"Recapitation" of *nido*-Metallacarboranes as a Synthetic Tool: Preparation of Apically Substituted CoC_2B_4 Clusters via Boron Insertion[1]

Michael A. Curtis, Michal Sabat, and Russell N. Grimes*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

Received June 17, 1996[⊗]

Derivatives of $Cp^*Co(2,3\text{-}Et_2C_2B_4H_4)$ containing substituents at the apex boron atom [B(7)], the first examples of apically functionalized small metallacarborane clusters, have been prepared in good yield via boron insertion into the *nido*-$Cp^*Co(2,3\text{-}Et_2C_2B_3H_3)^{2-}$ dianion. Reaction of this substrate with BX_3 (X = Cl, Br, I) or $PhBCl_2$ in toluene at room temperature gave the corresponding $Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}7\text{-}X)$ derivatives (**2a**−**c** and **3** in which X = Cl, Br, I, and Ph, respectively), all of which were isolated via column chromatography as air-stable yellow solids and characterized via ^1H, ^{11}B, and ^{13}C NMR, infrared, UV−visible, and mass spectra. Treatment of the same dianion with $1,4\text{-}(Br_2B)_2C_6H_4$ afforded air-stable orange crystalline $[Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}7)]_2C_6H_4$ (**4**). The structure of this compound was defined via spectroscopy and X-ray crystallography as a bis(cobaltacarborane) complex linked at the apex borons via a 1,4-phenylene bridge. Crystal data for **4**: space group *Pbca*; $a = 15.056(7)$ Å, $b = 21.612\ (8)$ Å, $c = 11.641\ (3)$ Å; $Z = 4$; $R = 0.045$ for 1582 independent reflections having $I > 3\sigma(I)$.

Introduction

A major theme in the evolution of metallacarborane chemistry, especially as it relates to the synthesis of new materials and reagents, is the development of controlled routes to specific classes of substituted derivatives. Much has been accomplished in the derivatization of large (12- and 13-vertex) metallacarboranes over a 30-year period, led by the pioneering work of Hawthorne, Zakharkin, Stone, and others.[2] In the small metallacarborane area, which has centered primarily on 7-vertex *closo*-MC_2B_4 and 6-vertex *nido*-MC_2B_3 clusters,[3] considerable effort in our laboratory has been directed toward finding efficient methods for introducing organic and inorganic substituents at boron,[4] carbon,[5] and metal[6] locations on the cage framework and for effecting direct cage-to-cage linkage.[7] Such reactions are indispensable to any serious attempt at designed synthesis of metallacarborane-based electronic materials or catalysts.

Some limitations remain in this methodology, one of which is the difficulty of placing organic substituents at boron locations on *closo*-MC_2B_4 cages. Halogenation at equatorial boron atoms can be accomplished,[8] but no rational procedure for introducing alkyl, alkenyl, alkynyl, aryl, or other functional groups has been reported for such clusters; moreover, to our knowledge, derivatives substituted at the apex [B(7)] position have been completely inaccessible. Functionalization at the apex boron appeared a worthy synthetic goal, opening possibilities for new types of macromolecular architectures based on linearly aligned metallacarborane clusters (vide infra). Accordingly, we report here the directed synthesis of B(7)-substituted derivatives of $Cp^*Co(2,3\text{-}Et_2C_2B_4H_4)$ via insertion of a BX unit (X = aryl or halogen) into the *nido*-$Cp^*Co(Et_2C_2B_3H_3)^{2-}$ dianion. This approach resembles boron-insertion reactions previously employed to generate B-substituted derivatives of icosahedral C_2B_{10}[9] or CB_{11}[10] carboranes from anionic *nido*-C_2B_9 and *nido*-CB_{10} substrates, respectively, and is also conceptually related to the cluster expansion of *nido*-$2,3\text{-}Et_2C_2B_4H_6$ via interaction with $RBCl_2$ and other monoboron reagents.[11] Similarly, boron insertion into metal clusters via reaction with $BH_3{\cdot}L$ complexes is well-known.[2e,12] Controlled boron additions do not seem to have been reported for metallacarboranes, although *metal*

[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1996.

(1) Organotransition-Metal Metallacarboranes. 47. Part 46: Franz, D. A.; Houser, E. J.; Sabat, M.; Grimes, R. N. *Inorg. Chem.*, in press.

(2) Representative recent reviews: (a) Harwell, D. E.; Nabakka, J.; Knobler, C. B.; Hawthorne, M. F. *Can. J. Chem.* **1995**, *73*, 1044 (Venus flytrap complexes). (b) Jelliss, P. A.; Stone, F. G. A. *J. Organomet. Chem.* **1995**, *500*, 307 (nonspectator carborane ligands in icosahedral complexes). (c) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081 (metallacarboranes of d- and f-block metals). For comprehensive reviews of transition-metal metallacarborane chemistry, see: (d) Grimes, R. N. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, England, 1995; Vol. 1, Chapter 9, pp 373−430 (literature 1982−1995, metallacarboranes). (e) Grimes, R. N. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press, Oxford, England, 1982; Vol. 1, Chapter 5.5, pp 459−542 (literature to 1982, including metalloboranes).

