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nido-Carborane Building-Block Reagents. 3. Cyclic and Open-Chain Oligomers Incorporating $-\overline{\mathrm{CB_4H_6C}}-$ Units. "Crown" Carboranes[1]

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The open-chain dialkynes $\mathrm{EtC{\equiv}C(CH_2)_nC{\equiv}CEt}$ (n = 4, 6), the trialkyne $\mathrm{HC{\equiv}C(CH_2)_5C{\equiv}C(CH_2)_5C{\equiv}CH}$, and the cyclic dialkynes $\overline{\mathrm{CH_2(CH_2)_4C{\equiv}C(CH_2)_nC{\equiv}C}}$ (n = 4–6) were treated with B_5H_9 and $(C_2H_5)_3N$ to give the corresponding *nido*-carborane oligomers, in which the original $-\mathrm{C{\equiv}C}-$ units are converted to $-\overline{\mathrm{CB_4H_6C}}-$ *nido*-carborane cages. In each case, all available $-\mathrm{C{\equiv}C}-$ groups were transformed to carborane moieties. No "partially converted" products (having both carborane and $-\mathrm{C{\equiv}C}-$ groups in the chain) were found; when the $B_5H_9/-\mathrm{C{\equiv}C}-$ ratio employed was <1, only "completely converted" products and unreacted starting materials were recovered at the end of the reaction. The open-chain carborane oligomers are viscous air-sensitive liquids that undergo bridge deprotonation on treatment with NaH in THF solution; with excess NaH, one proton per carborane unit is removed. The resulting ionic species undergo complexation with Fe^{2+} and oxidative fusion, forming products incorporating C_4B_8 cages. The cyclic bis(carborane) $\overline{\mathrm{CH_2(CH_2)_4\underline{CB_4H_6C}(CH_2)_5\underline{CB_4H_6C}}}$ is an air-stable oil that can be deprotonated but does not undergo metal-promoted oxidative fusion. All products were characterized by ^{11}B and ^1H NMR, infrared, visible–UV, and mass spectroscopy, and the ^{13}C NMR spectra of linear bis(carboranes) are reported.

Introduction

In the preceeding papers in this series[1,2] and in other recent publications from our laboratory,[3] methods have been described for the preparation of multilevel carborane–metal–arene sandwich complexes that are envisioned as precursors to extended electron-delocalized arrays.[3a] In these compounds, carborane and hydrocarbon ligands are linked by transition-metal ions such as Fe^{2+}, which in various species coordinate to C_2B_3 carborane faces, to carborane-bound aryl substituents, and/or to arene molecules. In this work the emphasis has been on *controlled* synthesis of specifically designed molecules via rational preparative routes. A different type of multicage system can be envisioned, in which the carborane units are connected by $-(CH_2)_n-$ chains. If the individual *nido*-$(-\overline{\mathrm{CB_4H_6C}}-)$ cages undergo bridge deprotonation and η^5 complexation to transition metals as do the monomeric species, oligomers or polymers of this type may serve as precursors to novel kinds of multimetal sandwich complexes. Also, one would have the opportunity of exploring metal-promoted oxidative fusion[3a,4] of the chain-linked C_2B_4 cages under severely constrained conditions and, if fusion does occur, obtaining heretofore unknown multicage oligomers incorporating C_4B_8 units.

We conjectured that hydrocarbon-linked $-\overline{\mathrm{CB_4H_6C}}-$ oligomers could be directly prepared by conversion of linear or cyclic polyalkynes, several of which are commercially available, to the corresponding poly(carboranes) via boronation of the acetylenic units with B_5H_9. The success of this approach and the chemistry of the oligomers obtained are the subject of this paper.

Results and Discussion

Synthesis of Open-Chain Bis- and Tris(carboranes). The reactions of B_5H_9 with the dialkynes $\mathrm{EtC{\equiv}C(CH_2)_4C{\equiv}CEt}$ and $\mathrm{EtC{\equiv}C(CH_2)_6C{\equiv}CEt}$ and the trialkyne $\mathrm{[HC{\equiv}C(CH_2)_5C{\equiv}]_2}$ in the presence of triethylamine yield the anticipated linked-carborane products via conversion of each $-\mathrm{C{\equiv}C}-$ unit to a *nido*-$C_2B_4H_6$ cage. In contrast to the mono(carborane) syntheses,[5] in which solvent is normally absent, we have found that the poly(carborane) preparations must be conducted in a nonreactive medium such as *n*-hexane; in the absence of solvent the reaction mixture becomes so viscous as to be unstirrable. By the method[1a] utilized in the preparation of $(n\text{-}C_4H_9)_2C_2B_4H_6$, workup of the reaction mixtures gave the respective carborane products $\mathrm{Et\overline{CB_4H_6C}(CH_2)_4\overline{CB_4H_6C}Et}$ (**1**), $\mathrm{Et\overline{CB_4H_6C}(CH_2)_6\overline{CB_4H_6C}Et}$ (**2**), and $\mathrm{H\overline{CB_4H_6C}(CH_2)_5\overline{CB_4H_6C}(CH_2)_5\overline{CB_4H_6C}H}$ (**3**) in 6–10% isolated yields.

