Variable-temperature (2–300 K) magnetic susceptibility measurements for solid **1**[10] reveal reduction in the effective magnetic moment from 7.33 to 0.62 μ_B/molecule (2.99 to 0.25 μ_B/iron) with decreasing temperature, indicative of net antiferromagnetic coupling within the Fe_6 aggregate. Extrapolation of the μ_{eff} vs T curve (Figure S1, supplementary material) to 0 K yields a value of ~0.07 μ_B/iron, indicating a diamagnetic ground state having $S_T = 0$. The room-temperature effective moment of 2.94 μ_B/iron,[10] obtained by the Evans method,[18] is consistent with the persistence of the hexanuclear structure in solution. The optical spectrum of the $\{Fe_6O_2(OH)_2\}^{12+}$ unit in **1** has a characteristic maximum at 524 nm not present in its $\{Fe_3O\}^{7+}$ constituents, in further support of the solution integrity of **1**. Zero-field Mössbauer spectra at 80 K can be fit as a symmetric quadrupole doublet with isomer shift $\delta = 0.511$ mm/s (relative to iron metal at room temperature) and quadrupole splitting $\Delta E_Q = 0.575$ mm/s ($\Gamma = 0.370$ mm/s).

Interestingly, hydrolysis of both **1** and "basic iron(III) benzoate" in MeCN, layered with wet THF (0.8% H_2O) at room temperature, gives the known molecule $[Fe_{11}O_6(OH)_6(O_2CPh)_{15}]$[7] in >80% yield, suggesting that **1** might be an intermediate in the formation of the undecairon(III) aggregate or even the ferritin core itself. Use of higher temperatures in the synthesis of polynuclear iron–oxo aggregates thereby seems to favor the assembly of smaller clusters.[5] This limitation in the extent of hydrolysis may be caused by reduced availability of water molecules.

In conclusion, the reported synthesis, reactions, and structural and physical properties of **1** clearly expand our knowledge of the class of polynuclear iron–oxo complexes. The $Fe_3 \rightarrow Fe_6 \rightarrow Fe_{11}$ conversions observed here provide some indication of the nucleation processes that might be involved in formation of the ferritin core.

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Supplementary Material Available: Tables of atomic positional and thermal parameters of **1**·1,4-dioxane·2MeCN and Figure S1, showing temperature-dependent magnetic susceptibility data for compound **1** (10 pages). Ordering information is given on any current masthead page.

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Articles

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nido-Carborane Building-Block Reagents. 1. Polycyclic Arene $RR'C_2B_4H_6$ Derivatives: Synthesis via Indenyl and Fluorenyl Alkynes and Metal-Promoted Oxidative Fusion

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The preparations of *C*-mono- and *C,C'*-bis(indenylmethyl) and *C*-mono- and *C,C'*-bis(fluorenylmethyl) derivatives of *nido*-2,3-dicarbahexaborane(8) ($C_2B_4H_8$) are described. These carboranes are multifunctional, presenting several aryl and carboranyl sites for metal η^5 or η^6 coordination, and are designed as structural modules for use in the construction of multiunit metal sandwich complexes and proposed electron-delocalized solid-state arrays. The carborane syntheses were conducted via the method of Hosmane and Grimes, involving the reaction of alkynes with B_5H_9 in the presence of $(C_2H_5)_3N$. However, these preparations required a priori the syntheses of the first known difluorenyl and diindenyl alkynes, as well as an improved synthesis of (9-fluorenylmethyl)acetylene. In the formation of the bis(indenylmethyl)acetylene from 1-lithioindene, an unexpected 1 → 2 rearrangement occurred to give the 2-substituted product exclusively. The new alkynes and carboranes were characterized via multinuclear NMR, IR, and mass spectroscopy, and the properties of the *nido*-$RR'C_2B_4H_6$ carboranes toward bridge deprotonation, complexation with Fe^{2+}, and subsequent fusion to generate $R_2R'_2C_4B_8H_8$ products were explored. All of the new $RR'C_2B_4H_6$ species are deprotonated by NaH in THF to give the $RR'C_2B_4H_5^-$ anions, and the monosubstituted anions (R = indenylmethyl, fluorenylmethyl; R' = H) undergo slow Fe^{2+}-promoted fusion to form $R_2C_4B_8H_{10}$. However, the disubstituted $R_2C_2B_4H_5^-$ anions do not fuse, owing to steric hindrance by the bulky R groups; the diindenyl species forms a complex of the type $(R_2C_2B_4H_4)Fe(THF)_x$ (x = 2 or 3), which does not react further. Treatment of the neutral diindenyl carborane with $FeCl_2$ gave in low yield an apparent intramolecular sandwich complex in which the iron is proposed to be η^5-coordinated to the C_5 rings of both indenyl groups.

Introduction

The *nido*-carborane 2,3-$C_2B_4H_8$ and its organosubstituted $RR'C_2B_4H_6$ derivatives are clearly useful to chemists in the boron cluster field, as the starting point in the synthesis of many diverse species including triple-decker sandwiches, large carboranes (e.g. C_4B_8 cages), and numerous transition-metal and main-group-metal complexes.[1] Recently, however, it has become apparent that the pyramidal $RR'C_2B_4H_4^{2-}$ and cyclic $RR'C_2B_3H_5^{2-}$ groups (generated from the neutral compounds) are also superb ligands for organometallic synthesis and open the way to construction of new types of complexes and extended π-systems that would be difficult or impossible to attain with hydrocarbon ligands alone.[2] The open C_2B_3 face of the pentagonal-pyramidal $RR'C_2B_4H_4^{2-}$ unit is

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[†] Undergraduate research participant, 1985–1987.

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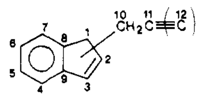
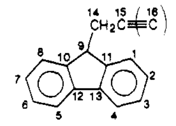
Table I. ^{1}H (360 MHz) and ^{13}C (90.5 MHz) NMR Data on Alkynes **1–4**

