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.

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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]

Henry A. Boyter, Jr., and Russell N. Grimes*

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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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(1) (a) Part 1: Fessler, M. E.; Spencer, J. T.; Lomax, J. F.; Grimes, R. N. *Inorg. Chem.*, preceding paper in this issue. (b) Based in part on Boyter, H. A., Jr.; Ph.D. Thesis, University of Virginia, 1987.

(2) (a) Grimes, R. N. *Pure Appl. Chem.* **1987**, *59*, 847. (b) Whelan, T.; Spencer, J. T.; Pourian, M. R.; Grimes, R. N. *Inorg. Chem.* **1987**, *26*, 3116. (c) Spencer, J. T.; Pourian, M. R.; Butcher, R. J.; Sinn, E.; Grimes, R. N. *Organometallics* **1987**, *6*, 335. (d) Spencer, J. T.; Grimes, R. N. *Ibid.* **1987**, *6*, 328. (e) Spencer, J. T.; Grimes, R. N. *Ibid.* **1987**, *6*, 323. (f) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Ibid.* **1985**, *4*, 896. (g) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Ibid.* **1985**, *4*, 890.

(3) (a) Onak, T. P.; Drake, R. P.; Dunks, G. B. *Inorg. Chem.* **1964**, *3*, 1686. (b) Maynard, R. B.; Borodinsky, L.; Grimes, R. N. *Inorg. Synth.* **1983**, *22*, 211. (c) Maynard, R. B.; Grimes, R. N. *J. Am. Chem. Soc.* **1982**, *104*, 5983.

(4) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 3294.

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

compd	solvent[a]	δ (J_{BH}, Hz)[b,c]	rel areas
(n-C_4H_9)$_2C_2B_4H_6$ (**1**)	A	−1.68 (154), −4.74 (137), −47.84 (176)	1:2:1
	B	−2.09 (151), −5.36 (138), −48.19 (174)	1:2:1
	C	−2.14 (148), −5.25 (117), −48.16 (176)	1:2:1
(i-C_5H_{11})$_2C_2B_4H_6$ (**2**)	B	−1.92 (158), −5.36 (151), −48.30 (181)	1:2:1
	C	−0.46 (146), −3.56 (138), −46.48 (175)	1:2:1
(n-C_6H_{13})$_2C_2B_4H_6$ (**3**)	A	−1.70 (155), −4.74 (128), −47.82 (179)	1:2:1
	B	−1.98 (153), −5.38 (154), −48.20 (184)	1:2:1
(n-C_4H_9)$_4C_4B_8H_8$ (**4**)	A	15.0, 12.5, −21.35, −25.6 (closed isomer)	2:2:2:2
		0.44, −8.31 (135) (open isomer)	6:2
	B	9.25, −25.54 (153), −30.12 (144) (closed isomer)	4:2:2
		−4.09 (138), −13.12 (139) (open isomer)	6:2
(i-C_5H_{11})$_4C_4B_8H_8$ (**5**)	A	12.09, 9.11, −24.75, −28.59 (162) (closed isomer)	2:2:2:2
		−2.32, −11.71 (138) (open isomer)	6:2
	B	11.15, 8.27, −24.92 (137), −28.67 (144) (closed isomer)	2:2:2:2
		−2.92, −12.07 (128) (open isomer)	6:2
(n-C_6H_{13})$_4C_4B_8H_8$ (**6**)	A	11.38, 9.01, −24.81 (146), −28.68 (139) (closed isomer)	2:2:2:2
		−2.50, −11.84 (115) (open isomer)	6:2
(C_6H_5)$_2C_2B_4H_6$ (**7**)	B	−1.75 (179), −3.56 (168), −46.91 (177)	1:2:1
	D	−1.70 (189), −3.59 (162), −46.74 (178)	1:2:1
	E	−1.03 (198), −2.60 (162), −45.62 (179)	1:2:1
(C_6H_5)$_2C_2B_4H_5^-$ (**7**$^-$)	D	4.50, −10.08, −50.72	2:1:1
[(C_6H_5)$_2PCH_2$]$_2$(Cl)Co[(C_6H_5)$_2C_2B_4H_4$] (**8**)	A	8.80, 4.45, −3.39	1:2:1

[a] Key: A = hexane, B = CH_2Cl_2, C = benzene, D = THF, E = CH_3CN. [b] Shifts relative to $BF_3 \cdot OEt_2$; positive values downfield. [c] Signals for which no J value is given are overlapped, unresolved doublets in H-coupled spectra.

