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Organotransition-Metal Metallacarboranes. 29.[1] Synthesis of Selectively C- and B-Substituted Double- and Triple-Decker Sandwiches. $(\eta^5\text{-}C_5Me_5)Co^{III}(\eta^5\text{-}R_2C_2B_3R'_3H_2)$ Cobaltocenium Analogues

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In earlier publications from our laboratory, methods were described for the regiospecific introduction of organic substituents onto cage boron and carbon atoms in small metallacarborane clusters. Here we report the selective application of these approaches in the targeted synthesis of several double-decker, triple-decker, and tetradecker sandwich compounds including the parent species $(C_5Me_5)Co(C_2B_3H_7)$ and $(C_5Me_5)Co(C_2B_3H_5)Co(C_5Me_5)$. The peralkyl species $(C_5Me_5)Co^{III}[(Me_2C_2B_3Me_3(\mu\text{-}H)_2]$ (**5**), an isostructural and isoelectronic analogue of the decamethylcobaltocenium ion $[(C_5Me_5)_2Co^{III}]^+$, was prepared and structurally characterized via X-ray diffraction. The C_2B_3 and C_5 rings in **5** are staggered and nearly parallel, and the metal is approximately centered over each ring. The cobalt–C_5Me_5 centroid distance (1.68 Å) in **5** is virtually identical to that reported in the literature for $(C_5Me_5)_2Co^+$, but the cobalt–C_2B_3 centroid vector is much shorter (1.54 Å), indicating greater covalent character in the Co–carborane vs the Co–C_5Me_5 interaction. In **5** the C_5Me_5 methyl groups are bent out of the C_5 plane away from the metal, in accord with theoretical predictions, but the methyls on the carborane ligand are bent *toward* the metal atom, an observation that probably reflects differences in orbital hybridization in the two rings. The permethyl triple-decker complex $(C_5Me_5)Co(Me_2C_2B_3Me_3)Co(C_5Me_5)$ was synthesized via deprotonation and metal-capping of $(C_5Me_5)Co(Me_2C_2B_3Me_3H_2)$. The unsubstituted triple-decker complex $(C_5Me_5)Co(C_2B_3H_5)Co(C_5Me_5)$ was prepared via two routes: (i) desilylation of the *C,C′*-bis(trimethylsilyl) derivative and (ii) deprotonation and metal capping of the parent double-decker $(C_5Me_5)Co(C_2B_3H_7)$. Attempted tetradecker stacking of $(C_5Me_5)Co(C_2B_3H_5\text{-}5\text{-}Cl)^-$ ion with $NiBr_2$ led to the fusion product $(C_5Me_5)_2Co_2C_4B_6H_8Cl_2$, but $(C_5Me_5)Co(Me_2C_2B_3H_3\text{-}5\text{-}Me)^-$ and $NiBr_2$ gave the desired tetradecker $[(C_5Me_5)Co(Me_2C_2B_3MeH_2)]_2Ni$ in low yield. New compounds were isolated as air-stable solids and characterized via ^1H and ^{11}B NMR, IR, and mass spectra.

Introduction

Metal–carborane sandwich compounds (metallacarboranes) are electronic analogues of metallocenes, a relationship that was recognized at the inception of this field more than two decades ago[2] and is well grounded in experimental and theoretical studies in this area.[3] The analogy is particularly apt for complexes of the pyramidal $C_2B_4H_4^{2-}$, planar $C_2B_3H_5^{2-}$, and planar $C_2B_3H_3^{4-}$ ligands and their derivatives, which are closely similar in size and shape to cyclopentadienyl and arene rings and can function as surrogates for them in sandwich systems.[4a] In our group, these properties have allowed us to design and construct a variety of multidecker and multilevel metal sandwich and linked-sandwich systems that utilize both small carborane and aromatic hydrocarbon building-block ligands.[4]

Direct structural and spectroscopic comparison of metallocenes and their small-carborane metal sandwich counterparts has been complicated by the fact that most known examples of the latter family are heterosubstituted, typically having alkyl groups on one or both cage carbon atoms and hydrogens on boron. In such species, properties associated with the C_2B_3 ring system itself cannot be clearly distinguished from effects arising from the substituent groups. Double- or triple-decker metallacarborane sandwiches bearing unsubstituted or homosubstituted ligands, e.g., $(C_5R_5)M[R_2C_2B_3R_3(\mu\text{-}H)_2]$ or $(C_5R_5)M(R_2C_2B_3R_3)M(C_5R_5)$, would be of particular interest; until now, few such complexes have been reported[5] and none has been crystallographically studied per se. However, the recent development in our laboratory of controlled synthetic routes[1,6] to C- and B-substituted derivatives of $Cp^*Co(H_2C_2B_3H_5)$ ($Cp^* = \eta^5\text{-}C_5Me_5$) has made it possible to prepare such species as desired. Here we apply these approaches to the synthesis of specific homosubstituted target complexes of the types mentioned, including a permethylated cobaltocenium analogue that has been structurally characterized.