compd	^{1}H[a–d]	^{13}C[b–e]
1	2.47 [H(1), 1 H, dt, $J = 8.28, 7.92$], 6.73 [H(2), 1 H, d, $J = 5.40$], 6.99 [H(3), 1 H, d, $J = 5.04$], 7.50 [H(4), 1 H, d, $J = 7.20$], 7.43 [H(5), 1 H, t, $J = 7.38$], 7.68 [H(7), 1 H, d, $J = 7.20$], 2.76 [H(10), 2 H, m], 3.75 [H(12), 1 H, t, $J = 7.56$]	49.50 [C(11)], 132.22 [C(2)], 130.18 [C(3)], 119.62 [C(4)], 126.67 [C(5)], 125.54 [C(6)], 124.41 [C(7)], 144.69 [C(8)], 145.13 [C(9)], 18.13 [C(10)], 71.49 [C(11)], 70.54 [C(12)]
2[f]	3.38 [H(1), 2 H, s], 6.50 [H(3), 1 H, s], 7.42 [H(4), 1 H, d, $J = 7.56$], 7.31 [H(5), 1 H, t, $J = 7.38$], 7.23 [H(6), 1 H, t, $J = 7.38$], 7.48 [H(7), 1 H, d, $J = 7.20$], 3.52 [H(10), 2 H, s]	37.61 [C(1), td, $^1J = 128.2$, $^3J = 6.0$], 140.37 [C(2), s], 129.68 [C(3), dt, $^1J = 167.6$, $^3J = 5.0$], 119.44 [C(4), dd, $^1J = 158.8$, $^3J = 8.2$], 126.39 [C(5), dd, $^1J = 159.4$, $^3J = 7.2$], 125.19 [C(6), dd, $^1J = 157.5$, $^3J = 7.1$], 124.12 [C(7), dd, $^1J = 156.9$, $^3J = 8.3$], 144.63 [C(8), s], 144.92 [C(9), s], 18.32 [C(10), t, $^1J = 129.7$], 78.78 [C(11), s]
3	7.77 [H(1,8), 2 H, d, $J = 7.56$], 7.34 [H(2,7), 2 H, t, $J = 7.20$], 7.41 [H(3,6), 2 H, t, $J = 7.38$], 7.74 [H(4,5), 2 H, d, $J = 7.20$], 4.08 [H(9), 1 H, t, $J = 7.02$], 2.72 [H(14), 2 H, dd, $J = 2.52$, $J = 2.16$], 2.08 [H(16), 1 H, t, 2.52	125.39 [C(1,8)], 127.74 [C(2,7)], 128.23 [C(3,6)], 120.55 [C(4,5)], 46.43 [C(9)], 142.33 [C(10,11)], 143.99 [C(11,13)], 23.33 [C(14)], 82.94 [C(15)], 71.04 [C(16)]
4	7.73 [H(1,8), 2 H, d, $J = 7.56$], 7.28 [H(2,7), 2 H, t, $J = 8.28$], 7.37 [H(3,6), 2 H, t, $J = 7.38$], 7.58 [H(4,5), 2 H, d, $J = 7.20$], 3.96 [H(9), 1 H, t, $J = 7.00$], 2.72 [H(14), 2 H, d, $J = 6.84$]	125.44 [C(1,8)], 127.76 [C(2,7)], 128.09 [C(3,6)], 120.43 [C(4,5)], 46.93 [C(9)], 141.65 [C(10,11)], 147.12 [C(12,13)], 23.74 [C(14)], 80.18 [C(15)]

[a] In $CDCl_3$; in ppm relative to $SiMe_4$. [b] Coupling constants given in Hz. [c] Numbering scheme



1 and 2



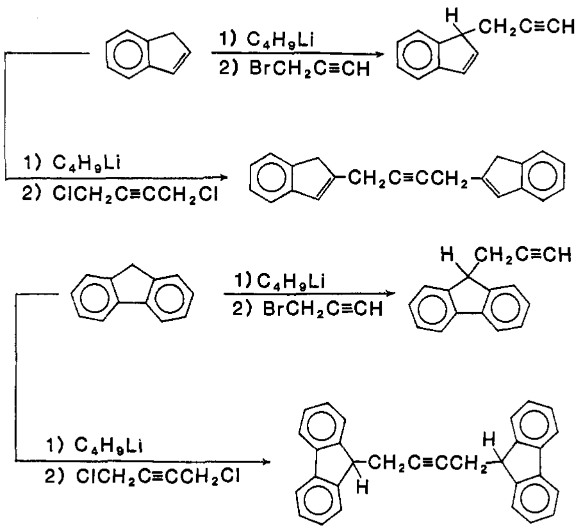
3 and 4

[d] Legend: t = triplet, d = doublet, s = singlet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets. [e] In acetone-d_6; in ppm relative to $SiMe_4$. [f] The ^{1}H and ^{13}C (^{1}H decoupled and undecoupled) spectra of **2** and indene, as well as the complete assignments of the peaks and schematic spin–spin splitting diagrams, are available as supplementary material.

electronically analogous to cyclopentadienides ($C_5R_5^-$) and arenes (all being formal six-electron donors), but the carboranes offer several practical advantages over the hydrocarbon ligands. The most significant are (i) their ability to stabilize metal–cyclic hydrocarbon complexes (particularly with high metal oxidation states) and to allow the isolation of neutral arene–metal–carborane species; (ii) their considerable synthetic versatility, of value in designed synthesis; (iii) the electron delocalization of the C_2B_4 framework, which should facilitate electron transfer between metal centers in polymetallic systems. These attributes are further enhanced if one attaches reactive substituents such as aryl groups to the C_2B_4 cage, thus broadening the synthetic possibilities still further.[2]

In several recent papers we have described how these properties of the $RR'C_2B_4H_6$ carboranes can be exploited to prepare multilevel arene–metal–carborane sandwich complexes[2,3] and have also reported on the bench-scale preparation of the dibenzyl derivative $(PhCH_2)_2C_2B_4H_6$, an air-stable liquid, and its metal chemistry.[2b,3b,e] From this work, it is apparent that a considerable potential exists for the systematic construction of multiligand, multimetal arrays of specified design based on carboranyl and carbocyclic building-block units. However, progress in this area clearly requires that one be able to prepare $C_2B_4H_8$ derivatives having desired functional groups attached at designated cage locations, and the present series of papers deals with this synthetic challenge. In this article we are concerned with derivatives having polycyclic aryl substituents, in which the properties of the organic ligands are reflected in the chemistry. Since the *C,C'*-dibenzyl derivative was shown in an earlier study[3b] to undergo bridge deprotonation to form the $(PhCH_2)_2C_2B_4H_5^-$ ion, Fe^{2+} complexation at the C_2B_3 face, and oxidative fusion to form $(PhCH_2)_4C_4B_8H_8$, as well as $Cr(CO)_3$ coordination at the phenyl rings, it was of interest to examine the corresponding properties of species having larger (especially polycyclic) aryl substituents. Accordingly, a study of indenyl- and fluorenylcarboranes was conducted as an appropriate next step in our investigation.

Scheme I



Results and Discussion

Preparation of Indenyl and Fluorenyl Alkynes and Carboranes. The reaction[4] of alkynes with B_5H_9 in the presence of triethylamine to form $RR'C_2B_4H_6$ via the net process

$$RC\equiv CR' + B_5H_9 \xrightarrow{Et_3N} RR'C_2B_4H_6 + Et_3N\cdot BH_3 \qquad (1)$$

is general and has worked with nearly all alkynes tried thus far, at least in our laboratory. However, alkynes containing indenyl or fluorenyl groups are not available from commercial sources and indeed are almost unknown, the only previously reported compounds being 3-(prop-2-ynyl)indene[5] and 9-(prop-2-ynyl)fluorene.[5] Consequently, the syntheses of *C,C'*-diindenyl- and *C,C'*-difluorenylcarboranes were dependent upon finding routes to their alkyne precursors. This was accomplished as shown in Scheme I, which depicts the routes to the monofluorenyl and monoindenyl compounds as well. Products **2** and **4** are the first

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Table II. Infrared Absorptions (cm^{-1})[a]

