In the present study, thermolyses of **2** with fluorene and [2.2]paracyclophane gave the corresponding products **6** and **10** respectively (Scheme II); in addition, **3** was found to undergo a similar displacement with 9,10-dihydroanthracene to give **5**. Compounds **5**, **6**, and **10** are new species, all obtained as colored air-stable crystalline solids. The naphthalene complex (η^6-$C_{10}H_8$)Fe($Et_2C_2B_4H_4$) (**4**), also air-stable, has been prepared previously in our laboratory via the thermal displacement method.[2h] In the present work this compound was obtained, for the first time, directly from the parent carborane by treatment with the naphthalene dianion as shown in Scheme II. Although the percentage yield of **4** obtained via the new direct route is lower than that realized via displacement[2h] (18.4% vs. 39.7% based on the $Et_2C_2B_4H_6$ reagent), we regard the new route as superior since it affords larger quantities of pure **4** (400 mg vs. 13 mg) in a single step. This procedure was also successfully employed in a one-step synthesis of the fluorene complex **6**, reported below.

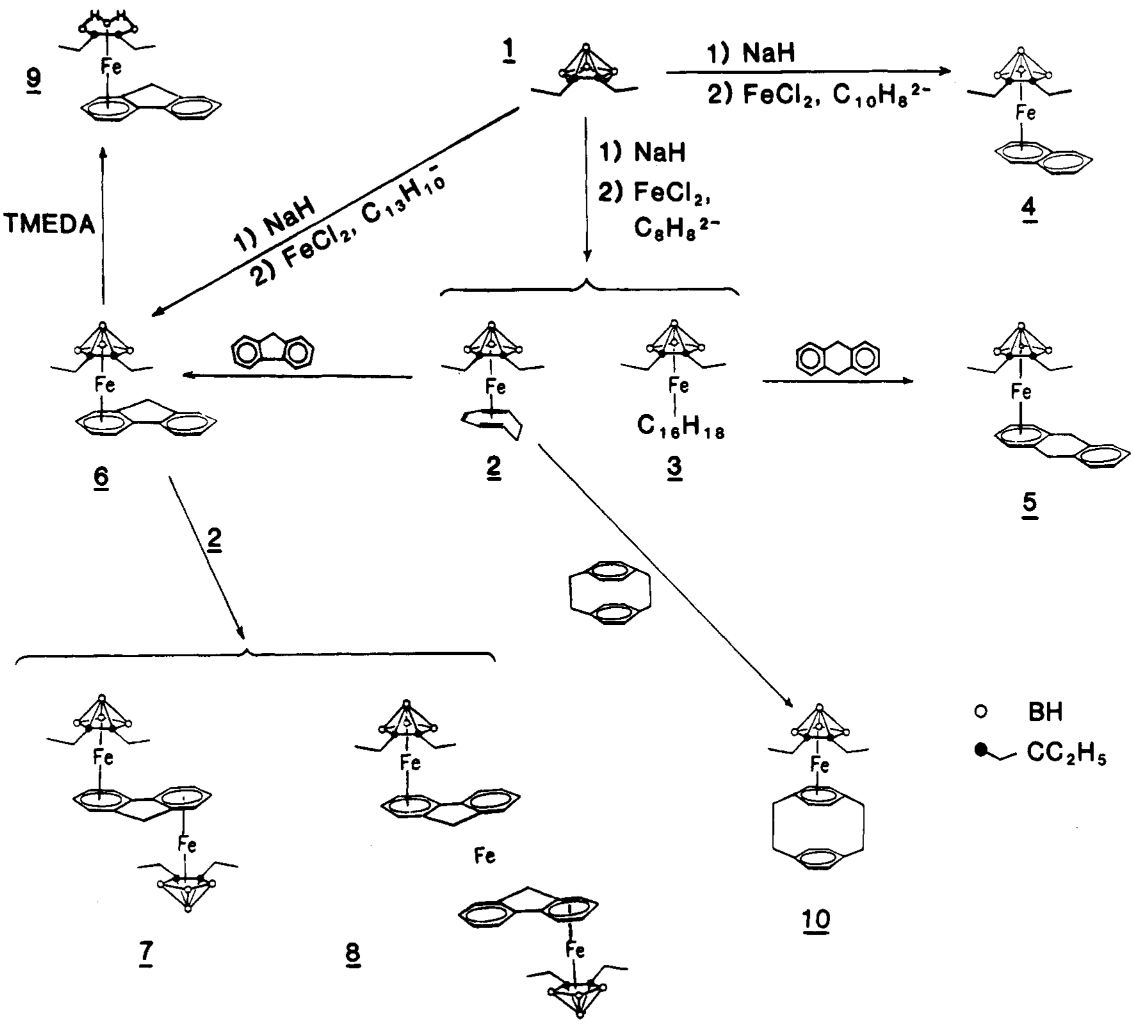
The new polyarene–ferracarboranes **5**, **6**, and **10** were characterized from their high-resolution ^{11}B and ^1H FT NMR spectra (Tables I and II), infrared spectra (Table III), and mass spectra (supplementary material), supported by X-ray crystallographic data on **6**. In general, the 115.8-MHz ^{11}B spectra exhibit the 1:1:2 (or 2:2) pattern typical of $R_2C_2B_4H_4^{2-}$ metal π-complexes, reflecting the local mirror symmetry of the carborane ligand; however, the 1:1:1:1 spectrum of the fluorene complex **6** is unusual and indicates inequivalence of B(4) and B(6), the basal borons adjacent to carbon. Normally this is not seen in