Results and Discussion

Stepwise B-Methylation of $Cp^*Co(Me_2C_2B_3H_5)$ (2). The known compound[7] **1**, an orange solid, was readily converted in high yield to the yellow nido species **2** by decapitation with wet TMEDA (an earlier synthesis[7] of this complex via treatment of **1** with concentrated NaOH in acetonitrile required 2 days). Bridge-deprotonation of **2** with butyllithium followed by reaction with methyl iodide gave the yellow crystalline *B*(5)-methyl

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(1) (a) Part 28: Benvenuto, M. A.; Grimes, R. N. *Inorg. Chem.*, preceding paper in this issue. (b) Based in part on the Ph.D. Thesis of M.A.B., University of Virginia, 1992.

(2) Hawthorne, M. F.; Dunks, G. B. *Science* **1972**, *178*, 462.

(3) (a) Mingos, D. M. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, England, 1982; Chapter 19. (b) Grimes, R. N. *Ibid.*, Chapter 5.5. (c) O'Neill, M. E.; Wade, K. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum Press: New York, 1982; Chapter 1 and references therein.

(4) Recent reviews: (a) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251. (b) Grimes, R. N. *Pure Appl. Chem.* **1991**, *63*, 369. (c) Grimes, R. N. *Electron-Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; John Wiley and Sons: New York, 1991; Chapter 11, pp 261–285.

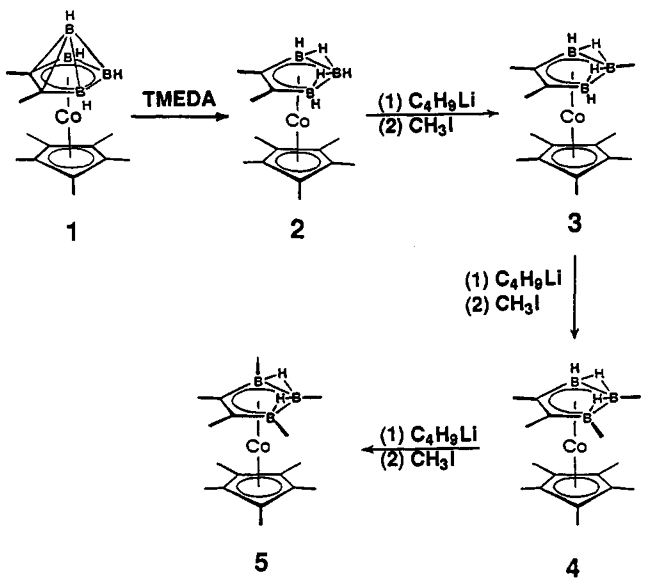
(5) $(C_5H_5)_2Co_2C_2B_3H_5$ (two isomers) and $(C_5H_5)Co(C_2B_3H_7)$ are known: Grimes, R. N.; Beer, D. C.; Sneddon, L. G.; Miller, V. R.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 1138.

(6) (a) Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1990**, *9*, 1171. (b) Attwood, M. D.; Davis, J. H., Jr.; Grimes, R. N. *Organometallics* **1990**, *9*, 1177. (c) Piepgrass, K. W.; Davis, J. H., Jr.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1991**, *113*, 680. (d) Piepgrass, K. W.; Grimes, R. N. *Organometallics*, **1992**, *11*, 2397. (e) Piepgrass, K. W.; Stockman, K. E.; Sabat, M.; Grimes, R. N. *Organometallics* **1992**, *11*, 2404.

(7) Finster, D. C.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1981**, *103*, 1399.

0020-1669/92/1331-3904$03.00/0

Scheme I



derivative **3** in almost quantitative yield (Scheme I). In an application of the previously described approach,[6a] this sequence was repeated twice more to give the *B*(4/6,5)-dimethyl and *B*(4,5,6)-trimethyl complexes (**4** and **5**, respectively), each of which was isolated as yellow crystals. These derivatives were characterized from their NMR, infrared, and mass spectra (Tables I–III and Experimental Section), which are consistent with the structures shown. In the infrared spectra, the characteristic B–H stretching band near 2500 cm^{-1} is very strong in **2** and **3**, of medium intensity in **4**, and absent in **5**, which lacks terminal BH hydrogens. The proton NMR spectra clearly reflect the presence of a mirror plane in **2**, **3**, and **5** and the asymmetry of **4**.

Structural Characterization of $Cp^*Co(Me_2C_2B_3Me_3H_2)$ (5). The permethyl species **5** is of interest given its isoelectronic and isostructural relationship to decamethylcobaltocenium ion, $Cp^*_2Co^+$ (both complexes contain formal Co(III); **5** has a dinegative carborane ligand and hence is neutral). Formally, **5** is derived from $Cp^*_2Co^+$ by isoelectronic replacement of three ring carbon atoms with three B^- and two bridging protons. Since the 10 ring atoms bear identical substituents, detailed structural comparison of this complex with the decamethylcobaltocenium ion provides a direct measurement of the consequences of interchanging carbon and boron atoms in the rings. Accordingly, an X-ray crystallographic analysis was conducted on **5**. Table IV lists information on the data collection and structure determination, and the atom coordinates, bond distances and bond angles are presented in Tables V–VII.