1[b]	3320 vs, 3090 vs, 3050 sh, 2990 sh, 2930 vs, 2890 sh, 2150 vs, 1960 w, 1920 w, 1810 w, 1710 w, 1665 w, 1620 m, 1580 w, 1470 vs, 1440 s, 1405 w, 1375 m, 1320 m, 1280 m, 1235 sh, 1205 w, 1180 m, 1160 sh, 1120 m, 1080 m, 1060 w, 1030 m, 1010 m, 950 s, 900 m, 880 m, 830 sh, 785 vs, 765 vs, 725 vs, 650 vs
2[c]	3100 m, 3070 m, 3050 m, 2930 m, 2910 m, 2840 w, 2800 w, 1960 w, 1935 w, 1905 w, 1880 w, 1850 w, 1825 w, 1790 w, 1790 w, 1710 m, 1680 w, 1640 w, 1625 s, 1590 w, 1570 sh, 1540 w, 1520 sh, 1475 vs, 1430 vs, 1415 s, 1400 s, 1375 sh, 1345 m, 1320 sh, 1310 sh, 1280 s, 1260 w, 1215 w, 1180 m, 1160 sh, 1130 w, 1110 w, 1045 m, 1025 m, 1000 w, 970 s, 960 sh, 930 s, 870 w, 850 w, 785 vs, 765 s, 730 vs, 705 sh, 630 w, 590 w, 560 w, 455 m, 425 m, 370 w, 275 sh
3[c]	3320 vs, 3090 s, 3060 s, 3040 sh, 2950 sh, 2920 m, 2860 w, 2140 m, 1960 m, 1920 m, 1865 w, 1820 m, 1750 s, 1725 s, 1660 w, 1630 sh, 1620 m, 1590 m, 1520 w, 1485 s, 1455 vs, 1435 s, 1375 m, 1325 m, 1305 m, 1280 m, 1245 m, 1230 m, 1215 m, 1180 w, 1160 w, 1110 m, 1040 m, 1010 m, 960 m, 940 w, 870 w, 790 sh, 765 vs, 745 vs, 650 s, 600 sh, 550 m, 450 m, 430 m, 340 m
4[c]	3100 m, 3070 m, 3050 m, 2780 sh, 2950 m, 2930 m, 2880 sh, 2860 w, 1950 w, 1925 w, 1910 w, 1855 w, 1805 w, 1730 w, 1660 w, 1615 w, 1590 w, 1490 m, 1460 vs, 1440 s, 1345 sh, 1320 m, 1285 m, 1255 w, 1215 w, 1180 w, 1160 w, 1110 w, 1040 m, 1015 m, 1000 w, 980 w, 960 sh, 940 m, 890 w, 860 w, 825 w, 795 sh, 770 vs, 750 vs, 735 sh, 680 w, 660 w, 630 m, 605 m, 560 m, 440 m, 320 w, 295 sh
5[b]	3010 w, 2960 m, 2900 vs, 2870 vs, 2800 s, 2550 s, 2330 w, br, 1780 m, 1430 s, 1350 m, 1140 m, 1095 w, 1075 w, 1055 w, 990 w, 950 m, 885 w, 815 m, 740 s, 730 w, 690 m, 570 w
6[b]	3057 s, 3042 s, 3019 s, 2955 s, 2923 s, 2885 s, 2856 w, 2597 vs, 1936 m, 1914 w, 1886 w, 1610 m, 1576 w, 1461 vs, 1397 s, 1364 m, 1257 m, 1158 m, 1122 m, 1104 m, 1048 m, 1019 m, 980 s, 951 s, 915 s, 900 m, 849 m, 822 m, 770 vs, 751 sh, 718 vs, 654 m
7[b]	3083 s, 3073 s, 3039 s, 3008 m, 2979 m, 2944 m, 2931 m, 2888 m, 2540 w, 2534 w, 2390 s, 2352 m, 2340 m, 2341 m, 1812 m, 1557 w, 1545 w, 1480 s, 1452 s, 1391 m, 1311 w, 1289 w, 1187 m, 1156 s, 1038 s, 1017 w, 1004 w, 828 vs, 807 vs, 803 vs, 797 vs, 785 vs, 774 vs, 759 vs, 738 vs, 725 vs, 677 vs
8[b]	3066 s, 3040 s, 3019 s, 2956 vs, 2924 vs, 2870 vs, 2855 vs, 2597 vs, 1944 m, 1908 m, 1607 m, 1581 m, 1478 vs, 1456 s, 1450 vs, 1403 w, 1378 m, 1355 m, 1340 m, 1337 m, 1318 m, 1300 m, 1271 w, 1232 w, 1198 m, 1187 m, 1154 m, 1100 m, 1032 m, 1008 m, 985 m, 953 m, 939 m, 914 m, 846 m, 789 m, 780 m, 774 m, 757 vs, 739 vs, 728 vs, 663 m, 653 m, 645 m, 638 m, 621 s
9[d]	3078 m, 3058 m, 2956 m, 2928 s, 2856 m, 2580 m, br, 1984 w, 1961 w, 1956 w, 1940 w, 1795 w, 1534 m, 1527 w, 1511 m, 1496 m, 1458 s, 1396 s, 1332 m, 1312 m, 1288 m, 1156 m, 1123 m, 1069 m, 1019 m, 949 m, 926 m, 915 m, 861 m, 775 vs, 692 s, 550 m
10[d]	3114 w, 3089 m, 3031 m, 2930 m, 2865 w, 2582 vs, 1944 w, 1929 w, 1600 m, 1590 w, 1488 s, 1455 s, 1432 w, 1323 w, 1268 m, 1088 m, 1060 m, 1050 m, 1015 w, 999 w, 919 w, 878 w, 830 s, 790 vs, 720 m, 703 s, 643 w, 603 w, 544 w, 511 w

[a] Key: s = strong, m = moderate, w = weak, v = very, sh = shoulder. [b] Neat liquid. [c] KBr pellet. [d] CCl_4 solution vs CCl_4.

Table III. 115.8-MHz ^{11}B FT NMR Data[a]

compd	δ (J_{BH}, Hz)[b]	rel areas
5	−0.01 (167), −2.62 (148), −49.92 (177)	1:2:1
6	−1.71,[c] −3.63 (140), −47.42 (175)	1:2:1
7	−0.64 (164), −3.33 (145), −50.95 (178)	1:2:1
8	−3.52,[c] −46.02 (184)	3:1
9	−2.17 (120), −12.17 (142)	3:1
10	−2.15 (120), −12.10 (141)	3:1
12	−0.98 (151), −5.44 (172), −46.59 (173)	1:2:1

[a] CH_2Cl_2 solution. [b] Shifts relative to $BF_3{\cdot}Et_2O$, positive values downfield. [c] Unresolved.

Table IV. 360-MHz ^1H FT NMR Data on Carboranes

compd[a]	δ[b,c] (J, Hz)	rel areas
5	[7.47 d (7.2 Hz), 7.38 d (7.2 Hz), 7.29 t (7.02 Hz), 7.20 t (7.4 Hz)] {indenyl C_6 ring}, 6.98 m {indenyl H(3)}, 6.29 s {indenyl H(2)}, 6.20 br {cage CH}, 3.74 m {indenyl H(1)}, 3.38 m {CH_2}	[4]:1:1:1:1:2
6	[7.45 d (8.3 Hz), 7.38 d (8.3 Hz), 7.29 t (7.4 Hz), 7.25 t (7.4 Hz)] {indenyl C_6 ring}, 6.17 s {indenyl H(3)}, 3.74 m {indenyl H(1)}, 3.28 m {CH_2}	[4]:1:2:2
7	[7.85 d (7.8 Hz), 7.77 d (7.8 Hz), 7.57 m, 7.40 m, 7.33 m] {fluorenyl C_6 ring}, 3.94 m {fluorenyl H(9)}, 2.31 m {CH_2}	[8]:1:2
8	[7.78 d (8.6 Hz), 7.73 d (9.7 Hz), 7.39 t (8.5 Hz), 7.32 m, 7.11 t (8.0 Hz)] {fluorenyl C_6 ring}, 4.38 t {fluorenyl H(9)}, 2.83 m {CH_2}	[8]:1:2
9	[7.49 d (7.2 Hz), 7.42 d (7.2 Hz), 7.28 t (7.2 Hz), 7.20 t (7.2 Hz)], 6.90 m {indenyl H(3)}, 6.57 m {indenyl H(2)}, 3.41 s {indenyl H(1)}, 2.18 s {CH_2}	[4]:1:1:1:2
10	[7.38 m, 7.32 d (7.9 Hz), 7.27 s, 7.21 s, 7.17 d 7.2 Hz), 6.99 d (7.2 Hz)] {fluorenyl C_6 ring}, 3.47 dd (69.1, 7.6 Hz) {fluorenyl H(9)}, 2.17 s {CH_2}	[8]:1:2