(3) (a) Hosmane, N. S.; Maguire, J. A. *J. Cluster Sci.* **1993**, *4*, 297. (b) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251. (c) Grimes, R. N. *Appl. Organomet. Chem.* **1996**, *10*, 209.

(4) (a) Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1990**, *9*, 1171. (b) Piepgrass, K. W.; Grimes, R. N. *Organometallics* **1992**, *11*, 2397. (c) Piepgrass, K. W.; Stockman, K. E.; Sabat, M.; Grimes, R. N. *Organometallics* **1992**, *11*, 2404.

(5) (a) Benvenuto, M. A.; Grimes, R. N. *Inorg. Chem.* **1992**, *31*, 3897. (b) Benvenuto, M. A.; Sabat, M.; Grimes, R. N. *Inorg. Chem.* **1992**, *31*, 3904.

(6) (a) Houseknecht, K. L.; Stockman, K. E.; Sabat, M.; Finn, M. G.; Grimes, R. N. *J. Am. Chem. Soc.* **1995**, *117*, 1163. (b) Stockman, K. E.; Houseknecht, K. L.; Boring, E. A.; Sabat, M.; Finn, M. G.; Grimes, R. N. *Organometallics* **1995**, *14*, 3014.

(7) Wang, X.; Sabat, M.; Grimes, R. N. *Organometallics* **1995**, *14*, 4668.

(8) Stockman, K. E.; Garrett, D. L.; Grimes, R. N. *Organometallics* **1995**, *14*, 4661.

(9) Hawthorne, M. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 896.

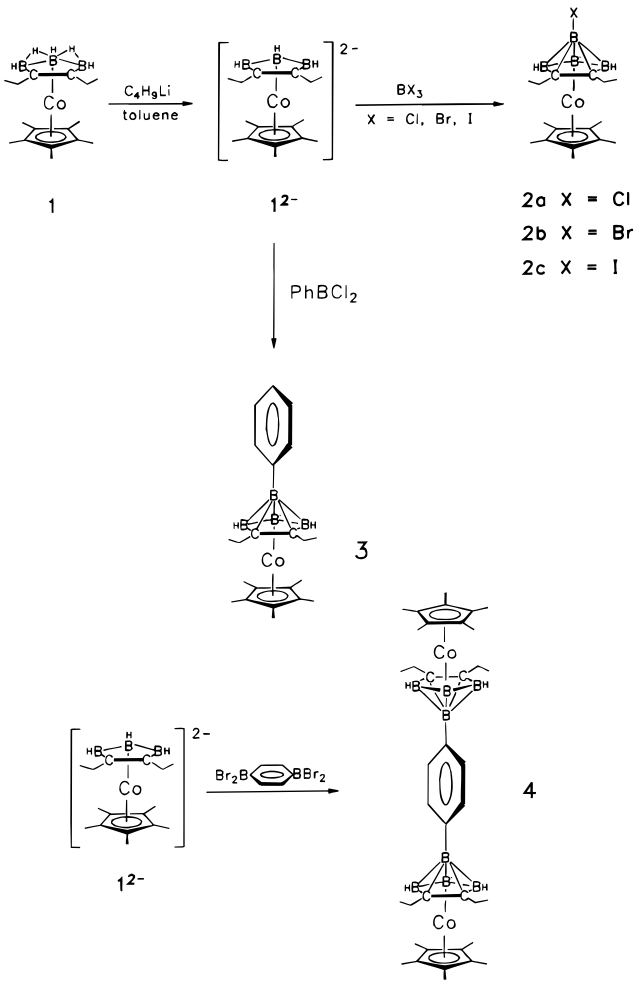
(10) Mair, F. S.; Morris, J. H.; Gaines, D. F.; Powell, D. *J. Chem. Soc., Dalton Trans.* **1993**, 135.

(11) Beck, J. S.; Sneddon, L. G. *Inorg. Chem.* **1990**, *29*, 295.

(12) Reviews: (a) Fehlner, T. P. *New J. Chem.* **1988**, *12*, 307. (b) Barton, L.; Srivastava, D. K. In *Comprehensive Organometallic Chemistry II*; Abel, E., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, England, 1995; Vol. 1, Chapter 8, pp 275−372. Some leading references: (c) Grebenik, P. D.; Leach, J. B.; Green, M. L. H.; Walker, N. M. *J. Organomet. Chem.* **1988**, *345*, C31. (d) Feilong, J.; Fehlner, T. P.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 424. (e) Grebenik, P. D.; Green, M. L. H.; Kelland, M. A.; Leach, J. B.; Mountford, P.; Stringer, G.; Walker, N. M.; Wong, L. L. *J. Chem. Soc., Chem. Commun.* **1988**, 799. (f) Hong, F.-E.; McCarthy, D. A.; White, J. P., III; Cottrell, C. E.; Shore, S. G. *Inorg. Chem.* **1990**, *29*, 2874.