Table II. 360-MHz ^1H NMR Data

compd	δ^{a-c}	rel areas
1	2.48 m [7.3 Hz] (CH_2), 2.31 m [7.3 Hz] (CH_2), 1.21 t [7.6 Hz] (CH_3)	1:1:3
2[d]	5.56 m (C_8H_{10}), 5.16 dd [2.5, 2.2 Hz] (C_8H_{10}), 4.68 m (C_8H_{10}), 1.95 m (CH_2), 1.72 m (CH_2), 1.68 m (C_8H_{10}), 1.06 t [7.4 Hz] (CH_3), −0.20 m (C_8H_{10})	1:1:1:1:1:1:3:1
3[d]	6.10 dt [d, 10.1 Hz; t, 2.5 Hz] ($C_{16}H_{18}$), 5.22 t [5.8 Hz] ($C_{16}H_{18}$), 4.67 q [3.6 Hz] ($C_{16}H_{18}$), 4.01 m ($C_{16}H_{18}$), 2.78 m ($C_{16}H_{18}$), 2.02 m (C_2H_5), 1.83 m (C_2H_5), 1.68 m (C_2H_5), 1.22 q [7.2 Hz] ($C_{16}H_{18}$), 1.07 m (C_2H_5), 0.90 m ($C_{16}H_{18}$), 0.27 m ($C_{16}H_{18}$), −2.87 m ($C_{16}H_{18}$)	2:2:2:2:1:1:1:2:1:2:6:2:2:2
4[e]	6.90 s ($C_{10}H_8$), 6.88 s ($C_{10}H_8$), 5.65 s ($C_{10}H_8$), 5.33 s ($C_{10}H_8$), 1.76 m (CH_2), 1.65 m (CH_2), 1.16 t [7.6 Hz] (CH_3)	1:1:1:1:1:1:3
5	7.31 m ($C_{14}H_{12}$, uncomplexed C_6H_4 ring), 5.38 m ($C_{14}H_{12}$, complexed C_6H_4 ring), 3.98 m ($C_{14}H_{12}$, methylene), 3.92 m ($C_{14}H_{12}$, methylene), 2.64 m (CH_2), 2.39 m (CH_2), 1.25 t [7.6 Hz] (CH_3)	2:2:1:1:1:1:3
6	7.67 m ($C_{13}H_{10}$, uncomplexed C_6H_4 ring), 7.56 ($C_{13}H_{10}$, uncomplexed C_6H_4 ring), 7.43 m ($C_{13}H_{10}$, uncomplexed C_6H_4 ring), 5.98 d [5.1 Hz] ($C_{13}H_{10}$, complexed C_6H_4 ring), 5.84 d [5.1 Hz] ($C_{13}H_{10}$, complexed C_6H_4 ring), 5.56 t [5.5 Hz] ($C_{13}H_{10}$, complexed C_6H_4 ring), 5.49 t [5.5 Hz] ($C_{13}H_{10}$, complexed C_6H_4 ring), 4.03 d [20.9 Hz] ($C_{13}H_{10}$, methylene), 3.72 d [20.9 Hz] ($C_{13}H_{10}$ methylene), 2.25 m (CH_2), 1.99 m (CH_2), 1.10 t [7.4 Hz] (CH_3), 0.89 t [7.4 Hz] (CH_3)	1:1:2:1:1:1:1:1:1:2:2:3:3
7	5.71 d [2.4 Hz] ($C_{13}H_{10}$), 5.60 d [2.4 Hz] ($C_{13}H_{10}$), 5.28 t [2.2 Hz] ($C_{13}H_{10}$), 5.20 t [2.2 Hz] ($C_{13}H_{10}$), 3.71 s ($C_{13}H_{10}$), 2.18 m (CH_2), 1.97 m (CH_2), 0.91 t [7.6 Hz] (CH_3), 0.77 t [7.2 Hz] (CH_3)	1:1:1:1:1:2:2:3:3
8	7.68 m ($C_{13}H_{10}$), 7.54 m ($C_{13}H_{10}$), 7.42 ($C_{13}H_{10}$), 5.98 d [5.4 Hz] ($C_{13}H_{10}$) 5.84 d [6.1 Hz] ($C_{13}H_{10}$), 5.56 t [5.8 Hz] ($C_{13}H_{10}$), 5.49 t [5.8 Hz] ($C_{13}H_{10}$), 4.02 d [21.3 Hz] ($C_{13}H_{10}$ methylene), 3.72 d [20.9 Hz] ($C_{13}H_{10}$ methylene), 2.24 m (CH_2), 2.03 m (CH_2), 1.10 t [7.6 Hz] (CH_3), 0.88 t [7.6 Hz] (CH_3)	1:1:2:1:1:1:1:1:1:2:2:3:3
9	7.80 d [7.6 Hz] ($C_{13}H_{10}$), 7.56 m ($C_{13}H_{10}$), 7.48 m ($C_{13}H_{10}$), 7.35 m ($C_{13}H_{10}$), 3.94 d [20.9 Hz] ($C_{13}H_{10}$), 3.76 d [20.9 Hz] ($C_{13}H_{10}$), 1.86 m (CH_2), 1.71 m (CH_2), 1.03 t [7.6 Hz] (CH_3), 0.91 t [7.6 Hz] (CH_3)	2:2:2:2:1:1:2:2:3:3
10	7.38 m ($C_{16}H_{16}$), 6.57 m ($C_{16}H_{16}$), 3.58 m ($C_{16}H_{16}$), 3.07 m ($C_{16}H_{16}$), 2.49 m (CH_2), 2.21 m (CH_2), 1.15 t[f] (CH_3)	4:4:4:4:2:2:6