Compounds **1**–**3** are moderately air-sensitive, colorless to light yellow oils that are slowly oxidized in solution on exposure to air and hence must be stored under an inert atmosphere (the reactivity of **3** is significantly greater than that of **1** and **2**). The structures depicted in Figure 1 are supported by unit- and high-resolution mass spectra, ^{11}B, ^1H, and (for **1** and **2**) ^{13}C FT NMR spectra, and IR visible–UV spectra. The ^{11}B data for **1** and **2** (Table I) exhibit the characteristic 1:2:1 pattern for *nido*-2,3-$R_2C_2B_4H_6$ species and indicate equivalence of the two carborane cages in each compound. In addition, both species show strong ultraviolet absorption at 226–228 nm (in *n*-hexane) or 232–234 nm (in CH_2Cl_2), which we have found to be diagnostic of the *nido*-2,3-C_2B_4 cage system.[6] However, we assume that **1** and **2** each exist as a mixture of spectroscopically indistinguishable isomers as indicated schematically in Figure 2. These can be described in terms of the apices of the respective carborane cages: if one considers a conformation in which the basal C_2B_3 rings are coplanar, then the apices will be on the same side of the plane (syn) or on opposite sides (anti). The former arrangement has mirror symmetry and would be optically inactive, but the latter isomer would exist as a pair of enantiomers (Figure 2). Since the linking methylene groups allow free rotation about the various C–C axes, an infinite number of conformations can exist, but the only possible stereoisomers are those just described. Given that the C≡C units in the dialkynes are well separated, their interaction with B_5H_9 can be assumed to proceed essentially independently, in which case the syn and anti species are about equally likely to form and hence should be present in a 1:1 ratio. However, this question was outside the scope of our investigation and was not pursued.

The characterization of the tris(carborane) **3** (Figure 1) is similarly based on spectroscopic data; in this case there are two different carborane cages as revealed in the ^{11}B NMR spectrum

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(1) (a) Part 2: Boyter, H. A., Jr.; Grimes, R. N. *Inorg. Chem.*, second of two preceding papers in this issue. (b) Based in part on: Boyter, H. A., Jr. Ph.D. Thesis, University of Virginia, 1987.

(2) Fessler, M. E.; Spencer, J. T.; Lomax, J. F.; Grimes, R. N. *Inorg. Chem.*, first of two preceding papers in this issue.

(3) (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.

(4) Maynard, R. B.; Grimes, R. N. *J. Am. Chem. Soc.* **1982**, *104*, 5983 and references therein.

(5) See ref 1a and references therein.

(6) Boyter, H. A., Jr.; Grimes, R. N., manuscript in preparation.

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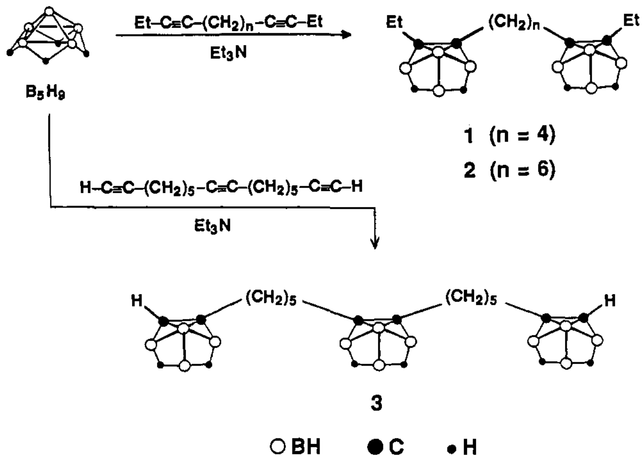

Figure 1. Synthesis and proposed structures of linear bis- and tris(carboranes) **1**–**3**.

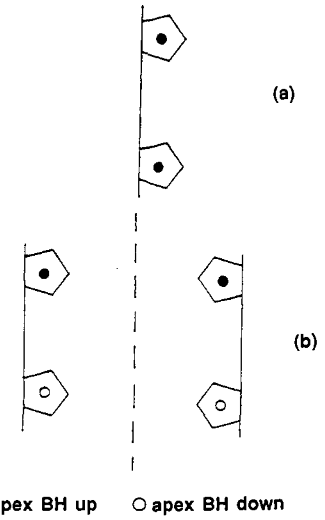

Figure 2. Schematic diagram of the proposed isomer geometries for bis(carboranes) **1** and **2**: (a) nonchiral isomer; (b) chiral isomer represented as an enantiomeric pair.