S0020-1669(96)00691-X CCC: $12.00

Scheme 1



insertions into metallacarborane cages have long been known[2d,13] and have been exploited in our laboratory to assemble multidecker metal-sandwich complexes containing MC_2B_3M' cluster units.[3b,c]

Results and Discussion

Synthesis of $Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}7\text{-}X)$ Complexes. The yellow air-stable complex[14] *nido*-$Cp^*Co(Et_2C_2B_3H_5)$ (**1**, $Cp^* = \eta^5\text{-}C_5Me_5$) was deprotonated with 2 equiv of *tert*-butyllithium in toluene solution at 0 °C, and the resulting orange dianion was reacted with BCl_3 (1.0 M solution in heptane) to give, following column chromatography, yellow air-stable $Cp^*Co(Et_2C_2B_4H_3\text{-}7\text{-}Cl)$ (**2a**) together with **1** (ca. 50% recovery). As shown in Scheme 1, analogous reactions of BBr_3 and BI_3 afforded the corresponding 7-bromo and 7-iodo derivatives **2b** and **2c**, respectively, which are also yellow air-stable solids. Isolated yields based on **1** consumed were 51, 65 and 57% for **2a**, **2b**, and **2c**.

The characterization of these compounds by multinuclear NMR, UV−visible, infrared, and mass spectroscopy (Tables 1−3 and Experimental Section) supports the assignment of these species as B(7)-halogenated derivatives. The unit-resolution mass spectra of all three species show intense parent envelopes that conform closely to the calculated patterns, as well as a strong fragment ion corresponding to loss of the halogen atom. The NMR data (Table 1) reveal mirror symmetry in each case, requiring that the substituent be located on either B(5) (the middle equatorial boron) or B(7); however, the spectra of **2a**−**c** are distinct from those of the known[8] B(5)−X derivatives in which X is Cl, Br, or I and hence establish that the new compounds are the apically substituted isomers. (For example, the ^{11}B NMR spectrum[8] of $Cp^*Co(Et_2C_2B_4H_3\text{-}5\text{-}Cl)$ in CH_2Cl_2 consists of two unresolved broad signals at δ 18.8 (1B) and 2.7 (3B), markedly different from that of **2a**.)

In the spectra of all three compounds, the B(7) resonance is shifted strongly upfield relative to the B(7)−H signal of the parent complex $Cp^*Co(2,3\text{-}Et_2C_2B_4H_4)$, whose spectral data recorded in the same solvent are included in Table 1 for comparison. This observation is notable in that the effect of chloro or bromo substitution on *closo*-carborane cages is usually to shift the resonance of the attached boron atom to lower field while an iodo group shifts it to higher (more negative) field,[15] presumably because of a particularly strong $+I$ (electron-donating) effect of the iodo substituent that dominates other types of interaction. Substituent effects in ^{11}B NMR spectra are complex and reflect a number of factors including inductive (I), resonance, conjugative, and other contributions from the ligand group, as well as the electronic environment of the substituted boron atom;[15] in **2a**−**c** an important contributor is, of course, the metal atom in the cage. In view of these complexities, we will not attempt an interpretation of the observed shifts other than to note that the increase in shielding of B(7) implies a strong $+I$ effect toward that boron atom in all three species.

Synthesis of $Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}7\text{-}Ph)$ (3) and $[Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}7)]_2C_6H_4$ (4). Treatment of the $\mathbf{1}^{2-}$ anion with phenylboron dichloride in toluene solution at 0 °C afforded the yellow *B*(*7*)-phenyl derivative **3**, an air-stable solid, in 79% isolated yield following chromatography on silica. The mass spectrum exhibits a strong parent group at *m/z* 400 and a fragment ion at *m/z* 322 reflecting loss of the phenyl group. The ^{11}B NMR spectrum of **3** (Table 1) differs from those of the halo derivatives **2a**−**c** in that there is no large shift of the B(7) resonance to high field; indeed, the equivalent B(4,6) equatorial peaks are more shielded than the B(7) resonance, which is identified by its appearance as a singlet in the B−H coupled spectrum.

An interesting question is whether there is significant electronic π-interaction between the phenyl ring and the cobaltacarborane cluster in this compound. Although there is a hint of this in the deshielding of B(7) in by ca. 7.6 ppm relative to the parent species (Table 1), the close similarity of the UV−visible spectrum to those of **2a**−**c** (Table 2) suggests that any such effect is small. However, a different situation may exist in the case of the phenylene-bridged bis(cobaltacarboranyl) complex **4**, discussed below.

Compound **4** was prepared via a similar route, allowing the $\mathbf{1}^{2-}$ dianion to react with 1,4-bis(dibromoboryl)benzene at room temperature. Chromatographic separation and workup gave orange air-stable crystals of **4** in 30% yield, characterized by NMR, UV−visible, IR, and mass spectroscopy and an X-ray diffraction analysis. The mass spectrum displays a strong parent envelope at *m/z* 721 with a fragment ion at *m/z* 399 corresponding to loss of a $Cp^*Co(Et_2C_2B_4H_3)$ unit. Although the NMR spectra resemble those of the phenyl-substituted complex **3**, the ^{11}B NMR signals are broad and the B−H coupling is unresolved; these features are attributed to slow tumbling motion of the bulky, rodlike molecules of **4** on the NMR time scale. There are indications that the electronic structure of **4** is significantly different from that of **3** and the *B*(*7*)-halo derivatives, starting

---

(13) Francis, J. N.; Hawthorne, M. F. *Inorg. Chem.* **1971**, *10*, 863.