[a] $CDCl_3$ solutions. [b] Legend: s = singlet, m = multiplet, d = doublet, dd = doublet of doublets, t = triplet, br = broad. [c] Relative to $SiMe_4$.

reported diindenyl and difluorenyl alkynes, respectively, and **1** is a new isomer; the synthesis of **3** represents an improvement over that in the literature.[6] The four alkynes were fully characterized from their ^1H and ^{13}C NMR spectra (Table I), IR spectra (Table II), and mass spectra. The isomer of the diindenyl alkyne **2** was surprising in that substitution occurs at the 2-position on the indene, indicating a 1 → 2 rearrangement in the course of the synthesis; this was not explored further, but the identity of **2** was unambiguously established (see Experimental Section).

The mono- and diindenylalkynes and their fluorenyl counterparts were converted to the respective *nido*-$RR'C_2B_4H_6$ carboranes **5**–**8** (Scheme II) by reaction with B_5H_9 and triethylamine according to reaction 1. The four products were purified by chromatography and obtained in 1–4-g quantities as yellow viscous liquids of low volatility that survive exposure to air for extended periods of time. The monosubstituted species **5** and **7** slowly degrade in air over several days, while the disubstituted compounds are stable to atmospheric oxygen for months. The structural characterization is supported by high-resolution ^1H and ^{11}B NMR spectra (Tables III and IV), IR spectra (Table II), and unit- and high-resolution mass spectra. The ^{11}B spectra of all four compounds exhibit the characteristic pattern of *nido*-C_2B_4 carboranes, with apex [B(1)] resonances appearing near δ −50.

Metal Complexation and Oxidative Fusion Properties of (Indenylmethyl)- and (Fluorenylmethyl)carboranes. Compounds **5**–**8** on treatment with NaH in THF each underwent clean deprotonation to remove a B–H–B bridging proton, forming the corresponding $RR'C_2B_4H_5^-$ anion (Scheme II). Although this reaction is typical of *nido*-$RR'C_2B_4H_6$ compounds, it proceeds more slowly in species such as **5**–**8**, which contain bulky R groups, in comparison to derivatives having small substituents such as $Et_2C_2B_4H_6$. This effect has been interpreted by us in a recent kinetic study[7] as primarily steric in nature insofar as **5**–**8** are concerned, with little indication of electronic influence by the organic groups. More profound steric consequences were observed when the anions **5**$^-$–**8**$^-$ were reacted with $FeCl_2$ and exposed to air. As shown in Scheme II, the monosubstituted carboranes **5**$^-$ and **7**$^-$ formed bis(carboranyl)iron(II) dihydride complexes that fused on oxidation to give the bis(indenylmethyl) and bis(fluorenylmethyl) tetracarbon carboranes **9** and **10**, respectively; these reactions parallel those previously observed for other *nido*-

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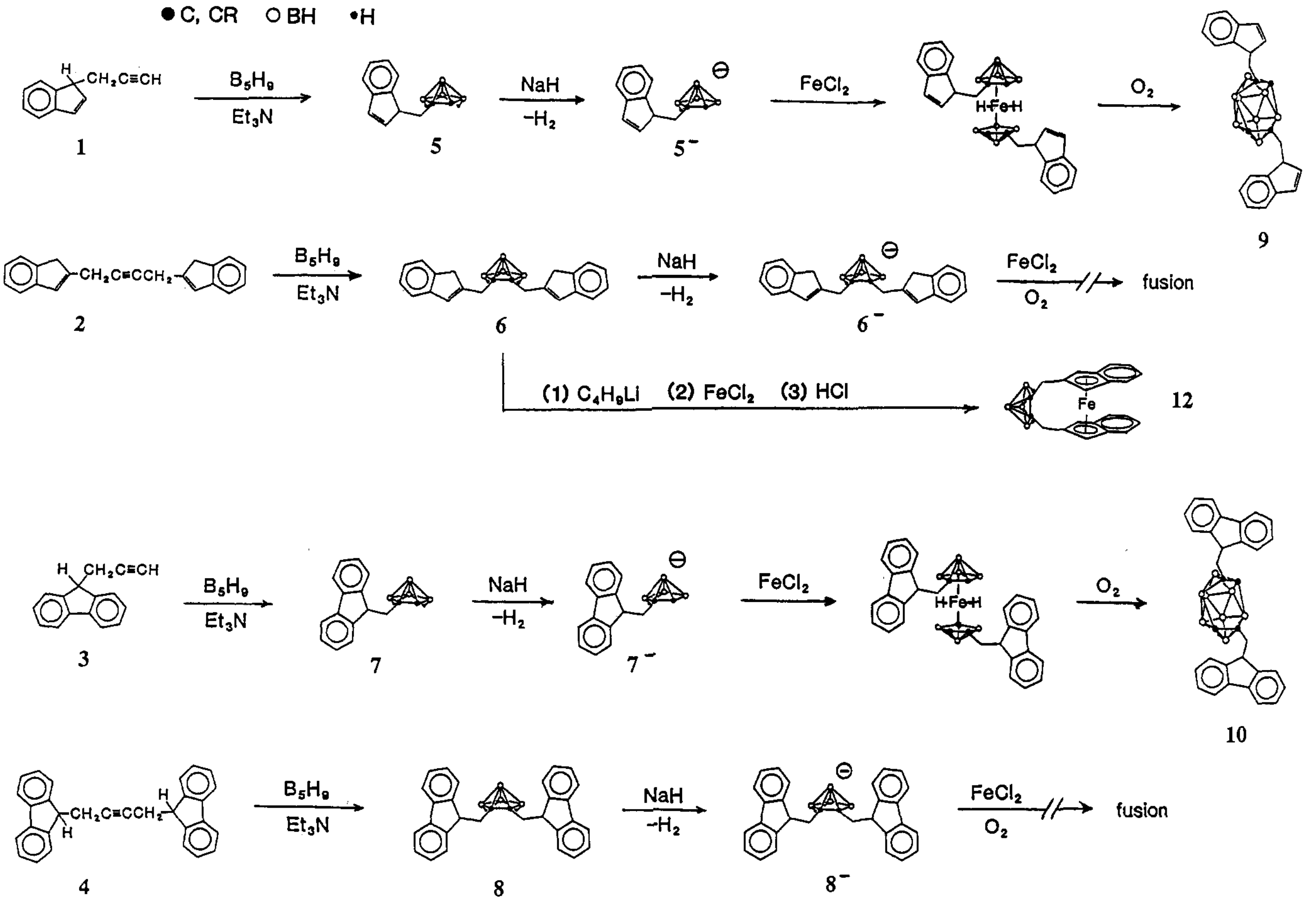
(6) Gautier, J. A.; Miocque, M.; Moskowits, H. *Bull. Soc. Chim. Fr.* **1965**, 1736.