(Figure 3a), which displays two partially overlapped sets of 1:2:1 resonances. Here the different apical boron signals near δ −50 arising from the end vs center cages are clearly evident. The UV–visible spectrum exhibits the characteristic band at 226 nm (vide supra), but in this case the peak is twice as broad as normal, suggesting that it is a composite of unresolved bands of slightly different frequencies arising from the inequivalent carborane cages. Applying the above stereochemical argument to **3**, a conformer with all three C_2B_3 basal planes coplanar has three possible patterns of apical BH groups as shown in Figure 4; two of these are optically inactive while the third, shown at the bottom, is chiral and must exist as an enantiomeric pair. If the three C≡C groups of the trialkyne react identically with B_5H_9, the three geometric isomers A, B, and C will be present in a ratio of 1:1:2, but the actual distribution cannot be determined from the available data. In each of the compounds **1**–**3** the $-\overline{CB_4H_6C}-$ cages are sufficiently well separated that electronic interactions between them are presumed to be negligible, in which case the isomers in each compound will exhibit virtually identical NMR spectra.

Synthesis of Cyclic Bis(carboranes). The reactions of the cyclic dialkynes $\overline{CH_2(CH_2)_4C{\equiv}C(CH_2)_nC{\equiv}C}$ (n = 4–6) with 2 equiv of B_5H_9 and excess triethylamine generated in each case the corresponding cyclic bis(carborane) $\overline{CH_2(CH_2)_4\underline{CB_4H_6C}(CH_2)_n\underline{CB_4H_6C}}$ (**4**, n = 4; **5**, n = 5; **6**, n = 6), which were isolated in 8–14% yields and characterized spectroscopically. The FT NMR and other data are consistent with the structures proposed in Figure 5 and exhibit ^{11}B NMR, electronic, and mass spectra characteristic of the *nido*-C_2B_4 cage system (vide supra) as well as bands in the ^1H and IR spectra that are diagnostic of B–H–B

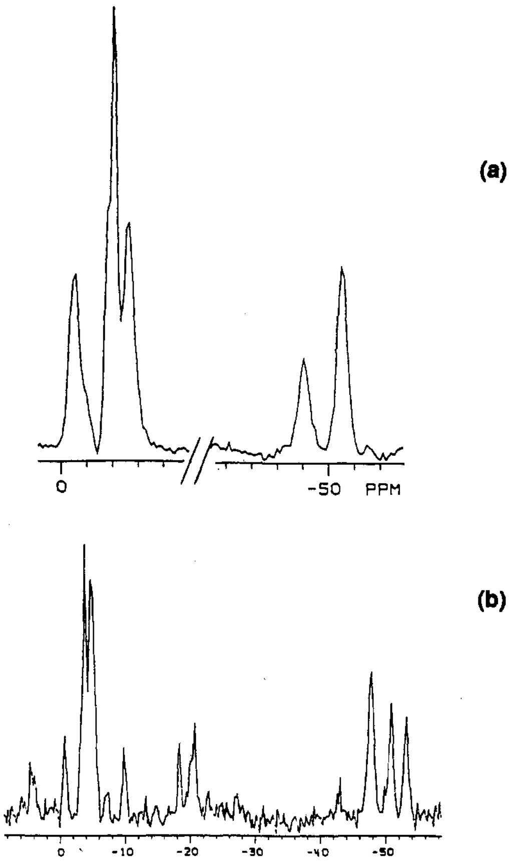

Figure 3. Proton-decoupled 115.8-MHz ^{11}B NMR spectra: (a) **3** in *n*-hexane solution; (b) partially deprotonated **3**, containing 3^{2-} isomers, in THF solution.

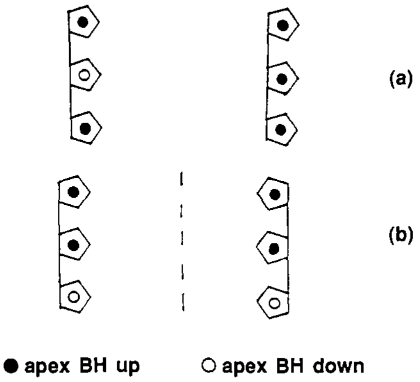

Figure 4. Schematic diagram of the proposed isomer geometries for the tris(carborane) **3**: (a) nonchiral isomers A and B; (b) chiral isomer C, represented as an enantiomeric pair.

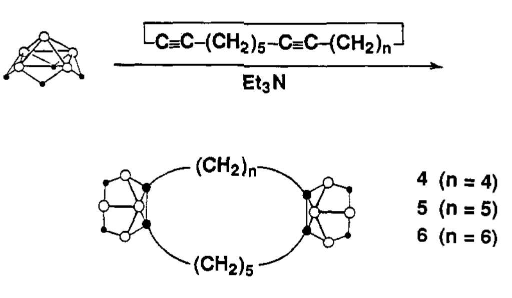

Figure 5. Synthesis and proposed structures of cyclic bis(carboranes) **4**–**6**. *Only one of the possible geometric isomers is shown (see text).*