Table II. 300-MHz ^{1}H FT NMR Data

compd	δ[a,b]	rel areas
1	2.44 m (α-CH), 2.28 m (α-CH), 1.59 m (β-CH), 1.43 m (γ-CH_2), 0.96 t (CH_3), −2.2 br (B−H−B)	2:2:4:4:6:2
2	2.46 m (α-CH), 2.28 m (α-CH), 1.67 m (CH), 1.49 (β-CH), 0.96 t (CH_3), −2.1 br (B−H−B)	2:2:2:4:12:2
3	2.43 m (α-CH), 2.27 m (α-CH), 1.60 m (β-CH), [1.30 m, 1.41 m] (CH_2), 0.92 t (CH_3), −2.0 br (B−H−B)	2:2:4:[12]:6:2
4	[2.18 m, 2.48 m] (α-CH), [1.20 m, 1.70 m] (CH_2), 0.96 t (CH_3), 0.90 t (CH_3)	[8]:[16]:6:6
5	[2.15 m, 2.50 m] (α-CH), [1.45 m, 1.70 m] (CH), [1.00 m, 1.43 m] (β-CH_2), 0.95 d (CH_3), 0.89 d (CH_3)	[8]:[4]:[8]:12:12
6	2.35 m[c] (CH_2), 1.28 m[c] (CH_2), 0.82 t (CH_3, J = 3 Hz)	8:64:12
7	[7.27 m,[d] 7.36 m[d]] (C_6H_5), −1.5 br (B−H−B)	10:2
8	[6.97 t,[d] 7.10 t,[d] 7.21 t,[d] 7.31 t,[d] 7.40 t,[d] 7.43 t,[d] 7.64 t,[d] 7.75 t[e]] (C_6H_5), 2.86 m[d] (CH_2), 2.35 m[d] (CH_2)	4:4:4:4:3:3:4:4:2:2

[a] $CDCl_3$ solution. [b] Shifts relative to $(CH_3)_4Si$. Legend: m = multiplet, t = triplet, d = doublet, br = broad. [c] Overlapped multiplets. [d] J = 7 Hz. [e] J = 8 Hz.

Table III. 75.5-MHz ^{13}C FT NMR Data

compd	δ[a,b]
1	138−140 (cage C's), 33.1 (α-C), 31.7 (β-C), 23.2 (γ-C), 14.4 (CH_3)
2	139−140 (cage C's), 40.1 (α-C), 29.8 (β-C), 28.6 (γ-C), 23.0 (CH_3), 22.9 (CH_3)
3	140−141 (cage C's), 32.1 (α-C), 30.9 (β-C), 30.2 (γ-C), 29.8 (δ-C), 23.1 (ϵ-C), 14.5 (CH_3)
7	141−143 (cage C), 128.96,[c] 128.83,[c] 126.42[c]
8	134.68,[c] 134.17,[c] 130.82,[c] 130.73,[c] 130.52,[c] 128.51,[c] 127.42,[c] 126.87,[c] 30.14 (CH_2)

[a] $CDCl_3$ solution. [b] Shifts relative to $(CH_3)_4Si$; all spectra broad-band decoupled. Assignments of β−ϵ-carbon shifts are tentative and are based on the assumption that deshielding decreases with increasing distance from the cage. [c] Phenyl carbon atoms.

Table IV. Infrared Absorptions (cm^{-1}, CCl_4 Solution vs CCl_4)[a]

compd	absorpns
1	2950 vs, 2935 vs, 2900 vs, 2600 s, 1938 m, 1470 s, 1465 s, 1389 m, 1363 m, 1360 w, 1233 w, 1165 m, 1127 w, 999 w, 994 sh, 945 w, 922 w, 912 w, 807 w, 765 w, 755 w, 670 m
2	2960 vs, 2931 vs, 2878 vs, 2605 s, 1940 m, 1480 sh, 1470 s, 1455 sh, 1389 m, 1368 m, 1342 w, 1264 w, 1217 w, 1172 m, 1125 w, 1032 w, 990 sh, 983 w, 972 w, 922 w, 912 w, 852 w, 807 w, 781 w, 765 w, 735 w, 660 m
3	2955 vs, 2932 vs, 2907 vs, 2603 s, 1944 m, 1475 s, 1465 s, 1395 m, 1361 m, 1122 w, 1035 w, 995 m, 994 sh, 945 w, 922 w, 919 w, 900 w, 875 w, 856 w, 776 w, 750 w, 690 m
4	2960 vs, 2930 vs, 2870 s, 2580 s, 2340 sh, 2320 w, 2300 w, 1470 m, 1460 m, 1390 w, 1120 m, 1090 m, 620 m
5	2960 vs, 2925 vs, 2870 vs, 2575 vs, 1470 vs, 1390 s, 1375 s, 1180 m, 1140 w, 1040 m, 970 w, 930 w, 700 m
6	2955 sh, 2915 vs, 2850 vs, 2590 s, 1465 s, 1385 w, 1120 m, 1080 m, 940 w, 675 w, 635 s
7	3060 vs, 3020 vs, 2940 vs, 2900 vs, 2840 vs, 2600 s, 2300 w, 1965 sh, 1950 m, 1895 w, 1870 w, 1820 w, 1735 w, 1670 w, 1600 vs, 1490 vs, 1440 vs, 1380 m, 1340 m, 1070 s, 1030 s, 940 w, 910 w, 615 m
8	3110 sh, 3070 s, 3015 w, 2970 m, 2930 vs, 2900 m, 2865 m, 2840 sh, 2620 sh, 2580 sh, 2560 vs, 2300 m, 1440 m, 880 m, 680 m