(7) Fessler, M. E.; Whelan, T.; Spencer, J. T.; Grimes, R. N. *J. Am. Chem. Soc.* **1987**, *109*, 7416.

Scheme II



$RR'C_2B_4H_6$ species.[8] However, the disubstituted ions **6⁻** and **8⁻** on similar treatment gave no evidence of fused products ($R_4C_4B_8H_8$), a result reminiscent of the behavior of the bis(tricarbonylchromium-benzyl)carborane $[(CO)_3Cr]_2(PhCH_2)_2C_2B_4H_5^-$, which also failed to fuse although its monometalated counterpart $(CO)_3Cr(PhCH_2)_2C_2B_4H_5^-$ did fuse.[3e]

In the case of the bis(fluorenylmethyl) carborane anion **8⁻**, there was little indication of reaction with $FeCl_2$, $CoCl_2$, or $NiBr_2$ and the starting material was recovered unchanged. The bis(indenylmethyl) anion **6⁻**, however, on treatment with $FeCl_2$ yielded unstable, dark purple **11**, whose mass spectrum indicated the composition $[(C_9H_7CH_2)_2C_2B_4H_4]Fe(THF)_x$ ($C_9H_7CH_2$ = indenylmethyl), suggestive of a "half-sandwich" complex; this material could not be further characterized and did not undergo further reaction to generate a bis(carboranyl)iron complex.

The fusion products **9** and **10** were isolated chromatographically and characterized from their NMR, IR, and mass spectra (Tables II–IV). In principle, three geometric isomers are possible for each compound arising from different locations of attachment of the two organic groups to the four cage carbon atoms, assuming that the geometry of the C_4B_8 skeleton is the same as that previously established in $Et_4C_4B_8H_8$[9] and $(PhCH_2)_2C_4B_8H_8$.[3b] However, there is no indication of isomers (other than enantiomers) in either case. Also, no evidence of cage rearrangement or fluxional behavior in solution, such as that observed[9] in $Me_4C_4B_8H_8$, $Et_4C_4B_8H_8$, and $Pr_4C_4B_8H_8$, was noted in **9** and **10**. All of these findings are readily explained in terms of steric effects arising from the bulkiness of the indenylmethyl and fluorenylmethyl substituents: the disubstituted carboranes **6** and **8** are prevented from forming bis(carboranyl)metal complexes, and hence from fusing, while the monosubstituted compounds **5** and **7** are able to fuse but form nonfluxional products. It is relevant to note that the tetrabenzylcarborane $(PhCH_2)_4C_4B_8H_8$ is similarly nonfluxional,[3b] as are its bis(tricarbonylchromium) complexes referred to above.

Preparation of a Ferrocenophane-Type Sandwich Complex. The geometry of **6** suggested that a first-row transition-metal atom could sandwich-bond to both indenyl groups, via the C_5 and/or C_6 rings, with good metal–ligand orbital overlap and with the indenes parallel to each other; however, η^5 coordination of the C_5 rings would require prior deprotonation to render them aromatic. Accordingly, neutral **6** was first treated with 3 equiv of *n*-butyllithium to remove the acidic indenyl protons and one B–H–B bridging proton.[10] After reaction with $FeCl_2$ followed by reprotonation of the cage with HCl, elution of the product mixture in hexane on silica gave **12** in low yield as a red solid. The composition of **12** was determined from its mass spectrum as $Fe[(C_9H_7CH_2)_2C_2B_4H_6]$, and the ^{11}B NMR spectrum is very similar to that of the original carborane **6**, indicating that the *nido*-C_2B_4 cage is not coordinated to the metal. Hence, it is proposed that the Fe^{2+} in this neutral, diamagnetic complex is sandwiched between the five-membered rings of the indenyl groups, as proposed in Scheme II. Crystallographic confirmation of this structure is clearly desirable.

The bulk of the product mixture was a red-orange material that resisted elution on silica and appeared to consist of high-molecular-weight species, possibly oligomers or polymers containing multiple indenylcarboranyl units linked by iron atoms.

Conclusions

The properties of the polycyclic aryl-substituted carboranes examined in this work are of interest on two levels. First, their behavior with respect to metal complexation and metal-promoted fusion extends and confirms the trends noted in earlier work on bulky-substituent $RR'C_2B_4H_6$ carboranes, in which the propensity

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(8) Maynard, R. B.; Grimes, R. N. *J. Am. Chem. Soc.* **1982**, *104*, 5983.

(9) Venable, T. L.; Maynard, R. B.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 6187.

(10) Since the B–H–B protons are more acidic than are the H(1) indenyl protons, **6** must first be converted to the monoanion **6⁻** via bridge deprotonation before the H(1)'s can be removed with *n*-butyllithium.

to undergo fusion decreases as the steric demands of R and R′ are increased.[2,3e] A fairly clear and consistent pattern is emerging: $RR'C_2B_4H_5^-$ ions having small R (R′) groups (e.g., methyl, ethyl) react rapidly with Fe^{2+}, and the resulting $(RR'C_2B_4H_4)FeH_2$ complexes, on exposure to air, form $R_2R'_2C_4B_8H_8$ via fusion almost instantaneously, while somewhat larger groups (e.g., benzyl) slow both processes but do not prevent them. Still bulkier substituents, such as $(CO)_3CrPhCH_2$, *when present as both R and R′*, block fusion completely; however, thus far we have not observed fusion blockage with any monosubstituted carborane ligand ($RC_2B_4H_5^{2-}$) even when R is quite large. Thus, in the present work, the mono(indenylmethyl)- and mono(fluorenylmethyl)carboranes are fusable but their disubstituted counterparts are not. It is apparent that large R groups interfere with the approach of metal ions to the open C_2B_3 face of the cage and in some cases, such as the bis(fluorenylmethyl) species **8**, evidently preclude even metal complexation.[11] The bis(indenylmethyl) carborane **6**⁻, on the other hand, does coordinate to Fe^{2+} but only to the extent of forming a half-sandwich; a second **6**⁻ ion does not bind to the metal. The fact that failure to complex and/or fuse has been observed only with certain disubstituted carborane ligands suggests that even when R is very large it is possible to η^5-coordinate two *mono*substituted $RC_2B_4H_5^{2-}$ ligands to a metal ion provided the R groups on the respective carborane units are attached to the "outer" cage carbon atoms, as proposed in Scheme II. Inspection of models confirms that the alternative placement of both very large R substituents on the "inner" carbons would create unacceptable steric crowding.

We have applied the same argument to the tricarbonylchromium–benzyl-substituted system,[3e] which on fusion yields two $[(CO)_3Cr]_2(PhCH_2)_4C_4B_8H_8$ isomers that are proposed to have "outer–outer" and "outer–inner" structures, respectively. The observation that fusion of **5** and **7** in the present work gave only one detectable $R_2C_4B_8H_{10}$ isomer in each case may reflect differences in the steric (or, less probably, electronic) influence of the organic substituents in the latter species, as opposed to that of tricarbonylchromium–benzyl compounds. There is also the possibility that isomers of **9** and **10** *are* present but could not be detected, so that caution is in order in comparing these results.