(14) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4776.

(15) Hermanek, S. *Chem. Rev.* **1992**, *92*, 325.

Table 1. ^{11}B, ^{1}H, and ^{13}C FT NMR Data

115.8-MHz ^{11}B NMR Data

compd	$\delta^{a,b}$	rel areas
$Cp^*Co(2,3-Et_2C_2B_4H_4)$	11.4 (138), 3.0 (150), 1.3 (190)	1:2:1
$Cp^*Co(2,3-Et_2C_2B_4H_3$-7-Cl) (**2a**)	9.0 (144), 2.4 (127), −5.4 (s)[c]	1:2:1
$Cp^*Co(2,3-Et_2C_2B_4H_3$-7-Br) (**2b**)	9.3 (139), 1.8 (129), −11.9 (s)[c]	1:2:1
$Cp^*Co(2,3-Et_2C_2B_4H_3$-7-I) (**2c**)	10.2 (176), 2.1 (127), −24.9 (s)[c]	1:2:1
$Cp^*Co(2,3-ET_2C_2B_4H_3$-7-Ph) (**3**)	12.7 (152), 8.9 (s)[c], 2.2 (136)	1:1:2
$[Cp^*Co(2,3-Et_2C_2B_4H_3-7)]_2C_6H_4$ (**4**)	13.2,[d], 10.2[d], 2.8[d]	1:1:2

300-MHz ^{1}H NMR Data

compd	δ^{e-g}
2a	2.36 m (ethyl CH_2), 2.14 m (ethyl CH_2), 1.79 s (C_5Me_5), 1.34 t (ethyl CH_3)
2b	2.33 m (ethyl CH_2), 2.07 m (ethyl CH_2), 1.78 s (C_5Me_5), 1.36 t (ethyl CH_3)
2c	2.34 m (ethyl CH_2), 1.97 m (ethyl CH_2), 1.77 s (C_5Me_5), 1.38 t (ethyl CH_3)
3	7.08−6.75 m (C_6H_5), 2.39 m (ethyl CH_2), 2.02 m (ethyl CH_2), 1.83 s (C_5Me_5), 1.36 t (ethyl CH_3)
4	6.38 s (C_6H_4), 2.30 m (ethyl CH_2), 1.88 m (ethyl CH_2), 1.78 s (C_5Me_5), 1.26 t (ethyl CH_3)

75.5-MHz ^{13}C NMR Data

compd	$\delta^{f,h}$
2a	91.3 (C_5 ring carbons), 21.2 (CH_2), 14.0 (ethyl CH_3), 9.9 (C_5Me_5 methyl carbons)
2b	91.4 (C_5 ring carbons), 21.3 (CH_2), 14.1 (ethyl CH_3), 9.9 (C_5Me_5 methyl carbons)
2c	91.6 (C_5 ring carbons), 22.1 (CH_2), 14.4 (ethyl CH_3), 10.2 (C_5Me_5 methyl carbons)
3	131.1 (C_6H_5), 126.8 (C_6H_5), 126.5 (C_6H_5), 90.5 (C_5 ring carbons), 21.7 (CH_2), 14.5 (ethyl CH_3), 10.0 (C_5Me_5 methyl carbons)
4	130.0 (C_6H_4), 90.6 (C_5 ring carbons), 21.9 (CH_2), 14.7 (ethyl CH_3), 10.2 (C_5Me_5 methyl carbons)

[a] Shifts relative to $BF_3 \cdot OEt_2$; positive values downfield. H−B coupling constants (Hz) are given in Parentheses. [b] CH_2Cl_2 solution. [c] s = singlet arising from substituted boron atom. [d] B−H coupling not resolved. [e] Shifts relative to $(CH_3)_4Si$. Integrated peak areas in all cases are consistent with the assignments given. Legend: m = multiplet, s = singlet, t = triplet. [f] $CDCl_3$ solution. [g] $B-H_{terminal}$ resonances are broad quartets and are mostly obscured by other signals. [h] Shifts relative to $(CH_3)_4Si$; all spectra proton-decoupled.

Table 2. UV−Visible Absorptions (CH_2Cl_2 Solution)

compd	λ, nm (rel intens)	ϵ^a
$Cp^*Co(Et_2C_2B_4H_4)^b$	418 (3), 292 (100), 248 (19)	
2a	412 (5), 306 (100), 278 (89), 238 (64)	10 500
2b	414 (4), 302 (100), 282 (92), 236 (53)	11 600
2c	418 (4), 308 (100), 286 (92), 236 (48)	13 300
3	412 (5), 312 (100), 280 (86), 242 (74)	12 400
4	318 (100), 240 (62)	24 100

[a] Extinction coefficient in cm^{-1} M^{-1} for the most intense band. [b] Reference 14 (spectrum recorded in $CHCl_3$ solution).