[a] Ppm relative to Me_4Si; coupling constants given in brackets. [b] Legend: s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, t = triplet, q = quintet, m = multiplet, br = broad. [c] $CDCl_3$ solution. [d] See ref 2d for spectrum analysis. [e] See ref 2 h. [f] Unresolved.

Scheme II



metal–$R_2C_2B_4H_4$ complexes, even in such closely related compounds as the 9,10-dihydroanthracene species **5** or in the previously characterized naphthalene (**4**) and phenanthrene analogues[2h] in which the hydrocarbon ligand introduces a high degree of overall asymmetry into the molecule. In those cases we presume that either (a) free rotation of the arene on the metal produces time-averaged equivalence of B(4) and B(6) (i.e., effective mirror symmetry) or (b) the difference in electronic environment of B(4) and B(6) in these species is too small to be observed in the ^{11}B spectrum, where line widths typically are larger than 50 Hz. Clearly neither rationale applies to **6**, where the asymmetry in the C_2B_4 group is so high as to render B(4) and B(6) inequivalent. In fact, X-ray diffraction data on this molecule[6] confirms that the fluorene ligand in the solid crystal is oriented such that a line connecting the centers of its C_6 rings is rotated well away (about 40°) from the local mirror plane bisecting the C_2B_4 ligand. Unfortunately, severe disorder in the fluorene group has prevented completion of a precise structure determination, but the data clearly establish the essential molecular features as depicted in Scheme II. In **6**, steric constraints arising from the bulky fluorene system may hinder ligand rotation, essentially locking the molecule into an asymmetric conformation even in solution and thereby accounting for the ^{11}B pattern observed for **6**. A similar argument accounts for the inequivalence of all three boron nuclei in the related complex $(\eta^3\text{-}C_{13}H_{10})Fe(Et_2C_2B_3H_5)$ (**9**), obtained from **6** by removal of the apex BH as described below.

The 360-MHz proton NMR spectra of **5**, **6**, and **10** are complex but indicate substantial shifts in both the metal-bound and unbound arene rings, relative to the uncomplexed hydrocarbons. In the 9,10-dihydroanthracene complex **5**, there is a pronounced (ca. 1.9 ppm) upfield shift of resonances assumed to arise from the complexed ring,[7] while the protons of the uncomplexed ring are shifted only slightly to higher field. The fluorene species **6** exhibits comparable upfield shifts of the protons on the metal-coordinated ring (ca. 1.7 ppm). The spectrum of the [2.2]-paracyclophane compound **10** indicates *downfield* shifts for the protons on both complexed and uncomplexed rings. The proton spectra of cyclophane-metal complexes in general are complex and difficult to interpret,[8] with shifts influenced by a number of factors including rehybridization of ring carbon atoms on complexation, reduction of ring current, and the magnetic anisotropy of the metal.[8b] In the case of **10**, one must add the influence of the $R_2C_2B_4H_4^{2-}$ carborane ligand, whose electronic influence

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(5) Leading references: (a) Burdett, J. K.; Canadell, E. *Organometallics* **1985**, *4*, 805. (b) Williams, J. M. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 235. (c) Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 843 and references therein.

(6) Crystal data: space group $P2_1/c$, a = 13.296 Å b = 15.87 Å, c = 8.860 Å, β = 99.40°; Z = 4; R = 0.13 for 2484 reflections having $F_o^2 > 3\sigma(F_o)^2$.

(7) Steele, B. R.; Sutherland, R. G.; Lee, C. C. *J. Chem. Soc., Dalton Trans.* **1981**, 529.

(8) (a) Boekelheide, V. *Top. Curr. Chem.* **1984**, 89. (b) Laganis, E. D.; Voegeli, R. H.; Swann, R. T.; Finke, R. G.; Hopf, H.; Boekelheide, V. *Organometallics* **1982**, *1*, 1415. (c) Swann, R. T.; Boekelheide, V. *J. Organomet. Chem.* **1982**, *231*, 143.