The second aspect on which we will comment briefly is the relevance of these findings to designed synthesis. Clearly, by selection of an appropriate *nido*-carborane ligand it is now possible to arrest the deprotonation–complexation–fusion sequence at a desired point; this should enable the preparation of some kinds of heretofore inaccessible species. For example, although the half-sandwich **11** will not accept a second bis(indenylmethyl)carborane ligand, it may well be feasible to displace the THF ligands with a less sterically demanding carborane (or noncarborane unit). Another possibility is to exploit the chemistry of bulky-ligand-monosubstituted carboranes such as **5** and **7** in asymmetric synthesis, via mixed-ligand (carborane–metal–organic ligand) diastereomeric complexes.

The observations on *nido*-$(polyarylCH_2)_2C_2B_4H_6$ species in this study raise further questions about the correlation between structure and reactivity in *nido*-C_2B_4 carborane derivatives, particularly as it concerns the use of these materials in tailored synthesis. Accordingly, we have investigated several related classes including (1) the diphenyl compound $Ph_2C_2B_4H_6$ (in which the aryls are attached directly to the cage), (2) long-chain dialkyl derivatives, (3) linear or cyclic oligomers incorporating two or more *nido*-$C_2B_4H_6$ units, and (4) systematically prepared boron-substituted $R_2C_2B_4H_xR'_{6-x}$ derivatives. These findings are described in the accompanying papers[12,13] and in other work.[14]

Experimental Section

Materials. Solvents were anhydrous grade and were stored over 4-Å molecular sieves prior to use. Deuteriated solvents were purchased from Aldrich. Indene, fluorene (*o,o′*-diphenylenemethane), propargyl bromide, 1,4-dichloro-2-butyne, and *n*-butyllithium, were obtained from Aldrich and used as received. B_5H_9 was obtained from a U.S. Government stockpile.

Instrumentation. ^1H (360 MHz), ^{11}B (115.8 MHz), and ^{13}C (90.5 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 recorded in chloroform-d_1 in 5-mm (o.d.) tubes. Routine ^1H 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-4600 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). Elemental analyses were obtained from the Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Preparation of 1-(Prop-2-ynyl)indene (1). The metalation of indene was carried out by using a procedure similar to that of Sommer and Marans.[15] To a stirred solution of 133 mL of a 2.6 M *n*-butyllithium–hexane solution (0.344 mol) under a dry nitrogen atmosphere was added dropwise a solution of 39.9 g of indene (0.344 mol) in 100 mL of dry hexane. The reaction was stirred for 3 h, during which time a slightly exothermic reaction occurred, producing a white precipitate. This mixture was diluted with 400 mL of *n*-hexane to allow more efficient stirring. After the reaction mixture had cooled to room temperature, a solution of 51.0 g of 80% propargyl bromide in toluene (0.344 mol) was added slowly to the reaction mixture. An exothermic reaction ensued in which the reaction mixture became light brown, and the mixture was stirred overnight. Water was then carefully added to the reaction mixture and the solution extracted with ether. The solvent was evaporated, and the resulting brown oil was distilled under vacuum to obtain 38.7 g of **1** (73% yield, bp 120 °C (0.01 Torr)). Material of high purity was obtained either by TLC or column chromatography using silica gel and a 15% methylene chloride in hexane solution as eluant (R_f 0.69). MS (*m/z* (relative intensity)): 155 (M^+ + 1, 9.5), 154 (M^+, 100), 129 (1.3), 128 (5.1), 117 (3.8), 115 (93.0), 113 (3.8). Anal. Calcd for $C_{12}H_{10}$: C, 93.5; H, 6.5. Found: C, 93.1; H, 6.4.

Preparation of 1,4-Bis(2-indenyl)-2-butyne (2). A 20.0-g amount of indene (0.172 mol) was reacted with 66.6 mL of 2.6 M butyllithium (0.172 mol) in a manner analogous to the lithiation reaction described in the previous synthesis. To the stirred solution of lithioindene at room temperature was added 10.5 g of 1,4-dichloro-2-butyne (0.085 mol) in 40 mL of hexane over a 1-h period. A vigorously exothermic reaction occurred during this addition and the mixture became light brown. After the reaction mixture cooled to room temperature, 1 L of ether and 1 L of water were added slowly and the mixture extracted. The organic layer was collected and excess ether evaporated. The remaining oil was then heated to 190 °C at 10^{-3} Torr to distill out low-boiling impurities. When it was cooled, the oil in the pot solidified and was recrystallized from ethanol to give 16.3 g (68%) of the pale yellow product, mp 81.5 °C.

Final purification was accomplished by TLC or column chromatography with silica gel, using 15% methylene chloride in hexane eluant (R_f 0.58), to yield a colorless, crystalline solid. MS (*m/z* (relative intensity)): 283 (M^+ + 1, 24.2), 282 (M^+, 98.7), 167 (40.1) 153 (18.5) 141 (12.7), 115 (100), 114 (15.3). Anal. Calcd for $C_{22}H_{18}$: C, 93.6; H, 6.4. Found: C, 93.4; H, 6.6.

Identification of **2** as the 2-substituted isomer was surprising but was established unambiguously from its ^1H and ^{13}C NMR spectra (supplementary material). In the 360-MHz ^1H NMR spectrum of **2** several features are noteworthy: (1) the H(2) resonance of indene[16] is absent;

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(11) The similarity in this trend to that previously observed[7] in the bridge deprotonation of these compounds by NaH is obvious and reinforces the idea that both types of processes are largely sterically controlled by the R groups.

(12) Boyter, H. A., Jr.; Grimes, R. N. *Inorg. Chem.*, following paper in this issue.

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(2) the H(1) and H(2) resonances of **2** are singlets, indicating nonadjacent locations of substitution; (3) the resonance for H(10) also appears as a singlet, further ruling out substitution at the 1-position. Other peaks are also consistent with the proposed structure and were assigned (with couplings) by analogoy to the literature assignments of indene.[16]

The 90.8-MHz ^{13}C NMR spectrum of **2** further confirms this structural assignment. In **2**, the resonance for C(2) shifts downfield relative to that for indene with a concomitant decrease in intensity, consistent with the quaternary character of C(2). Moreover, the C(3) resonance shifts slightly upfield, in agreement with the ^{13}C NMR spectra of other 2-substituted indenyl systems.[17] Further evidence is obtained from the ^{1}H-undecoupled ^{13}C spectrum of **2**, in which the C(2) resonance remains a singlet (indicating no directly bound hydrogen) while C(3) is split into a doublet with a coupling constant very similar to that seen in indene[17] itself. The C(1) and C(10) resonances are triplets with coupling constants (and chemical shifts) characteristic of methylene carbon atoms. All other peaks in the spectrum have been assigned and are consistent, in both chemical shifts and multiplicities, with 2-substitution.

Preparation of 9-(Prop-2-ynyl)fluorene (3). In a previously reported procedure[18] a solution of 50 mL of 2.6 M butyllithium (0.130 mol) was stirred under a dry nitrogen atmosphere and a total of 21.6 g of fluorene (0.130 mol) was added in 3-g quantities over 4 h. The slightly warm reaction mixture was stirred for an additional 2 h, after which 19.3 g of 80% propargyl bromide in toluene (0.130 mol) was added to the bright yellow solution and the reaction mixture was allowed to cool to room temperature. One liter of diethyl ether and 1 L of water were carefully added to the reaction mixture, and the organic layer was separated and dried over $MgSO_4$. Removal of solvent yielded a dark brown oil. From this residue was distilled a pale green fraction, which solidified upon standing to give 19.9 g (75% yield) of slightly light-sensitive, pale green crystals: mp 94–95 °C; bp 183 °C (0.01 Torr). High-purity material was obtained by TLC or column chromatography using silica gel eluted with 15% methylene chloride in hexane (R_f 0.56). MS (m/z (relative intensity)): 205 (M^+ + 1, 8.0), 204 (M^+, 39.5), 165 (100), 139 (7.0), 115 (5.7). Anal. Calcd for $C_{16}H_{12}$: C, 94.1; H, 5.9. Found: C, 92.5; H, 6.4.