The molecular structure of **5**, shown in Figure 1, is a double-decker sandwich in which the two rings adopt a staggered and nearly parallel (dihedral angle 2.7°) conformation, with an approximate mirror plane defined by B(5), Co, and C(13). Reflecting the homosubstitution on the 10 ring atoms, which would tend to even out electronic substituent effects on the structure, the cobalt atom is nearly centered over both rings. With respect to the carborane ligand, the mean Co–B distance of 2.050 (5) Å is only slightly shorter than the mean Co–C value of 2.065 (4) Å. These distances are within the ranges of corresponding bond lengths in other *nido*-MC_2B_3 clusters (where M = Co in all but one case);[8] however, the observed carborane ring C(2)–C(3) distance of 1.477 (8) Å in **5** is significantly longer than the previously observed[8] values of 1.35 (2)–1.43 (1) Å. The short carbon–carbon interaction normally observed in 2,3-C_2B_3 ring ligands, indicating multiple-bond character, has been discussed in earlier papers.[8d] The lengthening of this bond in **5**, with its implied lower C–C bond order, is evidently another consequence of the "evening-out" effect of homoalkylation mentioned above, whereby the differences in C–C, C–B, and B–B bonding within the ring are mitigated. Additionally, we surmise that the presence of five electron-donating methyl substituents raises the overall electron density in the ring, reducing the "electron deficiency" in the vicinity of the boron nuclei and thereby promoting a more uniform electron distribution in the heterocycle. These are, of course, questions that require investigation by quantitative calculations and, hopefully, crystallographic studies of other homosubstituted sandwich complexes.

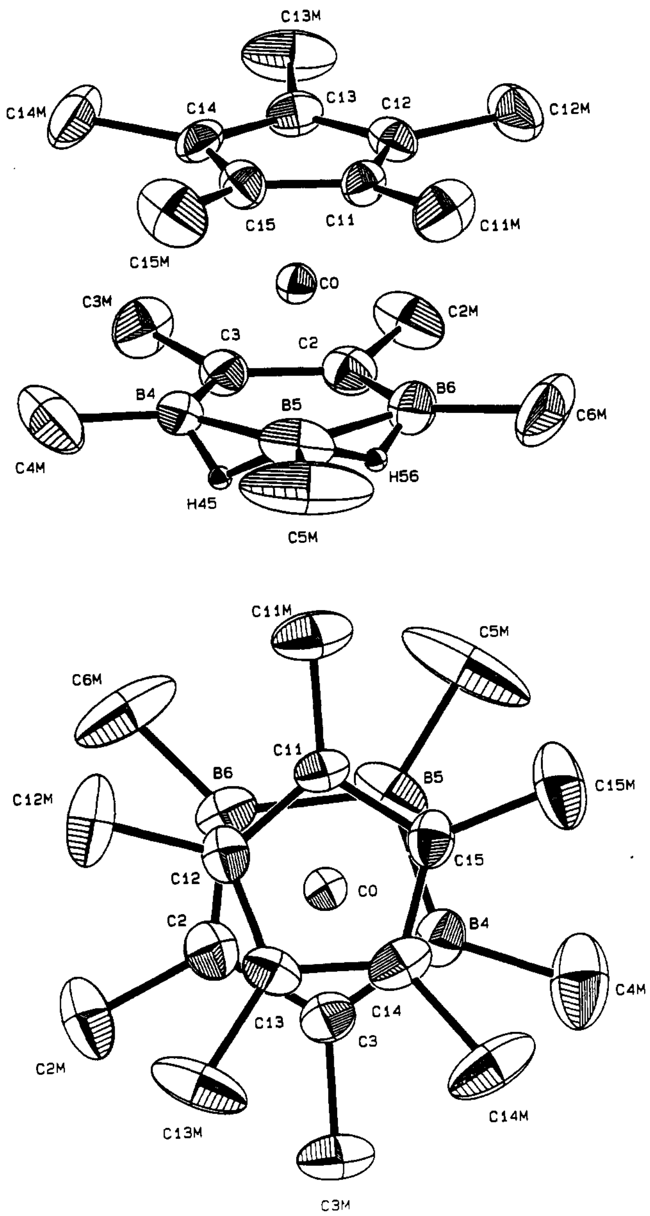


Figure 1. ORTEP views of the molecular structure of **5** employing 30% thermal ellipsoids, with terminal hydrogens omitted.

The most interesting aspects of this structure concern its relationship to the isoelectronic decamethylcobaltocenium ion, several salts of which have been characterized by X-ray crystallography.[9] The cobalt–C_5 ring bond lengths in **5** are nearly identical with a range of 2.052 (6)–2.064 (6) Å (mean value

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[8] (a) $Cp^*Co(Et_2C_2B_3H_4\text{-}5\text{-}C(=CH_2)OC(O)Me)$: see ref 6c,e. (b) $Cp^*Co(Me_2C_2B_3H_4)\text{-}\mu\text{-}HgCl$: Finster, D. C.; Grimes, R. N. *Inorg. Chem.* **1981**, *20*, 863. (c) $[CpCo(Me_2C_2B_3H_4)]_2Hg$: Finster, D. C.; Grimes, R. N. *Ibid.* (d) $(Cp_2Co{-}Me_2C_2B_4H_4)Co(Me_2C_2B_3H_4)$: Pipal, J. R.; Maxwell, W. M.; Grimes, R. N. *Ibid.* **1978**, *17*, 1447. (e) $(THF\text{-}B_9H_{12})Co(Me_2C_2B_3H_5)$: Borodinsky, L.; Sinn, E.; Grimes, R. N. *Ibid.* **1982**, *21*, 1928. (f) $(CO)_3Fe(C_2B_3H_7)$: Brennan, J. P.; Grimes, R. N.; Schaeffer, R.; Sneddon, L. G. *Inorg. Chem.* **1973**, *12*, 2276.