[a] Legend: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder.

n-hexylacetylene gave the corresponding *nido*-$R_2C_2B_4H_6$ products **1**–**3** in good yields as colorless to pale yellow nonvolatile liquids. These compounds are viscous oils that are unchanged by exposure to air as neat liquids but in solution slowly degrade over days or weeks; in these respects, **1**–**3** are notably different from their smaller (alkyl)$_2C_2B_4H_6$ homologues, which are volatile liquids that undergo air oxidation in a matter of hours.

The new compounds were characterized from their low- and high-resolution mass spectra, ^{11}B, ^{1}H, and ^{13}C FT NMR spectra (Tables I–III), IR spectra (Table IV), and visible–UV spectra (Experimental Section). Assignment of the structures (Figure 1) is straightforward on the basis of the NMR data and is further supported in each case by a characteristic visible–UV absorption at 226–228 nm in hexane that we have found to be diagnostic for *nido*-$R_2C_2B_4H_6$ derivatives.[6] The reactivity of **1**–**3** toward deprotonation, metal complexation, and oxidative fusion was investigated and found to be consistent with the sequence previously established[3c] for other *nido*-C_2B_4 species (eq 1). Bridge deprotonation of **1**–**3** by NaH in THF is slightly slower than is the case with $Et_2C_2B_4H_6$, the measured energies of activation being 4.3 and 4.5 kcal mol^{-1}, respectively, for **2** and **3** compared to 4.0 kcal

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[6] Boyter, H. A., Jr.; Grimes, R. N., manuscript in preparation.

$$R_2C_2B_4H_6 \xrightarrow[\text{THF}]{+NaH/-H_2} R_2C_2B_4H_5^- \xrightarrow{FeCl_2}$$

1: R = n-C_4H_9
2: R = i-C_5H_{11}
3: R = n-C_6H_{13}

$$\underset{\text{red}}{[(R_2C_2B_4H_4)_2FeH_2]} \longrightarrow \underset{\text{purple}}{[(R_2C_2B_4H_4)_2Fe_2(OC_4H_8)_2]}$$

$$\big\downarrow O_2$$

$$R_4C_4B_8H_8 \qquad (1)$$

4: R = n-C_4H_9
5: R = i-C_5H_{11}
6: R = n-C_6H_{13}

mol^{-1} for the diethyl derivative.[7] The $R_2C_2B_4H_5^-$ monoanions are quantitatively protonated to regenerate the neutral carboranes on treatment with gaseous HCl.

The reactions of **1**–**3** with $FeCl_2$ in THF proceeded with formation of the red and purple iron complexes indicated above; these species were not isolated, but their composition and structure can be inferred from those of the diethyl and dimethyl carboranes.[3c] In each case, the initial red monoiron complex changed to the royal purple diiron species after ca. 1 h at room temperature, and the latter color was maintained as long as the solution was held under vacuum. On exposure to air, the color instantly changed to yellow and solids were precipitated. Workup of the product mixture in each case gave, on chromatography on silica the corresponding $R_4C_4B_8H_8$ fusion product **4**, **5**, or **6**, accompanied by $R_2C_2B_4H_6$. The last species clearly arises from reprotonation of the $R_2C_2B_4H_5^-$ anion, since in each case the neutral $R_2C_2B_4H_6$ substrate was completely converted to its anion via treatment with NaH. The regeneration of $R_2C_2B_4H_6$ in the fusion reaction has not been observed for R = CH_3, C_2H_5, or C_3H_7 but does occur to some extent in a number of derivatives having larger R groups, e.g. $(CO)_3Cr(C_6H_5)CH_2$,[2b] indenylmethyl ($C_9H_7CH_2$),[1a] and fluorenylmethyl ($C_{13}H_9CH_2$),[1a] as well as in the present work. The proton source is evidently THF, and the protonation of the anion competes with complexation–fusion in systems where the latter process is relatively slow; this is the case for carboranes with large R substituents, which is consistent with the recovery of $R_2C_2B_4H_6$ in such systems. It has been observed that reprotonation is suppressed when the fusion is conducted in glyme rather than in THF.[8]