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

compd	solvent[a]	δ (J_{BH}, Hz)[b,c]	rel areas
$\mathrm{Et\overline{CB_4H_6C}(CH_2)_4\overline{CB_4H_6C}Et}$ (**1**)	A	−1.68 (153), −4.64 (149), −47.91 (177)	1:2:1
	B	−2.04 (148), −5.23 (139), −48.19 (175)	1:2:1
	C	−1.94 (151), −5.10 (141), −48.21 (175)	1:2:1
$\mathrm{Et\overline{CB_4H_6C}(CH_2)_6\overline{CB_4H_6C}Et}$ (**2**)	A	−1.67 (155), −4.64 (159), −47.86 (177)	1:2:1
	B	−1.97 (150), −5.12 (141), −48.21 (175)	1:2:1
$\mathrm{H\overline{CB_4H_6C}(CH_2)_5\overline{CB_4H_6C}(CH_2)_5\overline{CB_4H_6C}H}$ (**3**)	B	−1.14, −4.23, −5.39, −48.29, −51.29 (171)	2:5:2:1:2
	C	−0.78, −3.47, −3.99, −4.98, −47.91 (185), −51.04 (174)	2:1:4:2:1:2
$\overline{\mathrm{CH_2(CH_2)_4\underline{CB_4H_6C}(CH_2)_4\underline{CB_4H_6C}}}$ (**4**)	B	−1.66 (151), −5.00 (137), −48.24 (163)	1:2:1
$\overline{\mathrm{CH_2(CH_2)_4\underline{CB_4H_6C}(CH_2)_5\underline{CB_4H_6C}}}$ (**5**)	A	−0.62, −4.53 (155), −47.63 (187)	1:2:1
	B	−1.23 (125), −5.08 (145), −47.92 (175)	1:2:1
$\overline{\mathrm{CH_2(CH_2)_4\underline{CB_4H_6C}(CH_2)_6\underline{CB_4H_6C}}}$ (**6**)	B	−1.90 (143), −5.15 (137), −48.05 (170)	1:2:1
$\mathrm{Et\overline{CB_4H_6C}(CH_2)_6Et_2C_4B_8H_8(CH_2)_6\overline{CB_4H_6C}Et}$ (**7**)	B	−2.19, −4.18, −5.56, −12.23, −13.09, −25.62, −29.91, −48.38	2:4:4:1:1:1:1:2
$\mathrm{Et_2C_4B_8H_8[(CH_2)_6]_2Et_2C_4B_8H_8}$ (**8**)	B	9.96, 7.1, −3.9,[d] −12.70, −25.41, −29.90	1:1:8:2:2:2
$\mathrm{[Et\overline{CB_4H_6C}(CH_2)_6Et_2C_4B_8H_8]_2(CH_2)_6}$ (**9**)	B	−2.48, −4.02, −5.96, −13.1, −25.50, −29.95, −48.55	2:6:6:4:2:2:2
$\mathrm{[-Et_2C_4B_8H_8(CH_2)_6-]_3}$ (**10**)[e]	B	−4.0, −13.4, −25.7, −29.9	∼12:4:4:4

[a] Key: A = hexane, B = CH_2Cl_2, C = THF. [b] Shifts relative to $BF_3 \cdot OEt_2$; positive values downfield. [c] Signals for which no *J* value is given are unresolved doublets in proton-coupled spectra. [d] Broad peak with shoulder at ∼−5 ppm. [e] Broad peaks, poorly defined.

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

compd	δ[a,b]	rel areas
1	2.49 m[c] (α-CH), 2.34 m[c] (α-CH), 1.75 m[c] (β-CH), 1.22 t (CH_3), −2.2 br (B–H–B)	4:4:4:6:4
2	2.48 m (α-CH), 2.30 m (α-CH), 1.63 m (β-CH), 1.46 m (γ-CH), 1.21 t (CH_3), −2.3 br (B–H–B)	4:4:4:4:6:4
3	2.50–1.00 m[d] (CH_2 protons), 0.86[e] (carborane CH), −2.3 br (B–H–B)	20:2:6
4	2.95–1.25 m[d] (CH_2 protons), −2.3 br (B–H–B)	18:4
5	3.14 m (α-CH), 2.77 m (α-CH), 2.60–1.35 m[d] (β,γ-CH), −2.2 br (B–H–B)	4:4:12:4
6	2.80 m (α-CH), 2.40 m (α-CH), 1.65–1.20 m[d] (β,γ-CH), −2.3 br (B–H–B)	4:4:14:4
7	2.48–2.24 m[d] (α-CH), 1.55–1.30 m[d] (β,γ-CH), 1.25–0.85 t (CH_3), −2.4 br (B–H–B)	16:16:12:4
8	2.54–1.31 m[d] (CH_2 protons), 1.30–0.97 m[d] (CH_3)	32:12
9	2.50–1.28 m[d] (CH_2 protons), 1.20–0.97 m[d] (CH_3), −2.3 br (B–H–B)	48:18:4
10	2.43–1.30 m[d] (CH_2 protons), 1.25–0.82 m[d] (CH_3)	18:48