Table 3. Infrared Absorptions (cm^{-1}; NaCl Plates)[a]

compd	absorptions
2a	2972 s, 2927 s, 2872 m, 2538 vs, 1476 m, 1471 m, 1376 s, 1021 m, 770 s
2b	2964 s, 2934 s, 2909 s, 2870 m, 2550 vs, 1477 m, 1457 m, 1382 s, 1028 m, 763 s
2c	2969 s, 2929 s, 2909 s, 2870 m, 2545 vs, 1477 m, 1462 m, 1377 s, 1032 m, 748 s
3	3066 w, 3044 w, 2962 s, 2927 s, 2906 s, 2871 m, 2520 vs, 1475 m, 1462 m, 1379 s
4	3045 w, 2967 s, 2905 s, 2862 m, 2520 vs, 2503 vs, 1475 m, 1453 m, 1375 s

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

with the fact that **4** is orange while the others are all yellow. The UV−visible spectrum of **4**, in contrast to that of **2a**−**c** and **3**, consists of only two bands, the strongest of which (ϵ = 24 100 cm^{-1} M^{-1}) is about twice as intense as the corresponding absorptions in any of the other compounds; the factor of 2 may, of course, simply reflect the presence of two cobaltacarborane chromophores in **4**.

The crystal structure determination of **4** provides some support for the idea of a phenylene-cage interaction. Tables 4 and 5 present data collection and refinement parameters and bond distances and angles, respectively. The molecular geometry, shown in Figures 1 and 2, has a crystallographically imposed center of symmetry, so that the end Cp* rings are parallel; the overall length of the molecule is 14.7 Å and the metal−metal separation is 11.4 Å. The bond distances and angles in the CoC_2B_4 cluster are normal, and the C_5Me_5, C_2B_3, and C_6H_4 rings are planar within experimental error. The Cp* and carborane rings are almost parallel, with a dihedral angle of only 5.6°, and the phenylene ring plane is essentially perpendicular (87.7°) to the C_2B_3 rings. As can be seen in Figure 2, the phenylene ring is rotated about 30° away from a parallel orientation with the carborane C(2)−C(3) bond. The length of the phenylene-cage bond between C(4) and B(7) [1.563(8) Å] is sufficiently short to lend some plausibility to the idea of an arene−carborane cage π-conjugation as suggested earlier. This value is comparable to inter-ring B−C distances in *B*-phenyl derivatives of metal−borabenzene sandwich complexes in which conjugation has been invoked,[16] but we have been unable to find examples of *B*-aryl metallacarborane

Table 4. Experimental X-ray Diffraction Parameters and Crystal Data

empirical formula	$C_{38}H_{60}B_8Co_2$
fw	721.24
crystal color and habit	orange needle
crystal dimensions	0.24 × 0.23 × 0.47 mm
crystal system	orthorhombic
lattice parameters	a = 15.056(7) Å b = 21.612(8) Å c = 11.641(3) Å V = 3788(3) Å^3
space group	*Pbca* (No. 61)
Z	4
D_{calc}	1.26 g cm^{-3}
radiation	Mo Kα (λ = 0.170 69 Å)
μ(Mo Kα)	9.00 cm^{-1}
temperature	−120 °C
$2\theta_{max}$	46°
tot. no. of reflns measd	2992
no. of reflns with $I > 3\sigma(I)$	1582
no. of variables	217
residuals R, R_w[a]	0.045, 0.060
goodness of fit	1.62
max peak in final diff map	0.3 e/Å^3

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

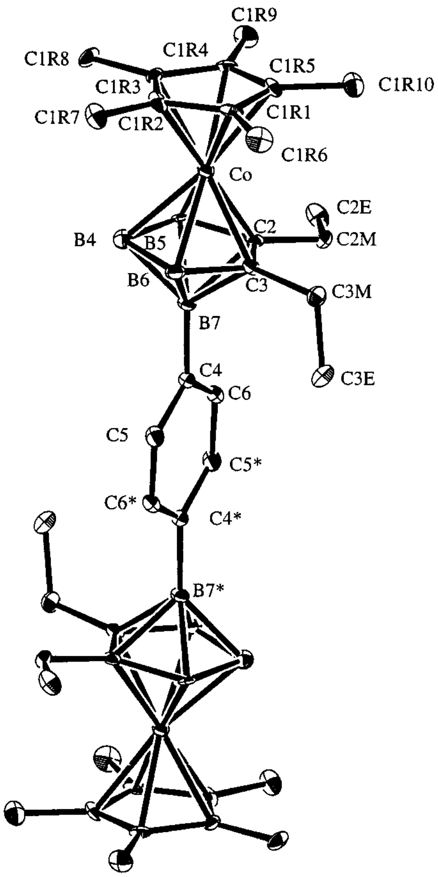


Figure 1. Molecular structure of [Cp*Co(2,3-$Et_2C_2B_4H_3$-7)]$_2C_6H_4$ (**4**; 30% thermal ellipsoids) with hydrogen atoms omitted for clarity.