The fusion products **4**–**6** were isolated chromatographically as air-stable colorelss oils and characterized from their ^{11}B and ^1H NMR, visible–UV, IR, and mass spectra. The most significant observation about these species is that their ^{11}B spectra (Figure 2) clearly reveal the presence of both "closed" (A) and "open" (B) cage isomers in solution. This has been observed previously for $R_4C_4B_8H_8$ species where R is methyl, ethyl, or propyl[9] but is *not* seen when R is larger (e.g., benzyl); in derivatives such as $(PhCH_2)_4C_4B_8H_8$, $(C_9H_7CH_2)_2C_4B_8H_{10}$, and $(C_{13}H_9CH_2)_2C_4B_8H_{10}$, only the open form has been detected.[1a,2c] The proportion of the A isomer in **4**–**6** is small (ca. 20–25%), as compared to equilibrium values of 64, 31, and 35% in $Me_4C_4B_8H_8$, $Et_4C_4B_8H_8$, and $Pr_4C_4B_8H_8$, respectively,[9] reflecting the inhibition of cage "closure" by the larger R groups in **4**–**6**. Clearly, the steric effects of large alkyl substituents, even in tetra-C-substituted species, are less drastic (at least for groups up to n-hexyl) than are those of the bulkier arylmethyl derivatives, allowing the coexistence of both closed- and open-cage isomers in solution. The ^{11}B NMR spectra of freshly prepared solutions of **4**–**6** do not change measurably over time, differing in this respect from the spectra of the tetramethyl and tetraethyl carboranes;[9] the last two species exist in the solid state as pure A and B isomers, respectively, and in solution A $\rightleftharpoons$ B equilibria are established within minutes ($Me_4C_4B_8H_8$) or hours ($Et_4C_4B_8H_8$). The tetra-n-propyl derivative exhibits both A and B forms immediately on dissolving, but the spectra do change slightly over several hours, reflecting adjustment of the [A]/[B] ratio as the equilibrium state is reached.[9] The behavior of **4**–**6** thus most closely approaches that of the propyl compound and indicates that in these carboranes *both cage isomers are present in neat samples* and, consequently, in their solutions. The absence of any change in the [A]/[B] ratio over time implies that there is no significant cage fluxionality in solution and hence that the relative amounts of A and B isomers one sees in the spectra are those in the isolated product mixture. (Alternatively, one might argue that dynamic interconversion of A and B isomers *is* occurring in solution but is not apparent because the [A]/[B] ratios in the pure liquid carboranes **4**–**6** are coincidentally at the thermodynamic equilibrium values to begin with; we discount this as highly improbable.)

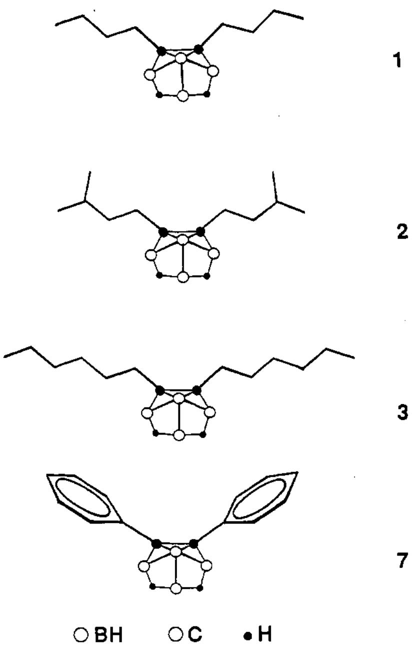

Figure 1. Structures of $R_2C_2B_4H_6$ derivatives **1** (R = n-C_4H_9), **2** (R = i-C_5B_{11}), **3** (R = n-C_6H_{13}), and **7** (R = C_6H_5).

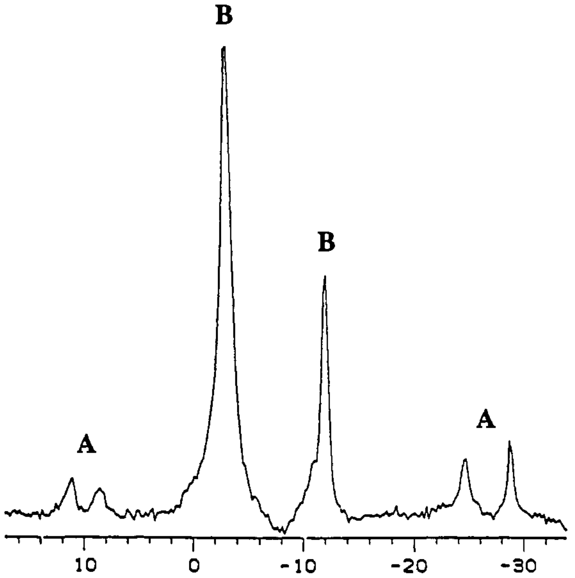

Figure 2. Proton-decoupled 115.8-MHz ^{11}B NMR spectrum of **5** in n-hexane at 45 °C. Peaks marked A and B arise from "closed" and "open" C_4B_8 cage isomers, respectively.[9] Spectra of **4** and **6** are similar.