Preparation of 1,4-Bis(9-fluorenyl)-2-butyne (4). A 26.1-g amount of fluorene (0.157 mol) was reacted with 60.5 mL of 2.6 M butyllithium (0.157 mol) following the procedure described in the preparation of **3**. To the solution of lithiofluorene was added slowly 9.66 g of 1,4-dichloro-2-butyne (0.079 mol). During the exothermic reaction a tan precipitate was produced, and the reaction mixture was stirred overnight. To the reaction mixture were carefully added 1 L of water and 1 L of diethyl ether, and the ether layer was separated and dried with $MgSO_4$. Removal of the ether gave a tan solid from which **4** was obtained by three crystallizations from ethanol or by dry column chromatography[19] with hexane as eluant (R_f 0.10). Pure **4** was obtained as 16.9 g (56% yield) of a tan powder, mp 112 °C. High-purity material was obtained by either TLC or column chromatography with silica gel and 15% methylene chloride–hexane as eluant (R_f 0.41). MS (m/z (relative intensity)): 383 (M^+ + 1, 11.5), 382 (M^+, 53.8), 217 (39.7), 203 (7.7), 179 (9.0), 165 (100). Anal. Calcd for $C_{30}H_{22}$: C, 94.2; H, 5.8. Found: C, 92.3; H, 5.9.

Preparation of 2-(1-Indenylmethyl)-*nido*-2,3-dicarbahexaborane(8) (5). Into a 500-mL Pyrex reactor bulb[4b] were placed 50 mmol (7.70 g) of **1**, 50 mmol (5.05 g) of triethylamine, and 150 mL of dry benzene. The bulb was degassed by evacuating at liquid-nitrogen temperature, after which the stopcock was closed, the reactor warmed to room temperature and then refrozen in liquid nitrogen, and the process repeated twice. Pentaborane(9) (50 mmol) was condensed into the bulb at −196 °C, and the reactor was warmed to 0 °C and maintained at that temperature overnight; the reaction mixture was a viscous, dark caramel liquid that could not be stirred at 0 °C. The bulb was placed in an oil bath and heated to 55 °C for 3 days with stirring, during which a colorless, clear liquid refluxed on the reactor walls. Following this period, the bulb was placed on a vacuum line, evacuated to remove excess B_5H_9, and opened under nitrogen in a hood, the contents were extracted with warm hexane to give a pale yellow oil, which was purified by repeated chromatography on silica in hexane. The yield of pure **5** was 2.01 g (9.93 mmol, 20% based on B_5H_9 employed). Exact mass for $^{12}C_{12}{}^{11}B_4{}^{1}H_{16}{}^+$: calculated, 204.1624; found, 204.1628.

Preparation of 2,3-Bis(2-indenylmethyl)-*nido*-2,3-dicarbahexaborane(8) (6). The above procedure was followed to effect reaction of 50 mmol of the diindenyl alkyne **2** with 50 mmol each of B_5H_9 and triethylamine in 150 mL of benzene. Extraction with benzene followed by chromatography in hexane on silica gave 3.85 g (11.6 mmol, 23%) of **6** as a pale yellow oil. Exact mass for $^{12}C_{22}{}^{11}B_4{}^{1}H_{24}{}^+$: calculated, 332.2250; found, 332.2264.

Preparation of 2-(9-Fluorenylmethyl)-*nido*-2,3-dicarbahexaborane(8) (7). The above procedure was used to react 30 mmol each of the monofluorenylalkyne **3**, B_5H_9, and triethylamine in 50 mL of hexane. Extraction of the reaction mixture with THF and chromatography in hexane on silica gave 1.21 g (4.76 mmol, 16%) of **7** as a yellow-orange oil. Exact mass for $^{12}C_{16}{}^{11}B_4{}^{1}H_{18}{}^+$: calculated, 254.1781; found, 254.1804.

Preparation of 2,3-Bis(9-fluorenylmethyl)-*nido*-2,3-dicarbahexaborane(8) (8). A bulb was charged with 50 mmol each of the difluorenylalkyne **4**, B_5H_9, and triethylamine and 150 mL of benzene, and the reaction was conducted as above. Extraction of the mixture with hot hexane and purification with hexane on silica gave 3.92 g (9.11 mmol, 18%) of **8** as a yellow-orange oil. Exact mass for $^{12}C_{30}{}^{11}B_4{}^{1}H_{28}{}^+$: calculated, 432.2563; found, 432.2572.

Conversion of 5 to $(C_9H_7CH_2)_2C_4B_8H_{10}$ (9) via Metal Complexation and Fusion. In a procedure previously described for other *nido*-carborane fusions,[20] 0.72 g (3.55 mmol) of **5** was deprotonated via reaction with excess NaH in 50 mL of anhydrous THF. After H_2 evolution had ceased, the solution containing **5**$^-$ ion was filtered in vacuo onto 0.22 g (1.78 mmol) of $FeCl_2$ and this mixture was stirred. After 20 min no undissolved $FeCl_2$ remained, and the solution was deep purple; this color remained through 4 h of stirring. On removal of solvent, the purple solid was analyzed mass spectroscopically to confirm that it was in fact $[(C_9H_7CH_2)_2C_2B_4H_4]_2FeH_2$ (Scheme II), analogous to previously reported bis(carboranyl)iron dihydride complexes that are intermediates in the fusion process.[8] A unit-resolution spectrum gave an intense parent group (base peak at m/z 461, cutoff at 463) with a profile matching almost exactly the calculated pattern for the above composition, based on natural isotopic distributions. On exposure of the solid to air, the solid turned brown within seconds. Chromatography of this material on a silica plate in hexane gave 0.29 g of recovered **5** and 79 mg (0.172 mmol, 17% based on carborane consumed) of **9** as a white solid. The composition of **9** was established from its mass spectrum (parent-group cutoff at m/z 405 with a profile consistent with the calculated peak intensities), ^{11}B NMR spectrum, and ^{1}H NMR spectrum; the ^{11}B pattern is typical of *nido*-C_4B_8 cage frameworks of the "open" type,[9] as depicted in Scheme II. TLC and NMR observations gave no indication of the presence of more than one isomer.

Conversion of 7 to $(C_{13}H_9CH_2)_2C_4B_8H_{10}$ (10). The above procedure was employed to deprotonate 1.50 g (5.90 mmol) of **7** and fuse the resulting **7**$^-$ anion via complexation with Fe^{2+} to give, following air oxidation and purification on a silica TLC plate, 107 mg (0.21 mmol, 12%) of white **10**. The mass spectrum exhibits a parent group cutoff at m/z 506 with a pattern consistent with the calculated spectrum, and the two-peak ^{11}B NMR spectrum is indicative of an open-type C_4B_8 cage;[8] again, there was no evidence for more than one isomer.