Table 5. Bond Distances and Selected Bond Angles for [Cp*Co(2,3-$Et_2C_2B_4H_3$-7)]$_2C_6H_4$ (**4**)

Bond Distances, Å			
Co−C(2)	2.042(5)	C(4)−C(5)	1.410(8)
Co−C(3)	2.021(5)	C(4)−C(6)	1.404(8)
Co−C(1R1)	2.054(6)	C(4)−B(7)	1.563(8)
Co−C(1R2)	2.030(6)	C(5)−C(6)*	1.380(8)
Co−C(1R3)	2.024(5)	C(1R1)−C(1R2)	1.449(8)
Co−C(1R4)	2.050(6)	C(1R1)−C(1R5)	1.440(8)
Co−C(1R5)	2.070(6)	C(1R1)−C(1R6)	1.493(8)
Co−B(4)	2.106(7)	C(1R2)−C(1R3)	1.432(8)
Co−B(5)	2.082(7)	C(1R2)−C(1R7)	1.489(8)
Co−B(6)	2.110(7)	C(1R3)−C(1R4)	1.442(8)
C(2)−C(2M)	1.522(8)	C(1R3)−C(1R8)	1.484(8)
C(2)−C(3)	1.459(8)	C(1R4)−C(1R5)	1.412(8)
C(2)−B(5)	1.572(9)	C(1R4)−C(1R9)	1.504(8)
C(2)−B(7)	1.762(9)	C(1R5)−C(1R10)	1.503(9)
C(2M)−C(2E)	1.521(8)	B(4)−B(5)	1.69(1)
C(3M)−C(3)	1.526(8)	B(4)−B(6)	1.68(1)
C(3M)−C(3E)	1.523(8)	B(4)−B(7)	1.76(1)
C(3)−B(6)	1.550(9)	B(5)−B(7)	1.799(9)
C(3)−B(7)	1.801(8)	B(6)−B(7)	1.80(1)

Selected Bond Angles, deg			
Co−C(2)−C(2M)	134.3(4)	Co−C(3)−C(3M)	134.2(4)
C(2M)−C(2)−C(3)	121.3(5)	C(3M)−C(3)−B(6)	124.4(5)
C(2M)−C(2)−B(5)	125.8(5)	C(3M)−C(3)−B(7)	134.5(5)
C(2M)−C(2)−B(7)	134.0(4)	C(2)−C(3)−C(3M)	122.0(5)
C(3)−C(2)−B(5)	112.8(5)	C(2)−C(3)−B(6)	113.1(5)
C(2)−C(2M)−C(2E)	115.0(5)	C(3)−B(7)−C(4)	126.7(5)
C(3)−C(3M)−C(3E)	111.9(5)	C(5)−C(4)−C(6)	117.2(5)
C(4)−B(7)−B(5)	131.4(5)	C(5)−C(4)−B(7)	121.2(5)
C(4)−B(7)−B(6)	131.4(5)	C(6)−C(4)−B(7)	121.5(5)
C(2)−B(7)−C(4)	125.4(5)	C(4)−C(5)−C(6)*	121.1(5)
C(4)−B(7)−B(4)	136.8(5)	C(4)−C(6)−C(5)*	121.7(5)

derivatives that would afford a more direct comparison with **4**; it appears that **4** is the first structurally characterized example of this type. However, it will be noted that a PtB_5 platinaborane cluster[17] with a phenyl substituent on one of the borons exhibits a B−C(phenyl) bond length of 1.629(15) Å, substantially longer than that in **4**.

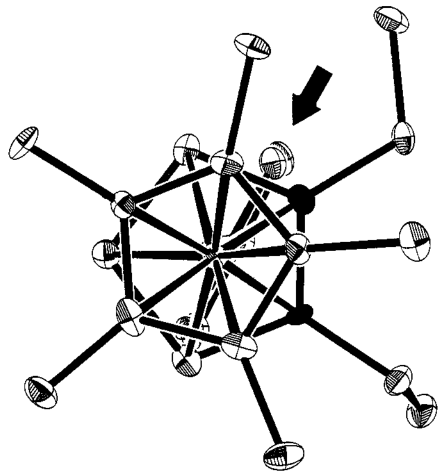


Figure 2. Top view of **4** showing the upper Cp*Co($Et_2C_2B_4$) unit and the phenylene ring (marked with an arrow). The carborane carbon atoms are shown in solid black.

Conclusions

The demonstration of a useful synthesis of apically functionalized small metallacarboranes completes an armory of synthetic tools developed in our group in recent years,[3b,c,4−8] by which one can tailor such compounds via the introduction of functional groups at any boron or cage carbon vertex and by selection of the metal and metal-bound ligands. We envision the B(7)-derivatized complexes as precursors to a new class of small-metallacarborane linked systems that are connected via the apex boron atoms. When combined with previously described approaches for cage substitution and coupling, this chemistry should give access to a wide variety of novel multicage geometries.[24] However, the Cp* ligands in compounds **2a**−**c**, **3**, and **4** are relatively inert (although a Cp*−Cp* linkage has recently been demonstrated[7]), and consequently these compounds *per se* are not well suited for construction of linear-chain polymers. To circumvent this problem, we anticipate that analogous B(7)-substituted complexes containing ($Et_2C_2B_4H_4$) ligands in place of Cp*, which should be accessible via boron insertion into the known complexes[18] ($Et_2C_2B_4H_4$)CoH($Et_2C_2B_3H_4$R) (R = H, Me) will afford a direct route to extended linear systems.