In summary, it appears that each of the fusion products **4**–**6** is formed as a mixture of open- and closed-cage isomers which are observable in the ^{11}B NMR spectra but which do not interconvert to a measurable extent in solution at room temperature. This behavior, viewed in comparison with that of other $R_4C_4B_8H_8$

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(7) Fessler, M. E.; Whelan, T.; Spencer, J. T.; Grimes, R. N. *J. Am. Chem. Soc.* **1987**, *109*, 7416.
(8) We thank Professor Larry Sneddon for useful discussions on this point.
(9) Venable, T. L.; Maynard, R. B.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 6187.

and $R_2R'_2C_4B_8H_8$ species, indicates that the *n*-butyl, isopentyl, and *n*-hexyl groups affect cage isomerization more strongly than do smaller alkyl substituents, but much less so than larger groups such as benzyl, which completely block the formation of the closed-cage isomer (A).

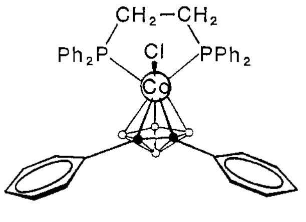
Synthesis and Chemistry of *nido*-$Ph_2C_2B_4H_6$. The alkyl and arylalkyl derivatives of *nido*-$C_2B_4H_8$ investigated in our laboratory all have $-CH_2-$ units attached to one or both cage carbon atoms, and in fact prior to this work the only known derivative having an aryl group bound directly to the cage was 2-Ph-2,3-$C_2B_4H_7$, originally prepared in the gas phase by Onak et al.[3a] and later obtained by Hosmane and Grimes on a gram scale from the base-promoted reaction of B_5H_9 and phenylacetylene.[4] We have been interested for some time in preparing the diphenyl compound 2,3-$Ph_2C_2B_4H_6$, in order to investigate the electronic and steric influence of the phenyl rings on the chemistry of the C_2B_4 system, particularly with respect to deprotonation, metal complexation, and cage fusion. However, the reaction of diphenylacetylene with B_5H_9 in the presence of Lewis base does not generate isolable carborane in more than trace amounts, giving instead nonvolatile, apparently polymeric products. Ultimately we found that the desired *nido*-$Ph_2C_2B_4H_6$ (7) could be produced in acceptable yield (10–40%) via the high-temperature reaction of diphenylacetylene and B_5H_9 in *n*-hexane solution in a steel cylinder.[10]

Pure 7 (Figure 1) was isolated by chromatography on silica and obtained as a colorless, slightly air-sensitive oil, characterized from its NMR, IR, visible–UV, and mass spectra. The band in the electronic spectrum arising from the *nido*-C_2B_4 cage appears at 222 nm, slightly blue-shifted from the usual position near 226–228 nm (vidre supra), indicating possible electronic ring–cage interaction; a broader absorption at 238–308 nm is attributed to the phenyl rings and is red-shifted in comparison to benzene. These observations imply transfer of electron density from the cage to the phenyl rings, a conclusion that correlates with the ^{11}B and ^1H NMR peaks arising from the equivalent BH(4) and BH(6) groups (adjacent to carbon), which exhibit substantial deshielding.

Given these electronic effects, and the relative rigidity of the phenyl–cage attachment (compared, for example, with the much more flexible benzyl units in ($(PhCH_2)_2C_2B_4H_6$[2d]), we anticipated that the chemistry of 7 would differ significantly from that of the alkyl and arylalkyl derivatives, and this is indeed the case as demonstrated by the following observations.

Bridge Deprotonation. The heterogeneous reaction of 7 in THF solution with suspended NaH proceeds cleanly and quantitatively to give the anion $Ph_2C_2B_4H_5^-$ (7^-), as shown by the ^{11}B NMR spectrum of 7^-, which exhibits just three sharp signals (Table I). This process has been shown in a recent kinetic study[7] to be strongly temperature-dependent, proceeding extremely rapidly at room temperature but much more slowly than for other *nido*-$R_2C_2B_4H_6$ derivatives below ca. −40 °C. The activation energy ΔE_a (12 kcal mol^{-1}) is higher by at least a factor of 2 than that of the other derivatives studied (where R is alkyl, arylalkyl, or $(CO)_3CrPhCH_2$), and the value of $-\Delta S^*$ is anomalously small. These findings have been interpreted[7] in terms of both inductive electron withdrawal by the phenyl rings, which increases the acidity of the B–H–B protons, and steric inhibition by the phenyls of the approach of the cage to the NaH surface; the latter effect is evidently more important at lower temperatures.