Table I. 300-MHz ^1H FT NMR Data

compd	δ^{a-c}
$(C_5Me_5)Co(Me_2C_2B_4H_4)$ (**1**)	1.80 s (C_5Me_5), 2.05 s (cage C–Me)
$(C_5Me_5)Co(Me_2C_2B_3H_5)$ (**2**)	1.80 s (C_5Me_5), 1.65 s (cage C–Me), –5.9 br s (B–H–B)
$(C_5Me_5)Co(Me_2C_2B_3H_4\text{-}5\text{-}Me)$ (**3**)	1.80 s (C_5Me_5), 1.65 s (cage C–Me), 0.35 s (B–Me), –5.2 br s (B–H–B)
$(C_5Me_5)Co(Me_2C_2B_3H_3\text{-}4/6,5\text{-}Me_2)$ (**4**)	1.80 s (C_5Me_5), 1.70 s (C_5Me_5), 1.65 s (cage C–Me), 0.35 s (B–Me), 0.25 s (B–Me), –5.3 br s (B–H–B), –4.9 br s (B–H–B)
$(C_5Me_5)Co(Me_2C_2B_3Me_3H_2)$ (**5**)	1.60 s (C_5Me_5), 1.55 s (cage C–Me), 0.40 s (B–Me), 0.15 s (B–Me), –5.0 br s (B–H–B)
$(C_5Me_5)Co(Me_2C_2B_3H_4\text{-}5\text{-}Cl)$ (**6**)	1.80 s (C_5Me_5), 1.65 s (cage C–Me), –3.9 br s (B–H–B)
$(C_5Me_5)Co(Me_2C_2B_3H_3\text{-}4/6\text{-}Me\text{-}5\text{-}Cl)$ (**7**)	1.80 s (C_5Me_5), 1.65 s (cage C–Me), 0.50 s (B–Me), –3.4 br s (B–H–B)
$(C_5Me_5)Co(Me_2C_2B_3H_2\text{-}4,6\text{-}Me_2\text{-}5\text{-}Cl)$ (**8**)	1.60 s (C_5Me_5), 1.50 s (cage C–Me), 0.50 s (B–Me), –3.6 br s (B–H–B)
$(C_5Me_5)_2Co_2(Me_2C_2B_3\text{-}4,6\text{-}Me_2\text{-}5\text{-}Cl)$ (**9**)	2.30 s (cage C–Me), 1.50 s (C_5Me_5), 1.36 s (B–Me)
$(C_5Me_5)_2Co_2(Me_2C_2B_3Me_3)$ (**10**)	2.20 s (cage C–Me), 1.60 s (B–Me), 1.40 s (C_5Me_5), 1.20 s (B–Me)
$(C_5Me_5)_2Co_2(C_2B_3H_5)$ (**14**)	4.40 br s (cage C–H), 1.60 s (C_5Me_5)
$(C_5Me_5)_2Co_2(C_4B_6Cl_2H_8)$ (**17**)	4.40 br s (cage C–H), 2.80 br s (cage C–H), 1.61 s (C_5Me_5), 1.57 s (C_5Me_5)
$[(C_5Me_5)Co(Me_2C_2B_3H_2Me)]_2Ni$ (**18**)	2.18 s (cage C–Me), 1.51 s (C_5Me_5), 1.16 s (B–Me)

[a] $CDCl_3$ solution. [b] Shifts relative to $(CH_3)_4Si$. Integrated peak areas in all cases are consistent with the assignments given. Legend: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet. [c] B–$H_{terminal}$ resonances are broad quartets and mostly obscured by other signals.

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

compd	δ (J_{BH}, Hz)$^{a-c}$	rel areas
1	11.4 (70), 5.3 (149), 2.9 (165)	1:2:1
3	19.8, –0.7 (131)	1:2
5	11.6, 7.1	1:2
8	12.8, 6.9	1:2
9	57.4, 10.5	1:2
13	60.8 (121), 8.1	1:2
14	51.7, 7.9	1:2
17	32.6, 21.4, 15.6, 13.7, –9.7	1:1:1:2:1
18	80.4, 10.0	1:2

[a] Shifts relative to $BF_3{\cdot}OEt_2$, positive values downfield. [b] Dichloromethane solution. [c] H–B coupling constant in Hz is given in parentheses, when resolved.