Experimental Section

Instrumentation. ^{1}H NMR spectra (300 MHz) and ^{11}B NMR (115.8 MHz) were recorded on GE QE-300 and Nicolet NT-360 spectrometers, respectively. Unit-resolution mass spectra were obtained on a Finnegan MAT 4600 spectrometer using perfluorotributylamine (FC43) as a calibration standard. In each case, a strong parent envelope whose intensity pattern was consistent with the spectrum calculated on the basis of natural isotopic abundances was observed. Elemental analyses were conducted on a Perkin-Elmer 2400 CHN Analyzer using (2,4-dinitrophenyl)hydrazone as a standard. Visible−ultraviolet spectra were obtained on a Hewlett-Packard 8452A diode array with a HP Vectra computer interface, and infrared spectra were recorded as thin films on a Mattson Cygnus FTIR spectrometer.

---

(16) (a) Huttner, G.; Gartzke, W. *Chem. Ber.* **1974**, *107*, 3786. (b) Herberich, G. E.; Raabe, E. *J. Organomet. Chem.* **1986**, *309*, 143.

(17) Bould, J.; Crook, J. E.; Greenwood, N. N.; Kennedy, J. D. *J. Chem. Soc., Dalton Trans.* **1991**, 185.

(18) Meng, X.; Waterworth, S.; Sabat, M.; Grimes, R. N. *Inorg. Chem.* **1993**, *32*, 3188.

Materials and Procedures. All reactions were conducted under an inert atmosphere unless otherwise indicated. Workup of products was generally carried out in air using benchtop procedures. Column chromatography was performed on silica gel 60 (Merck) or neutral alumina. The complex *nido*-$\mathrm{Cp^*(Et_2C_2B_3H_5)}$ was obtained via the literature synthesis.[14] The boron trihalides were obtained from Aldrich and used without further purification. Bis(dibromoboryl)benzene was prepared by the method reported by Haubold et al.[19] Solvents were distilled from appropriate drying agents under an inert atmosphere.

Synthesis of $\mathbf{Cp^*Co(Et_2C_2B_4H_3\text{-}7\text{-}Cl)}$ (2a). A solution containing 200 mg (0.64 mmol) of $\mathrm{Cp^*Co(Et_2C_2B_3H_5)}$ in 25 mL of toluene at 0 °C was treated with 0.75 mL (1.28 mmol) of 1.7 M *tert*-butyllithium. The solution turned dark red-orange as it was warmed to room temperature over a 1.5 h period. It was cooled to 0 °C, and 2.55 mL (2.55 mmol) of 1.0 M $\mathrm{BCl_3}$ in heptane was added dropwise. The resulting solution quickly became cloudy and turned orange as the flask was warmed to room temperature. The contents were stirred for 4 h, after which toluene was removed in vacuo. The residue was taken up in hexane and washed through 2 cm of silica, first with hexane and then with $\mathrm{CH_2Cl_2}$. The hexane wash contained only $\mathrm{Cp^*Co(Et_2C_2B_3H_5)}$ (103 mg). The $\mathrm{CH_2Cl_2}$ wash was column-chromatographed on silica in 1:1 hexane−$\mathrm{CH_2Cl_2}$, affording a major yellow band that was characterized as **2a** (56 mg, 0.16 mmol, 50.6% based on starting complex consumed). Anal. Calc for $\mathrm{CoClC_{16}B_4H_{28}}$: C, 53.68; H, 7.88. Found: C, 52.52; H, 8.04.

Synthesis of $\mathbf{Cp^*Co(Et_2C_2B_4H_3\text{-}7\text{-}Br)}$ (2b). The procedure described above for the synthesis of **2a** was followed using identical quantities of $\mathrm{Cp^*Co(Et_2C_2B_3H_5)}$ and *tert*-butyllithium to prepare the cobaltacarborane dianion. A 0.241 mL portion (2.55 mmol) of 1.0 M $\mathrm{BBr_3}$ was added at 0 °C, producing a cloudy solution that turned orange as the flask was warmed to room temperature. Stirring was continued for 4 h, after which the workup was conducted as before, yielding 66 mg of recovered $\mathrm{Cp^*Co(Et_2C_2B_3H_5)}$ from the hexane wash and 111 mg (0.28 mmol, 64.6%) of **2b** following chromatography on silica. Anal. Calc for $\mathrm{CoBrC_{16}B_4H_{28}}$: C, 47.75; H, 7.01. Found: C, 48.02, H, 7.57.