Attempted Fusion of the Bis(indenylmethyl)carborane 6. A number of experiments under a variety of conditions were conducted, typically involving deprotonation of 0.3–1.0 g of **6** with excess NaH in THF followed by addition of the filtered solution of **6**$^-$ ion to $FeCl_2$, $CoCl_2$, or $NiBr_2$. In a typical reaction with $FeCl_2$, the mixture was warmed from −53 °C to room temperature over 4 h and then stirred overnight. Within 20 min of reaching room temperature, the brown suspension began to change to a ruby red solution. When it was stirred overnight, the solution became deep purple. In different experiments, both the red and the purple solutions failed to give $R_4C_4B_8H_8$ products on exposure to air, nor was any further color change observed. When O_2 was bubbled through the purple solution, a trace of uncharacterizable brown material was obtained and 43% of the original carborane (**6**) was recovered. A mass spectrum of the purple solid exhibited a high-mass group with cutoff at m/z 533 and a pattern consistent with the composition $[(C_9H_7CH_2)_2C_2B_4H_4]Fe(THF)_2{}^+$ (**11**) with major fragments at m/z 461, corresponding to loss of one THF, and m/z 332, arising from uncomplexed **6**. Since the group at m/z 533 does not necessarily represent the molecular ion, the number of THF ligands cannot be precisely given.

No evidence of a fused product was seen on mass spectroscopic assays of the materials remaining even after treatment with other oxidants, including $FeCl_3$, permanganate ion, and dichromate ion.

Attempted Fusion of the Bis(fluorenylmethyl)carborane 8. A series of experiments similar to those described in the preceding section was conducted with $FeCl_2$ as the metal salt. Although a faint red color was produced on addition of the **8**$^-$ ion to $FeCl_2$, refluxing of this solution failed to produce a purple color analogous to that observed with the bis(indenylmethyl)carborane (above) or any other color change. No fused product was obtained after refluxing in air or under an O_2 atmo-

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sphere, and 50–60% of the original **8** was recovered.

Preparation of $Fe(C_9H_7CH_2)_2C_2B_4H_6$ (12). In an apparatus identical with that employed for the fusion reactions,[20] 0.15 g (0.40 mmol) of **6** was added to 30 mmol of *n*-butyllithium in 250–300 mL of THF and the solution warmed to 50 °C. After 8 h the solution was added to 0.05 g (0.40 mmol) of anhydrous $FeCl_2$ and refluxed for 8 h. After addition of a molar excess of dry HCl gas, the bulb was placed on a rotary evaporator and the solvent removed. Chromatography in hexane on preparative silica plates gave 18 mg of **12** as a bright red solid. The indicated composition was established from its mass spectrum (very strong parent group with a high mass cutoff at *m/z* 387), which matches the calculated spectrum virtually exactly, and its ^{11}B NMR spectrum, which is very similar to that of uncomplexed **6**. A considerable amount of orange-red material remained at the origin of the plate and did not elute with hexane, although a small portion moved very slowly in dichloromethane.

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Supplementary Material Available: Proton and ^{13}C NMR spectra for the diindenyl alkyne **2** with complete assignments of all shifts and couplings (3 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Virginia, Charlottesville, Virginia 22901

nido-Carborane Building-Block Reagents. 2. Bulky-Substituent $(alkyl)_2C_2B_4H_6$ Derivatives and $(C_6H_5)_2C_2B_4H_6$: Synthesis and Properties[1]

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The preparation and chemistry of *nido*-2,3-$R_2C_2B_4H_6$ carboranes in which R is *n*-butyl, isopentyl, *n*-hexyl, and phenyl was investigated in order to further assess the steric and electronic influence of the R groups on the properties of the *nido*-C_2B_4 cage, especially with respect to metal complexation at the C_2B_3 face and metal-promoted oxidative fusion. The three dialkyl derivatives were prepared from the corresponding dialkylacetylenes via reaction with B_5H_9 and triethylamine, but the diphenyl compound could not be prepared in this manner and was obtained instead in a thermal reaction of B_5H_9 with diphenylacetylene in the absence of amine. All four carboranes are readily bridge-deprotonated by NaH in THF, and the anions of the dialkyl species, on treatment with $FeCl_2$ and air oxidation, generate the respective $R_4C_4B_8H_8$ carborane fusion products where R = *n*-C_4H_9, *i*-C_5H_{11} or *n*-C_6H_{13}. In contrast to the tetrabenzylcarborane $(PhCH_2)_4C_4B_8H_8$, these $R_4C_4B_8H_8$ compounds exist in solution as mixtures of "open-cage" and "closed-cage" isomers. However, there is no indication of dynamic interconversion of the isomers, as occurs in the previously studied homologues $Me_4C_4B_8H_8$ and $Et_4C_4B_8H_8$. The diphenylcarborane anion $Ph_2C_2B_4H_5^-$ did not form detectable metal complexes with Fe^{2+}, Co^{2+}, or Ni^{2+}, and no evidence of a $Ph_4C_4B_8H_8$ fusion product has been found. Treatment of $Ph_2C_2B_4H_6$ with $Cr(CO)_6$ did not lead to metal coordination of the phenyl rings, unlike $(PhCH_2)_2C_2B_4H_6$, which had previously been shown to form mono- and bis(tricarbonylchromium) complexes. However, the reaction of $Ph_2C_2B_4H_5^-$, $CoCl_2$, and $(Ph_2PCH_2)_2$ did give 1,1-$(Ph_2PCH_2)_2$-1-Cl-1,2,3-$Co(Ph_2C_2B_4H_4)$, the only case in which metal complexation of the diphenylcarborane was observed. The properties of the three dialkylcarboranes studied are taken to reflect moderate steric effects of the alkyl substituents, while those of the diphenylcarborane are ascribed to both steric and electronic influence of the phenyls on the carborane cage. Evidence of withdrawal of electron density by the phenyls is found in the ^{11}B NMR and visible–UV spectra of $Ph_2C_2B_4H_6$.

Introduction

The first paper in this series describes the preparation and chemistry of *nido*-$RR'C_2B_4H_6$ species having polycyclic arylmethyl substituents at one or both cage carbon positions.[1a] Although the behavior of these molecules toward metal complexation and oxidative fusion appears to reflect primarily the steric effects of the R (R′) groups, the possibility of significant electronic interaction between the aryl substituents and the carborane framework cannot be discounted. In order to further illuminate the general question of steric vs electronic effects, it was desirable to examine the properties of $RR'C_2B_4H_6$ derivatives having large but electronically inactive R groups; to this end we have looked at a series of progressively bulkier *C,C′*-dialkylated species. In contrast to the behavior of these derivatives, the *C,C′*-diphenyl carborane (heretofore unreported) was anticipated to have strong ring–cage electronic interaction with significant chemical consequences but was previously unavailable owing to problems in synthesis. In this article we report the preparation, characterization, and properties of this important carborane derivative and contrast it with the alkyl and arylalkyl species described in this and earlier papers.[1a,2]

Results and Discussion

Synthesis and Chemistry of $(C_nH_{2n+1})_2C_2B_4H_6$ (n = 4–6) Derivatives. Prior to the present work, alkylated *nido*-C_2B_4 carboranes were limited to methyl, ethyl, and propyl mono- or disubstituted species.[3] In this study, we sought to prepare larger alkyl derivatives via reactions of symmetrical dialkylacetylenes with pentaborane(9) and triethylamine via the previously described approach.[3b,4] In two cases, with diadamantylacetylene and di-*tert*-butylacetylene, respectively, carborane products were not obtained in detectable amounts; together with cyclooctyne,[5] these are the only alkynes thus far examined in our laboratory that have failed to convert to the *nido*-carborane on reaction with B_5H_9. However, similar treatment of di-n-butyl-, diisopentyl-, and di-

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