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

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

compd	absorpns
1	2955 vs, 2947 vs, 2942 vs, 2933 vs, 2923 vs, 2920 vs, 2902 vs, 2874 vs, 2871 vs, 2605 vs, 2601 vs, 1954 w, 1941 w, 1677 w, 1653 w, 1550 s, 1366 m, 1334 m, 1295 w
2	2948 vs, 2945 vs, 2942 vs, 2938 vs, 2934 vs, 2929 vs, 2927 vs, 2920 vs, 2913 vs, 2884 vs, 2860 vs, 2603 vs, 2601 vs, 1946 w, 1941 w, 1741 w, 1653 w, 1576 s, 1550 s, 1373 m, 1351 m, 1342 m, 1270 s, 1220 s, 1100 m, 1080 m, 1010 s, 980 m, 960 w, 930 w
3	2960 sh, 2900 vs, 2840 vs, 2600 s, 1938 w, 1720 m, 1710 sh, 1700 w, 1680 w, 1250 m, 1140 w, 1080 w, 920 s
4	2990 sh, 2980 sh, 2930 vs, 2830 s, 2600 s, 1950 w, 1710 m, 1380 m, 1340 w, 1320 w, 1170 vs, 1120 w, 1100 w, 1060 m, 1040 m
5	2950 sh, 2940 sh, 2900 vs, 2830 vs, 2710 w, 2580 s, 1950 m, 1700 w, 1680 w, 1420 m, 1300 w, 1280 w, 950 w, 920 m, 900 w
6	2990 sh, 2920 vs, 2890 sh, 2850 s, 2600 s, 1980 w, 1790 w, 1750 w, 1720 s, 1710 s, 1680 w, 1280 w, 1170 s, 1120 w, 1100 w, 870 w
7	2970 vs, 2935 vs, 2865 vs, 2585 s, 1955 w, 1865 w, 1810 w, 1730 w, 1675 w, 1590 s, 1410 m, 1340 m, 1110 s, 1025 s, 910 w, 890 w
8	2990 m, 2980 sh, 2940 vs, 2920 sh, 2880 s, 2860 s, 2560 vs, 1400 m, 1380 m, 1330 w, 1300 w, 1280 w, 1160 w, 1120 w, 1080 w, 1020 m, 980 m, 880 m
9	2965 sh, 2960 vs, 2905 vs, 2590 s, 1955 m, 1940 w, 1870 w, 1820 w, 1765 w, 1750 w, 1670 w, 1570 w, 1430 m, 1330 m, 1090 s, 1040 s, 920 w, 860 w
10	2975 vs, 2950 vs, 2905 vs, 2610 s, 1990 w, 1900 w, 1740 w, 1730 w, 1660 w, 1510 w, 1490 w, 1310 w, 1080 m, 1005 m, 950 w, 910 w, 870 w, 860 w

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

bridges (Tables I–III and Experimental Section).

The cyclic bis(carboranes) **4**–**6** are slightly air-sensitive colorless oils that are soluble in nonpolar or moderately polar solvents. Since their proposed structures are somewhat reminiscent of crown ethers, and their bridge-deprotonated C_2B_4 cages can coördinate to metal ions (vide infra), we label these compounds informally as "crown carboranes" although this carries no implication of similarity in the metal-coordination properties of these classes. Once again, as in the case of the linear bis(carboranes) **1** and **2**, the *nido*-C_2B_4 cages in compounds **4**–**6** can have a syn or anti relative orientation, giving rise to two geometric isomers for each compound. However, while both isomers of **5** are nonchiral, in **4** and **6** the anti isomer of each compound is chiral (because of the inequivalent $-(CH_2)_n-$ chain lengths) and should exist as a racemic mixture of enantiomers. As with **1**–**3**, these isomers were not resolvable.

In an effort to prepare cyclic monocarborane–monoalkynes, the reactions of cyclic dialkynes (the precursors of **4**–**6**) were conducted with only 0.5 equiv of B_5H_9 per $-C{\equiv}C-$ unit. However, no such products were observed, and only the bis(carborane) species **4**–**6** and unreacted dialkyne were isolated. This suggests that the conversion of the first $-C{\equiv}C-$ functional group to a $-\overline{\mathrm{CB_4H_6C}}-$ cage enhances the reactivity of the remaining alkynyl unit toward B_5H_9, to a degree that boronation takes place preferentially at that site rather than on a competing dialkyne molecule. This observation contrasts with most base-catalyzed reactions of diacetylenes with $B_{10}H_{14}$, which yield alkynyl-1,2-$C_2B_{10}H_{11}$ derivatives as well as bis(carboranes);[7] however, a few dialkynes such as 1,6-heptadiyne[8] have been reported to form only bis(carborane) products.

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(7) (a) Grimes, R. N. *Carboranes*; Academic: New York, 1970; p 76. (b) Paxson, T. E.; Callahan, K. P.; Hawthorne, M. F. *Inorg. Chem.* **1973**, *3*, 708.

(8) (a) Fein, M. M.; Bobinski, J.; Mayes, N.; Schwartz, N. N.; Cohen, M. S. *Inorg. Chem.* **1963**, *2*, 1111. (b) Fein, M. M.; Grafstein, D.; Paustian, J. E.; Bobinski, J.; Lichstein, B. M.; Mayes, N.; Schwartz, N. N.; Cohen, M. S. *Inorg. Chem.* **1963**, *2*, 1115.