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

compd	absorptions
1[a]	2972 s, 2941 s, 2882 s, 2600 vs, br, 1951 w, 1918 w, 1462 s, 1382 m, 1311 w, 1210 w, 1072 w, 1000 w, 948 m, 924 m, 848 m, 799 w, 770 w, 722 w, 672 m
2	3035 w, 3005 w, 2980 s, 2945 s, 2890 m, 2850 m, 2560 s, 2530 vs, 1504 w, 1452 s, 1440 m, 1410 w, 1380 m, 1347 m, 1308 m, 1290 m, 1240 w, 1220 w, 1190 w, 1160 w, 1065 m, 1035 w, 980 w, 950 w, 930 w, 901 w, 888 m, 872 m, 852 m, 836 m, 810 w, 798 w, 735 m, 720 m, 618 m, 490 w, 465 m, 408 m
3	3038 m, 3009 m, 2978 s, 2940 s, 2880 m, 2541 vs, 1452 m, 1379 m, 1344 w, 1270 w, 1219 w, 1201 w, 1062 m, 965 m, 911 w, 876 s, 841 w, 824 w, 660 w
4	2960 s, 2930 s, 2893 m, 2511 vs, 1475 s, 1450 s, 1378 s, 1251 m, 1205 w, 1170 w, 1154 w, 1098 w, 1065 w, 991 w, 965 w, 933 w, 881 s, 850 s, 814 m, 796 w, 750 s, 733 w, 675 w, 631 w, 604 w, 538 w, 470 m, 411 m
5	3052 w, 3028 w, 2978 s, 2863 s, 2568 s, 1463 s, 1428 m, 1384 w, 1266 w, 1080 w, 1025 w, 882 w, 840 w, 810 w, 761 s, 739 s, 712 s, 514 w, 472 m, 420 w
6	3100 w, 2995 s, 2952 s, 2900 m, 2562 s, 2540 s, 1746 w, 1479 m, 1466 m, 1444 m, 1432 m, 1410 m, 1395 w, 962 w, 906 w, 888 s, 852 m, 822 w, 807 w, 778 s, 732 s, 672 w, 638 w, 620 w, 510 w, 478 m, 405 w
7	3082 w, 2978 s, 2942 s, 2880 m, 2562 sh, s, 2538 s, 1738 w, 1463 m, 1424 w, 1382 m, 1198 w, 1068 w, 878 w, 848 m, 815 w, 800 w, 728 w, 420 m
8	3088 m, 3079 sh, m, 3080 w, 2979 s, 2964 s, 2918 w, 2880 m, 2562 s, 2525 s, 2020 sh, m, 1512 m, 1472 m, 1458 m, 1439 s, 1428 s, 1405 m, 1388 w, 1360 w,, 1240 w, 1190 w, 1090 w, 1071 w, 1021 w, 960 m, 942 m, 900 m, 880 s, 871 sh, m, 849 m, 821 w, 801 w, 772 s, 728 s, 634 m, 568 w, 512 w, 500 w, 469 s, 422 w, 399 w, 370 w
9	3056 w, 2948 s, 2916 s, 2852 m, 2512 br, s, 2362 w, 1864 w, 1462 w, 1444 w, 1426 w, 925 w, 778 m, 758 s, 738 s, 718 s, 678 w, 622 w
10	2978 m, 2938 s, 2880 m, 2537 s, 2344 w, 2022 w, 1654 w, 1600 w, 1542 w, 1506 w, 1458 m, 1438 w, 1382 w, 1248 w, 1209 w, 1118 br, s, 1040 w, 879 m, 821 m, 796 w, 728 m, 678 w, 578 m, 501 w, 422 w, 342 w

[a] Neat sample.

on the metal–arene system is significantly dependent on the nature of R. This can be seen by comparing the ^1H and ^{11}B NMR spectra of **10** and its dibenzylcarborane analogue (compound **6** in the following paper[9]). The boron spectra are notably dissimilar, the shifts of the diethyl compound **10** being 7–12 ppm to low field of the dibenzyl complex resonances, consistent with greater shielding of boron nuclei in the latter compound.

Conversion of (η^6-$C_{13}H_{10}$)Fe($Et_2C_2B_4H_4$) (6) to Di- and Triiron Sandwich Complexes. In an attempt to generate a triple-decker complex by attaching a second Fe($Et_2C_2B_4H_4$) unit to the uncomplexed ring of **6**, the latter compound was heated with an excess of **2** at 180 °C in the absence of solvent. Extraction with dichloromethane gave two products which were isolated as air-stable orange solids and characterized as (η^6,η^6-$C_{13}H_{10}$)Fe_2($Et_2C_2B_4H_4$)$_2$ (**7**) and Fe[($C_{13}H_{10}$)Fe($Et_2C_2B_4H_4$)]$_2$ (**8**) (Scheme II). The staggered quadruple-decker structure which is depicted for **7** is consistent with its NMR and mass spectra. In the proton spectrum of **7**, the comparatively simple pattern indicates that the two aryl rings are equivalent and that both are coordinated to iron. The ^{11}B spectrum of **7** exhibits a normal 1:1:2 pattern, unlike that of **6** discussed above; this implies a more symmetrical electron density distribution in **7** compared to that in **6**, consistent with the proposed dimetallic structure for **7**. This molecular geometry has been confirmed by single-crystal X-ray diffraction data[10] on **7**, which established the presence of two ($Et_2C_2B_4H_4$)Fe moieties that are coordinated to fluorene in a trans configuration (Scheme II). As in the case of **6**, mentioned earlier, disorder in the fluorene ligand has prevented refinement of the structure to a satisfactory level of precision but nevertheless serves to establish the salient features of the molecule. Most importantly, alternative structures in which either (1) both irons are coordinated to a common C_6 ring or (2) the metals are located on the same side of the fluorene plane (attached to different C_6 rings) are eliminated.