Synthesis of $\mathbf{Cp^*Co(Et_2C_2B_4H_3\text{-}7\text{-}I)}$ (2c). The preceding procedure was followed using 160 mg (0.51 mmol) of $\mathrm{Cp^*Co(Et_2C_2B_3H_5)}$ and 0.60 mL (1.02 mmol) of *tert*-butyllithium. The cobaltacarborane dianion solution was stirred at room temperature for 1.5 h, after which 798 mg (2.04 mmol) of $\mathrm{BI_3}$ was added at 0 °C, producing a cloudy solution that turned orange as the flask was warmed to room temperature. Stirring was continued for 4 h, and workup as above yielded 131 mg (0.29 mmol, 57.2%) of **2c** following chromatography on silica. Anal. Calc for $\mathrm{CoIC_{16}B_4H_{28}}$: C, 42.76; H, 6.28. Found: C, 42.51; H, 6.50.

Synthesis of $\mathbf{Cp^*Co(Et_2C_2B_4H_3\text{-}7\text{-}Ph)}$ (3). A solution containing 100 mg (0.32 mmol) of $\mathrm{Cp^*Co(Et_2C_2B_3H_5)}$ in 25 mL of toluene at 0 °C was treated with 0.38 mL (0.64 mmol) of 1.7 M *tert*-butyllithium. The solution turned dark red-orange as it was warmed to room temperature over a 1.5 h period. It was cooled to 0 °C, and 202 mg (1.28 mmol) of $\mathrm{PhBCl_2}$ was added slowly via syringe. The resulting solution quickly became cloudy and turned orange as the flask was warmed to room temperature. Workup was conducted as in the case of **2a**, affording 36 mg of recovered $\mathrm{Cp^*Co(Et_2C_2B_3H_5)}$ and 65 mg (0.16 mmol) of **3** (79% based on starting cobaltacarborane consumed). Anal. Calc for $\mathrm{CoC_{22}B_4H_{33}}$: C, 66.11; H, 8.32. Found: C, 65.76; H, 8.58.

Synthesis of $\mathbf{[Cp^*Co(Et_2C_2B_4H_3\text{-}7)]_2C_6H_4}$ (4). The preceding procedure was followed using 400 mg (1.28 mmol) of $\mathrm{Cp^*Co(Et_2C_2B_3H_5)}$ in 25 mL of toluene and 1.50 mL (2.55 mmol) of 1.7 M *tert*-butyllithium. The solution turned dark red-orange as it was warmed to room temperature over a 1.5 h period. It was cooled to 0 °C, and 266 mg (0.64 mmol) of 1,4-$\mathrm{(BBr_2)_2C_6H_4}$ was added slowly via a sidearm attachment. The resulting solution quickly became cloudy and turned orange as the flask was warmed to room temperature. Workup as before gave 63 mg of recovered $\mathrm{Cp^*Co(Et_2C_2B_3H_5)}$ and 233 mg of **4** (0.32 mmol, 30.1% based on starting cobaltacarborane consumed). Anal. Calc for $\mathrm{Co_2C_{38}B_8H_{60}}$: C, 63.28; H, 8.38. Found: C, 61.47; H, 7.52.

X-ray Structure Determination of 4. Diffraction data were collected on a Rigaku AFC6S diffractometer at −120 °C using Mo Kα radiation. All calculations were performed on a VAX station 3500 computer employing the TEXSAN 5.0 crystallographic software package[20] and in later stages on a Silicon Graphics Personal Iris 4D35 computer with the teXsan 1.7 package.[21] Details of the data collection and structure determination are listed in Table 4. The unit cell dimensions were determined by least-squares refinement of the setting angles of 25 high-angle reflections. The intensities of three standard reflections, monitored at 3-h intervals, showed no significant variation. The intensities were corrected for absorption by applying the DIFABS program[22] with transmission factors between 0.79 and 1.24. The structure was solved by direct methods in SIR88.[23] Full-matrix least-squares refinement with anisotropic displacement parameters for all non-hydrogen atoms yielded the final *R* factors given in Table 4.

Acknowledgment. This work was supported by the National Science Foundation, Grant No. CHE 9322490, and the U.S. Army Research Office, Grant No. DAAH04-95-1-0145. We thank Mr. Shawn R. Wagner for assistance with the data collection and structure determination of **4**.

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, and calculated mean planes for **4** (3 pages). See any current masthead page for ordering information.

IC960691T

---

(19) Haubold, W.; Herdtle, J.; Gollinger, W.; Einholz, W. *J. Organomet. Chem.* **1986**, *315*, 1.

(20) TEXSAN 5.0: Single Crystal Structure Analysis Software (1989), Molecular Structure Corp., The Woodlands, TX 77381.

(21) teXsan 1.7: Single Crystal Structure Analysis Software (1995), Molecular Structure Corp., The Woodlands, TX 77381.

(22) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(23) SIR88: Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389.

(24) Note added in proof: Following the submission of this manuscript, collaborative work with chemists at the University of Heidelberg (Anorganisch-Chemisches Institut), applying the general synthetic approach outlined here, has yielded several additional structurally characterized species of the types 7,7′-$\mathrm{[Cp^*Co(2,3\text{-}Et_2C_2B_4H_3)]_2}$ (directly linked at the apices) and $\mathrm{[Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}7)]_2R}$, where R = MeCH, 1,4-$\mathrm{C_6H_4}$, *cis*-$\mathrm{C_2H_2}$, and CC: Curtis, M. A.; Pritzkow, H.; Siebert, W.; Grimes, R. N. To be published.