Interactions with Transition-Metal Reagents. In contrast to the behavior of most *nido*-$RR'C_2B_4H_5^-$ anions, which readily form $H_xM(RR'C_2B_4H_4)_2$ complexes and subsequently fuse to give $R_2R'_2C_4B_8H_8$ (vide supra), the addition of $FeCl_2$, $CoCl_2$, or $NiBr_2$ to THF solutions of $Ph_2C_2B_4H_5^-$ ion at room temperature gave virtually no evidence of reaction. No color changes were observed in 24 h, and neutral 7 was the only boron-containing material recovered; moreover, even at reflux in THF or glyme there was no indication of reaction. The failure to complex or fuse was previously seen in species where R = R′ = indenylmethyl, fluorenylmethyl, or $(CO)_3CrPhCH_2$ and in those cases[1a,2a,b] was attributed to steric hindrance, by the bulky R groups, of metal entry to the carborane open face. A similar argument applies to the diphenyl species, but in this case electron withdrawal from the C_2B_3 face by the phenyls, discussed above, might also somewhat deactivate the carborane toward metal complexation. It is relevant to note that the *mono*phenyl anion $PhC_2B_4H_6^-$ *does* complex with Fe^{2+} and on oxidation fuses to give $Ph_2C_4B_8H_{10}$,[11] so that the presence of just one C-bonded phenyl unit is not sufficient to block complexation or fusion.



8

Figure 3. Proposed structure of $[(C_6H_5)_2PCH_2]_2(Cl)Co[(C_6H_5)_2C_2B_4H_4]$ (8).

Notwithstanding its failure to form bis(carboranyl)metal complexes, metal coordination of 7^- was achieved in at least one instance. The reaction of $Ph_2C_2B_4H_5^-$ ion with $CoCl_2$ and $(Ph_2PCH_2)_2$ in THF yielded a dark purple product that has been characterized spectroscopically as 1,1-$(Ph_2PCH_2)_2$-1-Cl-1,2,3-$Co(Ph_2C_2B_4H_4)$ (8) (Figure 3). The NMR, IR, and mass spectra of 8 support the proposed structure, which is analogous to that of the previously reported diethylcarborane complexes[12] 1,1-$(Ph_2PCH_2)_2$-1-Cl-1,2,3-$M(Et_2C_2B_4H_4)$ where M = Fe and Co, both of which were crystallographically characterized. The visible–UV spectrum of 8 in CH_2Cl_2 exhibits bands at 232 and 280 nm, which are assigned to the C_2B_4 cage and phenyl rings, respectively, and also appear in the spectrum of the analogous diethylcarborane complex. However, the band arising from d–d transitions, which in the diethyl species appears at 460 nm, is shifted in 8 to 502 nm. Such a shift could be produced by an increase in π-donation from the carborane ligand to the metal (which would involve a concomitant decrease in ligand field strength). Alternatively, the shift to longer wavelength may simply reflect a lowering of symmetry in the environment of the metal, which would cause a redistribution of the metal d orbital energies; such asymmetry might well arise from skewing of the bulky diphenylcarborane and $(Ph_2PCH_2)_2$ ligands as a consequence of steric interactions between them.

In an attempt to coordinate $Cr(CO)_3$ groups to one or both of the phenyl rings, $Ph_2C_2B_4H_6$ was refluxed with excess $Cr(CO)_6$ in 10:1 dibutyl ether–THF, but no metalated carborane complexes were detected. This finding contrasts strongly with the behavior of $(PhCH_2)_2C_2B_4H_6$, which readily adds $Cr(CO)_3$ to both phenyls;[2c] the failure of the diphenylcarborane to do so is most easily explained in terms of steric hindrance of the approach of the metalating reagent to the C_6H_5 rings.

Experimental Section

Except where otherwise indicated, materials, instrumentation, and general procedures were identical with those described in the preceding paper.[1a] Tetrahydrofuran (THF) and glyme $(MeOCH_2)_2$ were dried over, and distilled from, Na-benzophenone. Alkynes were purchased from Farchan Chemical Co. Pulse Fourier transform ^{13}C (75.5 MHz) and ^1H (300 MHz) NMR spectra were recorded on a GE QE300 spectrometer, and broad-band decoupling was employed in obtaining $^{13}C\{^1H\}$ spectra. Visible–ultraviolet spectra were recorded on a Hewlett-Packard 8452 diode array spectrophotometer with HP Vectra computer interface.

Synthesis of $(n-C_4H_9)_2C_2B_4H_6$ (1), $(i-C_5H_{11})_2C_2B_4H_6$ (2), and $(n-C_6H_{13})_2C_2B_4H_6$ (3). The general procedure employed has been described previously[3b,4] but was modified in the present work, as follows. Typically, 50 mmol of the alkyne and 4.90 g (48.5 mmol) of triethylamine were placed in a 500-mL reactor,[3b] which was subsquently degassed three times as described earlier.[1a] The reactor was evacuated to $<10^{-5}$ Torr and placed in a liquid-nitrogen bath, and 3.15 g (50.0 mmol) of B_5H_9 was

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(10) We are indebted to Professor N. S. Hosmane for valuable discussions on the preparation of $Ph_2C_2B_4H_6$.

(11) Furia, J.; Hosmane, N. S.; Grimes, R. N., unpublished results.