Compound **8** is formulated from its mass spectrum as a triiron species containing two ($Et_2C_2B_4H_4$)Fe(fluorene) units (**6**) sandwiched around a central iron atom. However, the mode of coordination of the central iron to the fluorene ligands has not been established and may involve η^5- and/or η^6-binding (the former requiring loss of a methylene proton from fluorene, as a reviewer has suggested). The ^{11}B and ^1H NMR spectra are closely similar to those of **6**, and partial conversion of **8** to **6** may occur in solution. In the solid state, **8** appears stable and exhibits infrared and mass spectra distinct from those of **6** and **7**. An X-ray structure determination clearly would be of interest for **8**.

"Decapitation" of ($C_{13}H_{10}$)Fe($Et_2C_2B_4H_4$) (6). The extraction of the apex BH unit from seven-vertex transition-metal–$R_2C_2B_4H_4$ complexes in a controlled manner (i.e., without otherwise disrupting the cage) has been shown to be a general reaction for such molecules,[2e,11] and works particularly well with (arene)Fe($R_2C_2B_4H_4$) complexes.[2e,g] "Decapitation" has not, however, previously been demonstrated with polyarene species, and hence we explored its applicability to **6**. Treatment of **6** with refluxing *N,N,-N′,N′*-tetramethylethylenediamine (TMEDA) gave the desired product **9** in excellent yield, and characterization was straightforward via NMR, IR, and mass spectroscopy. Once again the tendency of the fluorene ligand to induce measurable inequivalence in the carborane borons (noted in **6** and **8** as discussed previously) is evident in the ^{11}B spectrum, this time as a 1:1:1 pattern; the arguments presented above should apply equally to **9**.

Since compound **9** has an open carborane face as well as an uncomplexed fluorene ring, **9** or its bridge-deprotonated anion is expected to lead to stacked polydecker complexes via sandwich bonding of metals to both ends of the molecule, a possibility we are currently exploring.

Conclusions

These studies, together with earlier work, further demonstrate the feasibility of designed synthesis of carborane–metal–arene sandwich complexes via general reactions, utilizing commercially available arenes and the readily accessible "bench reagent" *nido*-carborane $Et_2C_2B_4H_6$. It appeared to us that the next logical stage of development in this area lay in the use of $R_2C_2B_4H_6$ reagents containing R groups that are themselves capable of metal complexation and/or organic functionalization. The synthesis and chemistry of a particularly useful compound of this type, *C,C′*-dibenzylcarborane [$(PhCH_2)_2$-$C_2B_4H_6$], are described in the two papers which follow.

Experimental Section

Materials. All solvents used were of anhydrous reagent grade or better and were distilled, degassed with a dry nitrogen stream, and stored over 4-Å molecular sieves prior to use. Deuterated

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(9) Spencer, J. T.; Grimes, R. N., *Organometallics*, second of three papers in this issue.

(10) Crystal data: space group *Pbca*, $a = 6.800$ Å, $b = 13.500$ Å, $c = 29.700$ Å; $Z = 8$; $R = 0.12$ for 1952 reflections having $F_o^2 > 3\sigma(F_o)^2$.

(11) (a) Grimes, R. N.; Beer, D. C.; Sneddon, L. G.; Miller, V. R.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 1138. (b) Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *Ibid.* **1976**, *98*, 4818.

solvents were purchased from the Aldrich Chemical Co. Used as received were 3-hexyne (Farchan), triethylamine (Aldrich), B_5H_9 (U.S. Government stockpile), naphthalene (Aldrich), 9,10-dihydroanthracene (Aldrich), fluorene (*o,o'*-diphenylenemethane, Aldrich), [2.2]paracyclophane (tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene, Aldrich), tetramethylethylenediamine (Aldrich), potassium metal (Allied Chemical), and lithium wire (Aldrich). Sodium hydride (Alfa, 50% mineral oil) was washed twice with anhydrous hexane prior to use, and anhydrous iron(II) chloride (Alfa) was stored under dry nitrogen prior to use. Cyclooctatetraene (Aldrich, 98%) was stored cold and distilled in vacuo before being used. Dipotassium cyclooctatetraenide ($K_2C_8H_8$) was prepared in tetrahydrofuran (THF) by the procedure of Streitweiser et al.[12] *nido*-2,3-Diethyl-2,3-dicarbahexaborane(8) (1) was prepared by the method described elsewhere.[13] The complexes (η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$) (2) and ($C_{16}H_{18}$)Fe($Et_2C_2B_4H_4$) (3) were synthesized by previously reported procedures.[2d]