Table III. Infrared Absorptions (cm^{-1}; Neat Films on KBr Plates)^{a,b}

compd	absorptions
1	2960 m, 2918 m, 2861 w, 2530 vs, 1453 m, 1363 m, 1029 w, 868 m, 739 m
2	2960 m, 2910 s, 2858 m, 2501 vs, 1856 m, 1539 m, 1363 vs, 1003 m, 780 m
3	2941 m, 2908 m, 2854 w, 2498 m, 1930 w, 1364 m, 1302 w, 1074 w, 1025 m, 886 w, 770 w
4	2942 m, 2909 s, 2857 m, 2490 m, 1931 w, 1376 m, 1265 m, 1074 w, 1025 w, 706 vs
5	2914 m, 2899 s, 2852 m, 2490 vw, 2358 w, 2332 w, 1260 m, 1235 w, 1021 m, 884 s
6	2961 m, 2915 vs, 2864 m, 2519 s, 1890 w, 1364 s, 1012 m, 976 m, 846 s, 769 m
7	2952 m, 2907 s, 2857 m, 2502 m, 1869 w, 1364 s, 1297 w, 1023 m, 866 m, 817 w
8	2927 m, 2910 m, 2518 br m, 1245 m, 1077 w, 1029 w, 832 s
9	2954 m, 2918 s, 2853 m, 2500 w, 2340 w, 2323 w, 1379 m, 1292 m, 1123 w, 861 w
10	2924 m, 2920 s, 2854 m, 2423 w, 2358 m, 2343 m, 1290 w, 1080 w, 1023 w
14	2955 m, 2915 s, 2850 m, 2467 vs, 1375 m, 1255 w, 1026 m, 808 s, 735 m
17	3106 s, 2912 vs, 2527 vs, 2475 s, 2360 m, 2334 m, 1375 vs
18	2922 s, 2852 m, 2468 w, 1437 m, 1088 w, 1023 w, 865 w, 776 w

[a] Microcrystalline films obtained by evaporation of solutions. [b] Legend: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

Table IV. Experimental X-ray Diffraction Parameters and Crystal Data for **5**

empirical formula	$CoC_{17}B_3H_{32}$	Z	2
fw	327.8	μ, cm^{-1} (Mo Kα)	9.15
cryst color, habit	yellow, needle	transm factors	0.75–1.17
cryst dimens, mm	0.38 × 0.22 × 0.18	λ, Å	0.7107
		D(calcd), g cm^{-3}	1.18
space group	$P\bar{1}$	$2\theta_{max}$, deg	50
a, Å	9.088 (2)	reflecns measd	3347
b, Å	15.184 (3)	reflecns obsd	3127
c, Å	7.073 (2)	R	0.045
α, deg	90.46 (2)	R_w	0.051
β, deg	108.48 (2)	largest peak in final diff map, e/Å^3	0.20
γ, deg	90.86 (2)		
V, Å^3	925.6		

Table V. Final Positional Parameters

atom	x	y	z
Co	0.2617 (1)	0.24732 (6)	0.0524 (1)
C(2)	0.4124 (7)	0.2066 (4)	0.3221 (9)
C(2M)	0.5743 (8)	0.1630 (5)	0.359 (1)
C(3M)	0.2638 (9)	0.0513 (4)	0.234 (1)
C(3)	0.2677 (7)	0.1529 (4)	0.2623 (9)
C(4M)	–0.0536 (8)	0.1686 (7)	0.132 (1)
C(5M)	0.075 (1)	0.4015 (7)	0.211 (1)
C(6M)	0.510 (1)	0.3839 (6)	0.360 (1)
C(11M)	0.264 (1)	0.4328 (4)	–0.172 (1)
C(11)	0.2578 (7)	0.3343 (4)	–0.1717 (8)
C(12)	0.3842 (6)	0.2776 (4)	–0.1389 (8)
C(12M)	0.5540 (7)	0.3082 (6)	–0.094 (1)
C(13)	0.3307 (8)	0.1911 (4)	–0.1717 (9)
C(13M)	0.428 (1)	0.1112 (5)	–0.168 (1)
C(14M)	0.056 (1)	0.1127 (5)	–0.300 (1)
C(14)	0.1674 (8)	0.1912 (4)	–0.2275 (8)
C(15)	0.1219 (7)	0.2800 (5)	–0.2271 (9)
C(15M)	–0.0437 (8)	0.3131 (6)	–0.299 (1)
B(4)	0.1204 (9)	0.2060 (6)	0.213 (1)
B(5)	0.176 (1)	0.3141 (7)	0.245 (1)
B(6)	0.386 (1)	0.3064 (6)	0.319 (1)
H(45)	0.128 (6)	0.253 (4)	0.305 (8)
H(56)	0.293 (8)	0.330 (4)	0.34 (1)

2.060 Å). As in **5**, staggered ring conformations are found for $Cp^*_2Co^+$. The Co–Cp* centroid distance of 1.68 Å in **5** is virtually identical with that found[9] in $Cp^*_2Co^+$, but the Co–C_2B_3 centroid vector of 1.54 Å is much shorter, a typical feature[8] of metal–C_2B_3 complexes that clearly reflects the stronger Co–carborane vs Co–Cp* covalent bonding. The ring C–C and C–Me bond lengths in the Cp* ligand of **5**, whose mean values are respectively 1.407 and 1.519 Å, are close to the values reported[9] for $Cp^*_2Co^+$, although in the latter species the average ring C–C distances are slightly longer (1.422[9a] and 1.424 Å;[9b] all esd's are <0.01 Å).

An unusual feature of **5** is found in its methyl substituents. Although the methyl carbon atoms on the Cp* ligand are bent out of the C_5 ring plane by an average of 5.0° in a direction away from cobalt—in accord with the prediction of Hoffmann, Mingos, and co-workers[10] for η^n-C_nR_n ligands where $n < 6$—the methyls on the carborane ring are bent *toward* the metal by an average

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[9] (a) $(Cp^*_2Co^+)_2[TCNQI_2]^{2-}$: Miller, J. S.; Calabrese, J. C.; Harlow, R. L.; Dixon, D. A.; Zhang, J. H.; Reiff, W. M.; Chittipeddi, S.; Selover, M. A.; Epstein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 5496. (b) $(Cp^*_2Co^+)_2[(NC)_2CC(CN)_2]^{2-}$: Dixon, D. A.; Miller, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 3656.