(12) Boyter, H. A., Jr.; Swisher, R. G.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1985**, *24*, 3810.

added in several consecutive increments via distillation. The reactor was placed in an ice bath, stirred for 3 h, warmed to room temperature, and stirred for 2–4 days. the flask was opened on a vacuum line, volatiles were pumped away, the flask was opened to the air, and its contents were extracted with benzene (500 mL), *n*-hexane (500 mL), dichloromethane (500 mL), and acetone (250 mL). The combined extracts were rotary-evaporated to give a yellow-orange oily solid. This mixture was treated in one of three ways: (a) stirring in acetone for at least 6 h; (b) separating on 15-cm silica gel columns in *n*-hexane until the eluate, following rotary evaporation, remained clear on standing; or (c) allowing to stand for 3 days. The last of these treatments was found generally most satisfactory. Following any of these operations, the solution or oil was stirred in benzene, filtered, rotary-evaporated, and placed on a 30-cm silica gel/*n*-hexane column. The carborane product was eluted with at least 3 L of *n*-hexane, the eluate dried, and the remaining oil allowed to stand. If solids appeared, the material was rechromatographed until no solids appeared in the eluate on standing. Finally, the purity of the product was assayed by ^{11}B NMR spectroscopy. The main impurity encountered in all preparations was the amine–borane adduct, whose ^{1}H-coupled ^{11}B spectrum exhibits a quartet; this material was eliminated via repeated chromatography on silica columns. Yields of pure **1**–**3** in typical runs were 2.73, 3.97, and 4.49 g, respectively, corresponding to 30, 38, and 35% based on B_5H_9 employed. These compounds are slightly air-sensitive yellow oils that are best stored neat under vacuum. Visible–UV absorptions (nm): for **1**, 228 (*n*-hexane), 232 (dichloromethane), 236 (acetonitrile); for **2**, 234 (dichloromethane); for **3**, 226 (*n*-hexane). Exact mass for **1**: calculated for $^{12}C_{10}{}^{11}B_4{}^{1}H_{24}{}^{+}$, 188.2250; found, 188.2256. Exact mass for **2**: calculated for $^{12}C_{12}{}^{11}B_4{}^{1}H_{28}{}^{+}$, 216.2563; found, 216.2571. Exact mass for **3**: calculated for $^{12}C_{14}{}^{11}B_4{}^{1}H_{32}{}^{+}$, 244.2876; found, 244.2879.

Synthesis of $R_4C_4B_8H_8$ (R = *n*-C_4H_9 (4), *i*-C_5H_{11} (5), *n*-C_6H_{13} (6)) via Oxidative Fusion. The apparatus and general procedure have been described elsewhere.[13] In each case, carborane **1**, **2**, or **3** was deprotonated in THF solution via reaction with excess NaH, and the solution containing $R_2C_2B_4H_5^-$ ion was filtered in vacuo onto $FeCl_2$. The solution turned red initially and then purple, at which point it was opened to the air. After filtration, the solids remaining were extracted with benzene and the extract was combined with the filtrate and evaporated. The residue was chromatographed on a 10-cm silica column in *n*-hexane and eluted with dichloromethane, followed by purification of the product on a silica TLC plate in *n*-hexane. Yields were as follows: 0.251 g (1.34 mmol) of **1** and 0.200 g (1.58 mmol) of $FeCl_2$ gave 0.74 g (0.20 mmol, 30%) of **4** and 38 mg (15% recovery) of **1**; 0.420 g (1.95 mmol) of **2** and 0.311 g (2.45 mmol) of $FeCl_2$ gave 90 mg (0.21 mmol, 22%) of **5** and 0.18 g (42% recovery) of **1**; 0.451 g (1.85 mmol) of **3** and 0.252 g (1.99 mmol) of $FeCl_2$ gave 92 mg (0.19 mmol, 20%) of **6** and 0.14 g (30% recovery) of **3**. Products **4**–**6** are colorless oils, with R_f (hexane) 0.90, 0.80, and 0.90, respectively. Visible–UV absorptions in *n*-hexane (nm): for **4**, 224 (100%), 292 (10%); for **5**, 224 (90%), 256 (100%), 290 (95%); for **6**, 236 (81%), 256 (85%), 292 (100%). Exact mass for **4**: calculated for $^{12}C_{20}{}^{11}B_8{}^{1}H_{44}{}^{+}$, 372.4188; found, 372.4208. Exact mass for **5**: calculated for $^{12}C_{24}{}^{11}B_8{}^{1}H_{52}{}^{+}$, 428.4814; found, 428.4842. Exact mass for **6**: calculated for $^{12}C_{28}{}^{11}B_8{}^{1}H_{60}{}^{+}$, 484.5440; found, 484.5462.