Instrumentation. ^{1}H (360-MHz) and ^{11}B (115.8-MHz) high-resolution pulse Fourier transform NMR spectra were obtained on a Nicolet Magnetics Corp. NT-360/Oxford spectrometer, and data manipulation utilized standard Nicolet software with a 1280/293B data system. Proton spectra of all compounds were taken in chloroform-d_1 in 5-mm (o.d.) tubes. Routine ^{1}H spectra for identification and purity assessment were obtained on a varian EM-390 spectrometer operating at 90 MHz. ^{11}B spectra were obtained in methylene chloride solution in 10-mm (o.d.) tubes with $BF_3 \cdot O(C_2H_5)_2$ as reference standard. Broad-band heteronuclear decoupling was employed. Unit-resolution mass spectral measurements were recorded on a Finnigan MAT-4500 GC/MS spectrometer using perfluorotributylamine (FC43) as a calibration standard. Mass spectral simulations were performed on a Hewlett-Packard Model 87 computer. Except where otherwise indicated, the mass spectra of all boron-containing compounds exhibited intense parent envelopes, and intensity profiles in the parent region were consistent with calculated spectra on the basis of natural isotope distributions. High-resolution mass measurements were obtained on a Finnigan MAT 8230 instrument using an SSX 300 data system, with perfluorokerosene employed as a reference standard. Infrared spectra were recorded on a Perkin-Elmer Model 1430 spectrometer and were referenced to the 1601.8 cm^{-1} band of polystyrene. Column chromatography was conducted on silica gel 60 (Merck), and thin-layer chromatography was conducted on precoated silica gel plates (Merck).

One-Step Preparation of ($C_{10}H_8$)Fe($Et_2C_2B_4H_4$) (4) from $Na^+Et_2C_2B_4H_5^-$ and Naphthalene. In a side-arm flask connected to an apparatus previously described[14] was placed 0.988 g (7.71 mmol) of naphthalene and 0.274 g (39.5 mmol) of lithium wire. The apparatus was evacuated and 75 mL of dry, degassed THF condensed into the flask. The mixture was allowed to warm slowly to room temperature and stirred for 1 h at that temperature, during which time the color changed from colorless to dark green and finally to deep red. The solution was filtered in vacuo onto 0.963 g (7.59 mmol) of anhydrous $FeCl_2$ in a 250-mL round-bottom flask which was cooled in liquid nitrogen. In the other side-arm flask, a solution of $Na^+Et_2C_2B_4H_5^-$ was prepared from the reaction of 0.966 g (7.35 mmol) of $Et_2C_2B_4H_6$ (1) with 0.201 g (8.36 mmol) of NaH in 30 mL of THF using standard techniques.[13b] This solution was filtered in vacuo into the flask containing $FeCl_2$ at liquid-nitrogen temperature. The reactor was warmed to 0 °C and stirred for 2 h at this temperature, followed by warming slowly to room temperature with an additional 5 h of stirring. The mixture was opened to the atmosphere, the THF removed by rotary evaporation, and the residue dried in vacuo. The residue was dissolved in methylene chloride, filtered through a 3-cm layer of silica gel, and washed with methylene chloride until the washings were colorless. The solvent was removed and the residue chromatographed on a silica gel column (30 × 3.5 cm) which was eluted with 1:1 hexane–methylene chloride. Two bands were collected: a colorless band consisting of 0.0751 g (0.585 mmol) of unreacted naphthalene and an orange-red band which gave 0.411 g (1.31 mmol, R_f 0.40, 18.4% yield based on the amount of naphthalene consumed) of 4.

Preparation of ($C_{14}H_{12}$)Fe($Et_2C_2B_4H_4$) (5). Into a 25-mL sealed-end Pyrex tube equipped with a ball joint for attachment to a vacuum system were placed 0.184 g (0.465 mmol) of ($C_{16}H_{18}$)Fe($Et_2C_2B_4H_4$) (3) and 0.350 g (1.94 mmol) of 9,10-dihydroanthracene. The tube was evaculated, sealed with a torch, and heated at 175 °C for 8 h and then cooled to room temperature. The reactor was opened to the air and the residue extracted with methylene chloride and filtered, and the solvent removed. The residue was chromatographed on silica gel TLC plates which were developed with a 40% methylene chloride/hexane solution. Two reddish orange bands were collected. The first of these gave 0.0741 g (0.187 mmol) of unreacted 3. The second band gave 0.0227 g (0.062 mmol, R_f 0.48, 22.3% yield based on 3 consumed) of 5 as orange, air-stable crystals: mp 142–144 °C; exact mass calcd for $^{56}Fe^{11}B_4{}^{12}C_{20}{}^1H_{26}{}^+$ 366.176, found 366.179.

Preparation of ($C_{13}H_{10}$)Fe($Et_2C_2B_4H_4$) (6). Method A. Into a Pyrex tube identical with that employed in the synthesis of 5 were placed 0.171 g (0.585 mmol) of 2 and 0.489 g (2.95 mmol) of fluorene. The tube was evacuated, sealed, heated at 160 °C for 3 h, and cooled to room temperature, after which it was opened and the residue extracted with methylene chloride, filtered, and chromatographed on silica gel plates developed with a 1:1 benzene–hexane solution. Two orange bands were collected. The first band yielded 0.024 g (0.082 mmol, R_f 0.69) of unreacted 2. The second band provided 0.105 g (0.299 mmol, R_f 0.51, 59.3% yield) of 6 as an orange, air-stable, crystalline material: mp 130–132 °C; exact mass calcd for $^{56}Fe^{11}B_4{}^{12}C_{19}{}^1H_{24}{}^+$ 352.1600, found 352.1616.