Bridge Deprotonation of Bis- and Tris(carboranes). Since the removal of a B–H–B proton via the reaction

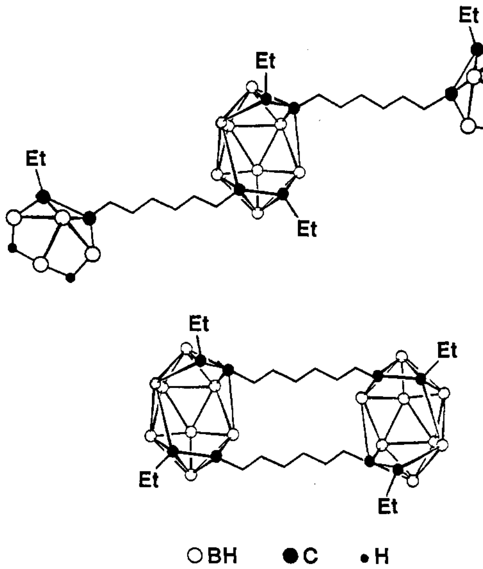
$$R\overline{CB_4H_6C}R + MH \rightarrow M^+R\overline{CB_4H_5C}R^- + H_2$$

is characteristic of *nido*-2,3-$R_2C_2B_4H_6$ monocarboranes and is the usual entry to the extensive metal-coordination chemistry based on these compounds,[3] the corresponding properties of the poly(carborane) oligomers are of interest. Accordingly, **1**, **2**, **3**, and **5** were treated with excess NaH in THF and the evolved hydrogen measured; in addition, the anion formation in each case was followed by ^{11}B NMR spectroscopy. The bis(carboranes) **1**, **2**, and **5** evidently undergo deprotonation of both cages at a similar rate, as indicated by the ^{11}B spectra of the respective dianions $\mathbf{1}^{2-}$, $\mathbf{2}^{2-}$, and $\mathbf{5}^{2-}$, which give no evidence of singly deprotonated (monoanionic) species containing both $-\overline{CB_4H_6C}-$ and $[-\overline{CB_4H_5C}-]^-$ units. This observation supports the view that in both **1** and **2** the two cages function as independent entities and do not measurably affect each other's chemistry.

In contrast, the behavior of the tris(carborane) **3** toward NaH clearly reveals a difference in the reactivity of the center $-\overline{CB_4H_6C}-$ cage vis-à-vis the end cages, which in this molecule are chemically inequivalent (vide supra). The ^{11}B NMR spectrum of the partially deprotonated product (Figure 3b) reveals that the signals near δ −52 arising from the apex borons of the equivalent end cages decrease in intensity relative to that of the central cage apex as the deprotonation proceeds, indicating that the reaction of the end cages is measurably faster. This observation is consistent with a recent kinetic study of deprotonation in *nido*-2,3-$RR'C_2B_4H_6$ carboranes which demonstrated that the rate in species where both R and R′ are bulky groups tends to be slower than in those where R = H (monosubstituted derivatives).[9] In compound **3**, the center $-\overline{CB_4H_6C}-$ unit corresponds to the former situation while the end cages are in the latter category. Under the reaction conditions employed, the dianionic deprotonation product is unstable and its degradation prevented our following the process to completion with the deprotonation of all three cages.

Metal-Complexation and Oxidative-Fusion Behavior of Bis- and Tris(carborane) Anions. The conversion of 2,3-$R_2C_2B_4H_5^-$ anions to $R_4C_4B_8H_8$ carboranes via formation of $H_xM(R_2C_2B_4H_4)_2$ complex intermediates has been extensively studied in our laboratory.[1,2,3a–c,4] The corresponding properties of multicage *nido*-carboranes have not been explored and are clearly of interest in a mechanistic sense (e.g., fusion might proceed via intermolecular and/or intramolecular pathways) and also as a synthetic route to novel oligomers incorporating C_4B_8 clusters. In this work, the reactions of the bis(carborane) dianions $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ with 1 molar equiv of $FeCl_2$ in THF, under the same conditions employed previously for mono(carboranes), gave red solutions that changed to royal purple within 1 h. On exposure to air the solutions turned colorless immediately and the products were isolated chromatographically as described elsewhere.[1] These findings correspond closely to the well-established sequence[4] for the complexation and fusion of mono(carborane) $R_2C_2B_4H_5^-$ anions (eq 1 in the preceding paper[1a]).