Table VI. Bond Lengths (Å)

Co–C(2)	2.070 (6)	C(6M)–B(6)	1.58 (1)
Co–C(3)	2.060 (6)	C(11M)–C(11)	1.496 (8)
Co–C(11)	2.064 (6)	C(11)–C(12)	1.407 (7)
Co–C(12)	2.057 (6)	C(11)–C(15)	1.420 (8)
Co–C(13)	2.064 (6)	C(12)–C(12M)	1.538 (8)
Co–C(14)	2.063 (6)	C(12)–C(13)	1.386 (8)
Co–C(15)	2.052 (6)	C(13)–C(13M)	1.510 (8)
Co–B(4)	2.059 (8)	C(13)–C(14)	1.409 (8)
Co–B(5)	2.037 (9)	C(14M)–C(14)	1.530 (9)
Co–B(6)	2.055 (9)	C(14)–C(15)	1.415 (8)
C(2)–C(2M)	1.569 (8)	C(15)–C(15M)	1.523 (8)
C(2)–C(3)	1.477 (8)	B(4)–B(5)	1.70 (1)
C(2)–B(6)	1.54 (1)	B(5)–B(6)	1.82 (1)
C(3M)–C(3)	1.553 (9)	B(4)–H(45)	0.95 (5)
C(3)–B(4)	1.52 (1)	B(5)–H(45)	1.17 (6)
C(4M)–B(4)	1.60 (1)	B(5)–H(56)	1.07 (6)
C(5M)–B(5)	1.60 (1)	B(6)–H(56)	0.98 (6)

Table VII. Bond Angles (deg)

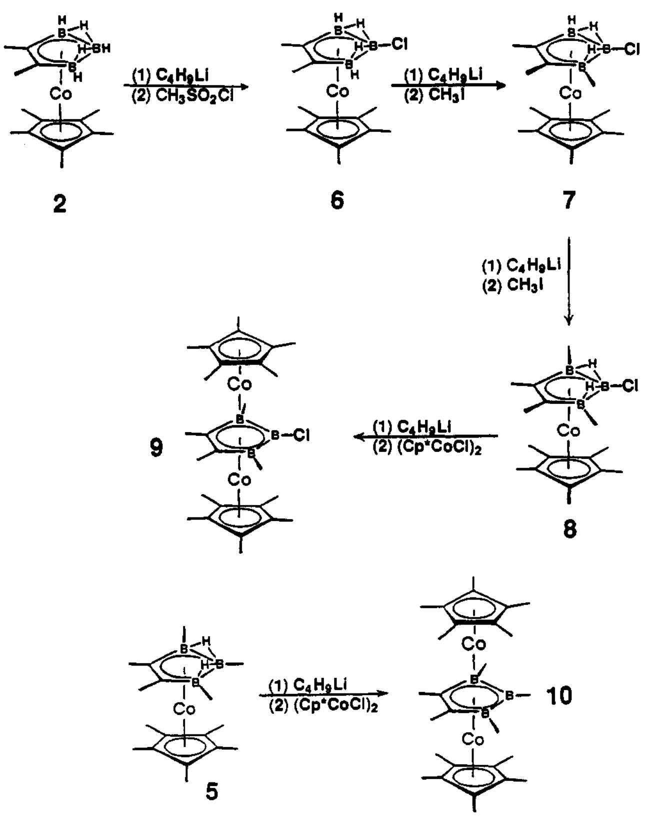
Co–C(2)–C(2M)	127.0 (4)	C(11M)–C(11)–C(12)	126.7 (6)
C(2M)–C(2)–C(3)	121.0 (6)	C(11M)–C(11)–C(15)	126.4 (6)
C(2M)–C(2)–B(6)	124.5 (6)	C(12)–C(11)–C(15)	106.5 (5)
C(3)–C(2)–B(6)	114.0 (6)	Co–C(12)–C(12M)	130.2 (4)
Co–C(3)–C(3M)	127.5 (4)	C(11)–C(12)–C(12M)	124.7 (6)
C(2)–C(3)–C(3M)	123.4 (6)	C(11)–C(12)–C(13)	109.7 (5)
C(2)–C(3)–B(4)	114.4 (6)	C(12M)–C(12)–C(13)	125.4 (6)
C(3M)–C(3)–B(4)	122.0 (6)	Co–C(13)–C(13M)	130.0 (5)
Co–B(4)–C(4M)	128.8 (6)	C(12)–C(13)–C(13M)	126.1 (7)
C(3)–B(4)–C(4M)	126.8 (8)	C(12)–C(13)–C(14)	108.1 (5)
C(3)–B(4)–B(5)	106.7 (6)	C(13M)–C(13)–C(14)	125.6 (7)
C(4M)–B(4)–B(5)	126.3 (7)	Co–C(14)–C(14M)	131.0 (5)
Co–B(5)–C(5M)	129.8 (6)	C(13)–C(14)–C(15)	107.5 (5)
C(5M)–B(5)–B(4)	130 (1)	C(14M)–C(14)–C(15)	124.7 (7)
C(5M)–B(5)–B(6)	128 (1)	C(13)–C(14)–C(14M)	127.4 (7)
B(4)–B(5)–B(6)	101.6 (5)	Co–C(15)–C(15M)	130.9 (5)
Co–B(6)–C(6M)	129.3 (6)	C(11)–C(15)–C(14)	108.2 (6)
C(2)–B(6)–C(6M)	128.7 (8)	C(11)–C(15)–C(15M)	125.2 (6)
C(2)–B(6)–B(5)	103.2 (6)	C(14)–C(15)–C(15M)	126.2 (6)
C(6M)–B(6)–B(5)	128.0 (8)	B(4)–H(45)–B(5)	107 (5)
Co–C(11)–C(11M)	130.8 (4)	B(5)–H(56)–B(6)	125 (6)