Method B. Compound 6 was also prepared by a direct method (B) analogous to that described above for 4. In a typical reaction, 0.8602 g (22.00 mmol) of potassium metal was placed into the side-arm flask and 75 mL of dry, degassed THF was added under vacuum. To this frozen solution was added 3.374 g (20.30 mol) of fluorene via a solid addition tube. The reaction was then allowed to warm to −63 °C and stirred at this temperature for 3 h, during which time the solution became dark green in color. This solution was filtered in vacuo onto 2.573 g (20.30 mmol) of anhydrous $FeCl_2$, previously cooled to liquid-nitrogen temperature. In the other side-arm flask, 2.499 g (19.01 mmol) of 1 was reacted with 0.5194 g (21.64 mmol) of NaH in 50 mL of THF by using standard procedures[13b] and the solution filtered onto the $FeCl_2$. The main reactor was allowed to warm to −63 °C with continuous stirring for 2 h, after which time it was slowly warmed to room temperature and stirred for an additional 12 h. The reaction mixture was opened to the air and the solvent removed by rotary evaporation. The residue was column chromatographed (2.5 × 60 cm) on silica gel and eluted with a 1:3 methylene chloride–hexane solution. Two red and one orange band were collected. The desired product was contained in the orange (third) band and yielded 0.950 g (2.70 mmol, R_f 0.41, 14.2%) of 6, which was spectroscopically identical with that prepared by method A above.

Preparation of ($C_{13}H_{10}$)Fe_2($Et_2C_2B_4H_4$)$_2$ (7) and Fe[($C_{13}H_{10}$)Fe($Et_2C_2B_4H_4$)]$_2$ (8). Into a Pyrex reaction tube identical to that used for the synthesis of 5 were placed 0.0972 g (0.272 mmol) of 6 and 0.398 g (1.37 mmol) of 2. The tube was evacuated, sealed, heated to 180 °C for 5.5 h, cooled to room temperature, and opened to the air. The residue was extracted with methylene chloride, filtered, and chromatographed on silica gel TLC plates which were developed with a 60% methylene chloride–hexane solution. Four orange bands were collected. The first yielded 0.0161 g (0.0551 mmol) of unreacted 2, and the second band gave 0.0141 g (0.040 mmol) of unreacted 6. The third band provided 0.0275 g (0.0511 mmol, R_f 0.65, 18.4% yield based upon the amount of 6 consumed) of 7 as an air-stable solid. The final band gave 0.0114 g (0.015 mmol, R_f 0.42, 5.4% yield) of a complex identified as 8.

Preparation of ($C_{13}H_{10}$)Fe($Et_2C_2B_3H_5$) (9) from 6. Into a two-neck 100-mL round-bottom flask attached to a vacuum line via a reflux condenser and equipped with a magnetic stirrer and rubber septum was placed 0.035 g (0.099 mmol) of 6. The entire apparatus was evacuated, and 10 mL of dry, degassed *N,N,N'*,-

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(12) Streitweiser, A.; Muller-Westerhoff, U.; Sonnichsen, G.; Mares, F.; Morrell, D. G.; Hodgson, K. O.; Harmon, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 8644.

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

(14) Borodinsky, L.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 1921, Fig. 6.

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N′-tetramethylethylenediamine (TMEDA) was added through the septum via a syringe. This mixture was stirred for 30 min at room temperature and then refluxed for an additional 30 min during which time the color changed from reddish orange to yellow. The solution was cooled to room temperature, the TMEDA removed in vacuo, and the reaction opened to the air. The residue was extracted with methylene chloride and chromatographed on silica gel TLC plates developed with a 20% methylene chloride–hexane solution. A single yellow band was collected which yielded 0.0243 g (0.0708 mmol, R_f 0.54, 71.2% yield) of **9** as an air-stable solid; exact mass calcd for $^{56}Fe^{11}B_3{}^{12}C_{19}{}^{1}H_{25}{}^{+}$ 342.1585, found 342.1585.

Preparation of ($C_{16}H_{16}$)Fe($Et_2C_2B_4H_4$) (10). A procedure analogous to that described above for the synthesis of **5** was employed to react 0.306 g (1.05 mmol) of **2** with 1.09 g (5.25 mmol) of [2.2]paracyclophane in 2 mL of dry, degassed triglyme at 175 °C for 6 h. The tube was treated as described above and the residue chromatographed on a 2.5 × 60 ccm silica gel column which was eluted with a 9:1 methylene chloride–hexane solution. Two orange bands were collected. The first provided 0.066 g (0.2265 mmol) of unreacted **2**. The second colored band gave 0.121 g (0.307 mmol, R_f 0.76, 37.3% yield) of **10** as air-stable crystals: mp 151–153 °C; exact mass calcd for $^{56}Fe^{11}B_4{}^{12}C_{22}{}^{1}H_{30}{}^{+}$ 394.2069, found 394.2072.