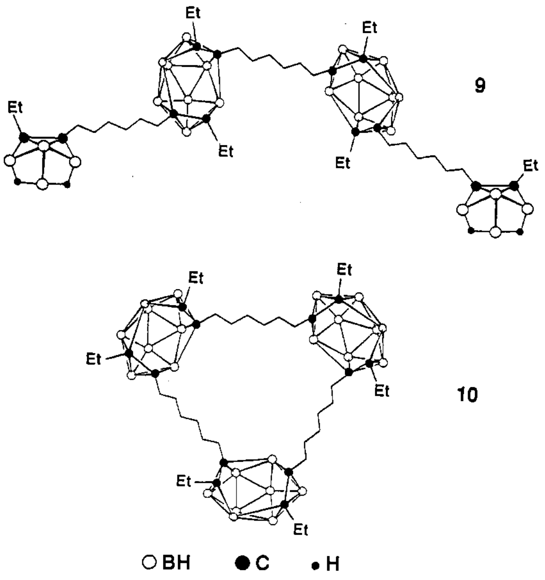
The product mixture from the reaction of $\mathbf{2}^{2-}$ contained the original carborane **2** (20% recovery) and four new compounds (**7**–**10**), which were isolated as air-stable colorless oils. While detailed structural assignments are not possible in the absence of crystal structure determinations (each species is presumed to consist of several isomers), mass spectroscopic, NMR, and electronic spectral data do permit identification of the principal features of each product. The proposed geometries of **7** and **8**, shown in Figure 6, are supported by low- and high-resolution mass spectra; in **7**, the ^{11}B NMR spectra clearly reveal the presence of both *nido*-C_2B_4 and C_4B_8 cages, while in **8** only the latter feature is seen. Similar analysis of **9** and **10** indicates that the former contains two C_2B_4 and two C_4B_8 clusters while the latter species is composed of three C_4B_8 cages (Figure 7). There is no indication of an intramolecular fusion product $[-(CH_2)_6Et_2C_4B_8H_8-]$, suggesting that the complexation of a metal ion to two C_2B_4 cages in the same molecule is kinetically disfavored relative to intermolecular coordination. Intramolecular fusion conceivably could be promoted by conducting the reaction in dilute solution, but we have not found that this affects the product mixture qualitatively. The corresponding reactions of $\mathbf{2}^{2-}$ gave similar C_4B_8-containing fused products, which are currently under study.



7

8

Figure 6. Proposed structures of fused carboranes **7** and **8**, formed via oxidative fusion of **2**. In each case only one geometric isomer is depicted.



9

10

Figure 7. Proposed structures of fused carboranes **9** and **10**, formed via oxidative fusion of **2**. Only one geometric isomer is depicted for each compound.

Attempts to induce fusion of the cyclocarborane dianion $\mathbf{5}^{2-}$ via complexation with Fe^{2+} gave no indication of reaction; no color change was observed in 48 h, and workup of the product mixture yielded only neutral **5**. The behavior of $\mathbf{5}^{2-}$ is consistent with observations on *nido*-$R_2C_2B_4H_5^-$ carboranes where both R groups are bulky substituents such as fluorenylmethyl, indenylmethyl, and $(CO)_3CrPhCh_2$, in which metal-promoted fusion is sterically blocked.[2,3a,3b] As the $-\overline{CB_4H_6C}-$ cages in $\mathbf{5}^{2-}$ must be similarly constrained (indeed more so), its failure to complex or fuse is understandable on a steric basis. In contrast, the fact that the open-chain bis(carboranes) $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ do undergo fusion can be ascribed to the fact that their cages are only partially hindered,

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[9] Fessler, M. E.; Whelan, T.; Spencer, J. T.; Grimes, R. N. *J. Am. Chem. Soc.* **1987**, *109*, 7416.

Table IV. Data for Syntheses of $-(\overline{CB_4H_6C})_n-$ Oligomers

alkyne; amt, mmol	amt of B_5H_9, mmol	amt of $(C_2H_5)_3N$, mmol	product	isolated yield, g (%)
1,9-dodecadiyne; 25.0	50.0	48.5	**1**	0.635 (10)
1,11-tetradecadiyne; 25.0	50.0	48.5	**2**	0.722 (10)
1,8,15-hexadecatriyne; 16.7	50.0	48.5	**3**	0.352 (6)
1,7-cyclotridecadiyne, 27.7	60.0	56.9	**4**	0.610 (8)
1,8-cyclotetradecadiyne; 25.0	50.0	48.5	**5**	1.010 (14)
1,8-cyclotetradecadiyne; 25.0	25.0	24.3	**5**	0.433 (12)
1,9-cyclopentadecadiyne; 27.7	60.0	56.9	**6**	0.837 (10)

inasmuch as the "end" cage carbons have only ethyl substituents. Again, this finding is in line with our recent observation that when only *one* R (R′) group in $RR'C_2B_4H_6$ is sterically demanding, complexation and fusion generally *do* occur.[2]

Conclusions

This work establishes that (1) the general preparative route to *nido*-C_2B_4 species via reaction of B_5H_9 with alkynes is applicable to polyalkynes, (2) dialkynes and trialkynes yield only bis- and tris(carboranes) even when the $B_5H_9/C{\equiv}C$ ratio is <1, with no evidence of alkynylcarborane products, (3) Fe^{2+}-assisted oxidative fusion of linear bis(carborane) dianions occurs to give multicage products containing C_4B_8 cages, but only intermolecularly, and (4) cyclic bis(carboranes) such as **5** can be deprotonated to give dianionic species but do not undergo observable transition-metal coordination or cage fusion. These findings should be capable of extension to the synthesis of higher molecular weight oligomers and polymers, and we are currently exploring such possibilities.