of 3.4°. This latter effect is uneven, with a deflection of 4.8° for the methyls bound to C(2) and C(3), 3.3° for B(4/6)–Me, and only 0.7° for B(5)–Me. Since a similar finding was reported earlier[8b] for two mercury-bridged complexes incorporating the *nido*-$Cp^*CoC_2B_3$ moiety, the effect is evidently intrinsic to the covalent binding between the metal and the carborane ring. Differences in orbital hybridization, approximating sp^3 for the C_2B_3 ring atoms and sp^2 in the formal Cp^{*-} ligand, provide a possible rationale for the observed out-of-plane bending patterns.

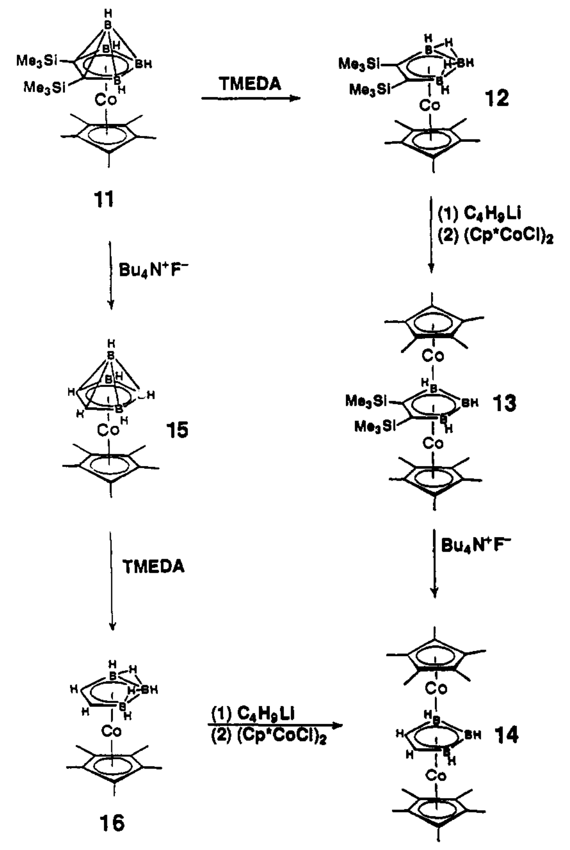
Synthesis of Selectively Substituted Triple-Decker and Tetradecker Sandwich Complexes. The double-decker species **2**–**5** are precursors to larger sandwiches via established stacking reactions,[4,11,12] and this approach was employed to construct specific target molecules that were previously inaccessible by controllable routes, including those with unsubstituted or homosubstituted C_2B_3 ring ligands. As outlined in Scheme II, **2** was regiospecifically B(5)-chlorinated to give **6**, which was in turn methylated at the remaining boron positions to form **7** and **8**. Deprotonation of the latter complex followed by treatment with $(Cp^*CoCl)_2$ afforded the *B*(5)-chloro triple-decker **9**. The black pentamethyl complex **10**, the first triple-decker metallacarborane sandwich having identical substituents on all ring atoms, was similarly prepared in low yield from **5**.

Another synthetic target, the unsubstituted triple-decker $Cp^*_2Co_2(H_2C_2B_3H_3)$ (**14**) was obtained via two different routes from the closo cluster[1a] $Cp^*Co[(Me_3Si)_2C_2B_4H_4]$ (**11**). As depicted in Scheme III, the decapitation of **11** (compound **3a** in the preceding paper[1a]) to give **12** (previously[1a] **9a**), and reaction of that species with butyllithium and $(Cp^*CoCl)_2$, produced the *C,C′*-bis(trimethylsilyl) sandwich **13**, which was desilylated with tetrabutylammonium fluoride (TBAF) to form black, crystalline,

Scheme II



Scheme III



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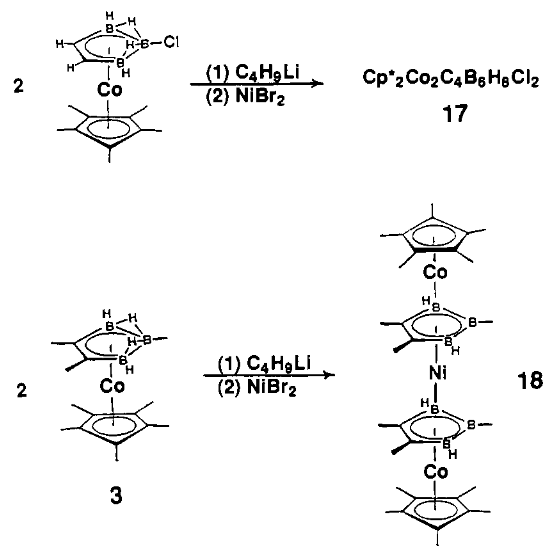
(10) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.