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Registry No. **1**, 8058-48-8; **2**, 84583-03-9; **4**, 95464-66-7; **5**, 105472-21-7; **6**, 105472-22-8; **7**, 105472-23-9; **8**, 105501-01-7; **9**, 105472-20-6; **10**, 105472-24-0; $FeCl_2$, 7758-94-3; [2,2]paracyclophane, 1633-22-3; flourene, 7782-41-4; naphthalene, 91-20-3; 9,10-dihydroanthracene, 613-31-0.

Supplementary Material Available: Tables of unit-resolution mass spectroscopic data on compounds **1**–**10** (5 pages). Ordering information is given on any current masthead page.

Organotransition-Metal Metallacarboranes. 9. *nido*-2,3-Dibenzyl-2,3-dicarbahexaborane(8) [$(PhCH_2)_2C_2B_4H_6$], a Versatile Multifunctional *nido*-Carborane: Iron–Polyarene Sandwich Compounds and Chromium Tricarbonyl π-Complexes[1]

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The title carborane **1**, a nearly nonvolatile air- and water-stable liquid, has been prepared in multigram quantities from dibenzylacetylene (1,4-diphenyl-2-butyne) and B_5H_9 in the presence of triethylamine. The multifunctional reactivity of **1** has been systematically explored via the preparation of a variety of mixed iron–carborane–polyarene complexes in which one or more of the three bonding rings in **1** (C_2B_3 and two C_6) are coordinated to metals. Thus, **1** was bridge-deprotonated to give the $(PhCH_2)_2C_2B_4H_5^-$ anion which in turn was treated with $FeCl_2$ and $C_8H_8^{2-}$ ion to form the cyclooctatriene complex (η^6-C_8H_{10})Fe[$(PhCH_2)_2C_2B_4H_4$] (**2**). The C_8H_{10} ligand in **2** is readily displaced by arenes on heating, affording sandwich complexes of general formula (arene)Fe[$(PhCH_2)_2C_2B_4H_4$] where the arene is [2.2]paracyclophane (**3**), 9,10-dihydroanthracene (**4**), or fluorene (*o,o′*-diphenylenemethane) (**6**). The reaction of **4** with **2** at elevated temperature yielded the staggered triple-decker diiron species (η^6,η^6-$C_{14}H_{12}$)Fe_2[$(PhCH_2)_2C_2B_4H_4$]$_2$ (**5**). Complexes **2**–**6** are air-stable orange crystalline solids. Treatment of **2** with chromium hexacarbonyl in refluxing butyl ether/tetrahydrofuran resulted in complexation of one phenyl ring with a $Cr(CO)_3$ group, forming (2-[$(CO)_3Cr(\eta^6$-$C_6H_5)CH_2$]-3-$PhCH_2$-2,3-$C_2B_4H_4$)Fe(η^6-C_8H_{10}) (**7**); reaction of **7** with $Cr(CO)_6$ gave the dichromium species (2,3-[$(CO)_3Cr(\eta^6$-$C_6H_5)CH_2$]$_2$-2,3-$C_2B_4H_4$)Fe(η^6-C_8H_{10}) (**8**) in which both of the phenyl rings and the carborane face are coordinated to metals. Complexes **7** and **8** are yellow, moderately air- and light-stable solids. Characterization of compounds **1**–**8** was achieved via ^{11}B and ^{1}H NMR, IR, and mass spectroscopy, supported by an X-ray diffraction analysis of a dichromium complex of **1** which is reported in the following paper.

Introduction

In the preceding paper[1a] and in earlier reports in this series,[1b] methods are described for the systematic construction of arene (or cyclic polyene)–transition metal–carborane π-complexes of specified design. These syntheses exploit several advantages afforded by *nido*-$R_2C_2B_4H_6$ carboranes as starting reagents,[2] including ease of preparation and handling, facile complexation by metal ions on the C_2B_3 face, and high chemical and thermal stability of the metal complexes formed. An additional synthetically important property of these complexes is their ability to undergo "decapitation" or base-induced removal of the apex BH unit (see Scheme I in the preceding report[1a]). This process forms a planar C_2B_3 ring which can η^5-bond to a second metal, as in the (η^5-C_5H_5)Co($C_2B_3H_5$)Co(η^5-C_5H_5) isomers which provided the first examples of electrically neutral triple-decker sandwich complexes.[3]

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[1] (a) Part 8: Spencer, J. T.; Grimes, R. N. *Organometallics*, first of three papers in this issue. (b) See ref 1a and references therein.

[2] Grimes, R. N. In Proceedings of the Anton Burg Symposium on Boron Chemistry, Los Angeles, CA, March 1985; Verlag Chemie International: Deerfield Beach, FL; in press.

[3] (a) Grimes, R. N.; Beer, D. C.; Sneddon, L. G.; Miller, V. R.; Weiss, R. *Inorg. Chem.* 1974, *13*, 1138. (b) Miller, V. R.; Grimes, R. N. *J. Am. Chem. Soc.* 1975, *97*, 4213.

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