Experimental Section

Except where otherwise indicated, materials, instrumentation, and general procedures were identical with those described in the two preceding papers.[1a,2]

Synthesis of $-\overline{CB_4H_6C}-$ Carborane Oligomers (1–6). Compounds **1–6** were prepared from the corresponding alkyne, B_5H_9, and triethylamine by the detailed procedure described elsewhere,[1] except for the following changes. In the present work, the high viscosity of the carborane products required the addition of 60–75 mL of benzene or *n*-hexane solvent in each case in order to facilitate the reaction (in the case of the tris(carborane) **3**, the product mixture was viscous even in the presence of solvent). Also, because of the air sensitivity of the open-chain products **1–3** while in solution, these compounds were isolated as quickly as possible via rotary evaporation of solvent. Table IV lists the quantities of reagents and yields of isolated products **1–6** obtained in typical runs. Visible–UV absorptions (nm, in CH_2Cl_2 except where otherwise indicated): for **1–3**, 226 in *n*-hexane; for **4**, 234; for **5**, 226 in *n*-hexane; for **6**, 232. ^{13}C FT NMR ($CDCl_3$ solution, 75.5 MHz, shifts in ppm relative to $SiMe_4$): for **1**, 138–142 (cage C's), 31.74 (α-CH_2), 30.75 (α-CH_2), 25.16 (β-CH_2), 15.32 (CH_3); for **2**, 138–143 (cage C's), 31.87 (α-CH_2), 30.78 (α-CH_2), 29.91 (β-CH_2), 25.12 (γ-CH_2), 15.31 (CH_3). Exact mass for **1**: calculated for $^{12}C_{12}{}^{11}B_8{}^1H_{30}{}^+$, 262.3092; found, 262.3098. Exact mass for **2**: calculated for $^{12}C_{14}{}^{11}B_8{}^1H_{34}{}^+$, 290.3405; found, 290.3425. Exact mass for **3**: calculated for $^{12}C_{16}{}^{11}B_{12}{}^1H_{40}{}^+$, 364.42747; found, 364.4242. Exact mass for **4**: calculated for $^{12}C_{13}{}^{11}B_8{}^1H_{30}{}^+$, 274.3092; found, 274.3107. Exact mass for **5**: calculated for $^{12}C_{14}{}^{11}B_8{}^1H_{32}{}^+$, 288.3249; found, 288.3257. Exact mass for **6**: calculated for $^{12}C_{15}{}^{11}B_8{}^1H_{34}{}^+$, 302.3405; found, 302.3424.

Synthesis of $-(Et_2C_4B_8H_8)_n-$ Carborane Oligomers via Metal Complexation and Oxidative Fusion. By a procedure described elsewhere,[1a] 0.722 g (2.5 mmol) of **2** was deprotonated via reaction with excess NaH (0.800 g) in dry THF and the resulting solution was filtered onto 0.444 g (3.5 mmol) of $FeCl_2$. The red solution was exposed to air, and the products were separated on silica columns and TLC plates[1a] to give four colorless, air-stable compounds that were characterized as the oligomers **7–10** (Table I). In addition, 0.144 g (0.50 mmol) of the original carborane **2** (20%) was recovered from the reaction mixture. R_f (25% CH_2Cl_2/*n*-hexane) values and yields: for **7**, 0.62 and 42 mg (0.070 mmol, 5.6%); for **8**, 0.50 and 51 mg (0.089 mmol, 7.1%); for **9**, 0.55 and 35 mg (0.041 mmol, 4.9%); for **10**, 0.45 and 23 mg (0.021 mmol, 3.2%). Visible–UV absorptions (nm, in CH_2Cl_2): for **7**, 232 (100%), 258 (50%), 266 (45%), 290 (50%); for **8**, 232 (100%), 252 (20%), 290 (20%); for **9**, 232 (100%), 256 (80%), 290 (80%); for **10**, 236 (80%), 256 (85%), 292 (100%). Exact mass for **7**: calculated for $^{12}C_{28}{}^{11}B_{16}{}^1H_{64}{}^+$, 576.6498; found, 576.6560. Exact mass for **8**: calculated for $^{12}C_{28}{}^{11}B_{14}{}^{10}B_2{}^1H_{60}{}^+$, 570.6257; found, 570.6297. Exact mass for **9**: calculated for $^{12}C_{42}{}^{11}B_{20}{}^{10}B_4{}^1H_{94}{}^+$, 858.9734; found 858.9730. Exact mass for **10**: calculated for $^{12}C_{42}{}^{11}B_{20}{}^{10}B_4{}^1H_{90}{}^+$, 854.9421; found, 854.9414.

Attempted Complexation and Fusion of the Cyclocarborane 5. Under conditions identical with those employed in the preceding experiments, 86 mg (0.30 mmol) of **5** was deprotonated with 1.173 g (10.2 mmol) of KH (35%) in THF and 0.482 g of $FeCl_2$ was added. No color changes or hydrogen evolution was observed, and at the end of several hours the only isolable material was the starting carborane (0.12 mmol recovered).

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