Synthesis of 2,3-$Ph_2C_2B_4H_6$ (7). The most satisfactory method was as follows. Diphenylacetylene (7.1 g, 40 mmol) and 60–80 mL of *n*-hexane were placed in a stainless steel cylinder (300–500 mL) equipped with a bellows valve and an 18/9 stainless steel ball joint. The cylinder assembly and contents were placed on a vacuum line and degassed to a pressure of 10^{-5} Torr, after which 3.15 g (50 mmol) of B_5H_9 was transferred to the cylinder in vacuo at −196 °C while the cylinder and valve were warmed to prevent condensation of the borane in the valve seat. After the borane was transferred, the valve was closed and the cylinder warmed to room temperature while still on the vacuum line to test for leakage through the valve. The cylinder was moved to a hood and immersed to a depth of 3 cm in an oil bath at 180 °C. This temperature was maintained for 3 days, after which the cylinder was cooled and reattached to the vacuum line and the volatile contents were removed by evacuation while the cylinder and valve were warmed with a heat gun. After removal of the volatiles, degassed *n*-hexane was transferred into the cylinder and then pumped off several times, to ensure that the cylinder valve was not clogged with solids. At this point 75–100 mL of *n*-hexane was transferred to the cylinder at −196 °C, the valve was closed, the cylinder was placed in the hood, filled with argon, and opened to the air, and its contents were extracted with benzene, dichloromethane, and acetone. The extract was dried and passed through two silica gel/*n*-hexane columns with benzene as eluant. Evaporation of the combined eluants gave an oily solid, which was placed in a short-path distillation apparatus[14] and heated to ca. 50 °C under vacuum. The distillate was determined by mass spectrometry to be a mixture of **7** and the alkyne reagent. A mass spectrum of the residue indicated a mixture of $Ph_4C_4B_4H_4$, $(Ph_2C_2)_4Ph_2C_2B_5H_7$, and $(Ph_2C_2)_5Ph_2C_2B_5H_7$, which are under investigation. The distillate was separated by thin-layer chromatography on silica in *n*-hexane, which gave a wide colorless band that was visible under short-wavelength UV light; under long-wavelength UV light the leading edge (high R_f) of this band was more clearly illuminated. This area contained the product **7**, which was separated and extracted from the silica gel. Visible–UV absorptions in *n*-hexane (nm): 222 (100%), 252 (20%), 294 (20%). Exact mass: calculated for $^{12}C_{14}{}^{11}B_4{}^{1}H_{16}{}^{+}$, 228.1624; found, 228.1628. Yields of **7** from this procedure ranged from 0.9 to 3.6 g (10 to 40%) and averaged 1.7 g (19%); the reasons for the variation have not been identified.

The preparation of **7** was attempted under a variety of other condtiions, including (a) exclusion of solvent, (b) inclusion of triethylamine with and without solvent, and (c) reaction temperatures from 25 to 180 °C. These experiments gave unsatisfactory results, because of either low yields of the diphenylcarborane product or its inseparability from the mixture.

Bridge Deprotonation of 7 and Attempted Oxidative Fusion. The reaction of **7** with suspended NaH in THF solution to generate $Na^+Ph_2C_2B_4H_5^-$ was conducted analogously to the dialkylcarborane deprotonations described above and described in ref 12. Rate measurements as a function of temperature and calculations of ΔH and ΔS^* for the deprotonation of **7** have been presented elsewhere.[7]

Many attempts were made to fuse the $Ph_2C_2B_4H_5^-$ anion by employing $FeCl_2$, $CoCl_2$, and $NiBr_2$, typically with ca. 1 mmol of the carborane anion and 2 mmol of the metal halide. No color change was observed in each case, and neutral $Ph_2C_2B_4H_6$ was the only boron-containing product recovered.

Synthesis of 1,1-$(Ph_2PCH_2)_2$-1-Cl-1,2,3-Co($Ph_2C_2B_4H_4$) (8). A procedure identical with that employed for the synthesis[12] of 1,1-$(Ph_2PCH_2)_2$-1-Cl-1,2,3-Co($Et_2C_2B_4H_4$) gave 27 mg of **8** (10% yield) as a purple crystalline solid. Visible–UV absorptions in dichloromethane (nm): 232 (100%), 280 (75%), 502 (2%). Exact mass: calculated for $^{12}C_{40}{}^{11}B_4{}^{31}P_2{}^{59}Co{}^{1}H_{38}{}^{+}$, 683.2154; found, 683.2164.

Attempted Reaction of 7 with $Cr(CO)_6$. A 0.250-g (1.10-mmol) sample of **7** was placed in a round-bottom flask fitted with a nitrogen bubbler and a reflux condenser. A 10% THF–dibutyl ether mixture was added to the flask after it had been purged with N_2 for 30 min. Excess $Cr(CO)_6$ (3.1 g, 14 mmol) was added and the mixture refluxed for 14 h, cooled, and opened to the air. After it was dried, the mixture was passed through a 15-cm silical gel/*n*-hexane column to separate the chromium carbonyl. Thin-layer chromatography of the eluate, following removal of solvent, gave only the starting carborane; no other boron-containing materials were detected via ^{11}B NMR and mass spectroscopic analysis.

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