(11) (a) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4776. (b) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *Ibid.* **1989**, *111*, 4784.

(12) (a) Piepgrass, K. W.; Davis, J. H., Jr.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1991**, *113*, 681. (b) Piepgrass, K. W.; Hölscher, M.; Meng, X.; Sabat, M.; Grimes, R. N. Submitted for publication.

Scheme IV



air-stable **14**. In an alternative approach that illustrates the versatility of this chemistry (Scheme III), **11** was first desilylated, affording **15** (compound **6a** in the accompanying article). Decapitation of **15** formed **16** (elsewhere[1a] **11a**), which was deprotonated and complexed with Cp*Co to generate **14**.

Attempts to determine the solid-state structure of **14** by X-ray crystallography were unsuccessful owing to extensive disorder in the rings; in several attempts to collect data at low temperatures the crystals shattered. However, the proposed triple-decker geometry is fully consistent with the spectroscopic data. The mass spectrum exhibits an intense parent group at m/z 450 with essentially no fragmentation, while the ^{1}H NMR spectrum shows single Cp* and cage C–H resonances; the ^{11}B NMR spectrum exhibits a low-field area-1 resonance typical of C_2B_3-bridged multidecker systems.[1a,5,6,11]

The recently discovered tetradecker-stacking reaction[12] involves coordination of two suitably tailored *nido*-MC_2B_3 units to a third metal, M′. In the earlier work it was shown that the reaction generates stable tetradeckers from Cp*Co($Et_2C_2B_3H_4$-5-X) clusters only if the substituent X on B(5) (the middle boron) is substantially less electron-donating than hydrogen, as measured by the proton NMR B–H–B signal;[12] the best results were obtained for X = Cl. The present study furnished an opportunity to determine whether this pattern extends to Cp*Co($RR'C_2B_3H_4$-5-X) species in which the R and R′ groups are H and/or $SiMe_3$. Accordingly, the *B*(5)-chloro *C*(2)-trimethylsilyl and *B*(5)-chloro *C*(2,3)-bis(trimethylsilyl) complexes (**10b** and **9b**, respectively, in the preceding paper) were deprotonated and treated with 0.5 equiv of $NiBr_2$ in an attempt to produce tetradeckers. No such products were obtained in either case, and considerable quantities of the neutral starting complexes were recovered. Similar treatment of the B(5)–Cl C(2,3)–H_2 species (**11b** in ref 1a) produced, on workup, not a tetradecker but rather a 12-vertex dicobaltacarborane, $Cp^*{}_2Co_2C_4B_6H_8Cl_2$ (**17**, Scheme IV).

Complex **17**, a black crystalline solid, is formally related to the previously characterized $Cp_2Co_2R_4C_4B_6H_6$ clusters (R = H, Me) whose structures have been established by X-ray crystallography.[13] It is not possible to assign a specific cage structure to **17** since the presence of chlorine substituents, and of Cp* rather than Cp ligands, precludes direct comparison of its NMR spectra with those of the earlier species. The observation of two Cp* signals and five boron resonances in the ^{1}H and ^{11}B NMR spectra, respectively, indicates an absence of molecular symmetry in **17**. However, it is reasonably certain that this product forms via metal-promoted fusion of the Cp*Co($C_2B_3H_5Cl^-$) anions, a process frequently encountered in working with complexes of this type.[14] If the nickel ion initially coordinates to two Cp*CoC_2B_3 cluster units to form a reactive intermediate, such a species could (1) lead directly to an isolable tetradecker, (2) undergo cluster fusion to produce species such as **17** with expulsion of nickel, or (3) revert to the starting cobaltacarborane species via reprotonation of the ligands. These are often competitive processes, as will be discussed in a forthcoming full paper on tetradecker sandwich synthesis.[12b]

When the *B*(5)-methyl derivative **3** was subjected to similar reaction conditions, the desired tetradecker complex [Cp*Co($Me_2C_2B_3MeH_2$)]$_2$Ni (**18**) was isolated, although in only 8% yield, as a red-black crystalline solid (Scheme IV). The spectroscopic data clearly point to a tetradecker structure, i.e., the mass spectrum exhibits a strong parent group at m/z 653, and the Cp*, C–CH_3, and B–CH_3 resonances are within the ranges found for structurally established tetradecker sandwich species.[12] A feature that is particularly diagnostic for an extended multidecker sandwich is the signal at very low field (δ 80) in the ^{11}B NMR spectrum.

Concluding Remarks

In this work we have applied methods for selective organosubstitution at ring boron and carbon atoms of small metallacarborane sandwich complexes, described previously,[1a,6] to prepare a number of designed species based on the Cp*CoC_2B_3 building-block unit. As a general observation, this tailorability increases the utility of these complexes as synthons for building larger multiunit systems. Moreover, the ability to vary independently both the C- and B-substituents extends the options available for circumventing problems encountered in synthesis with these ligands and should open up new possibilities as well. For example, we anticipate that it will be feasible to prepare externally cyclized species in which the C–C cage bonds of one or more MC_2B_n clusters (n = 3, 4) are incorporated into larger ring structures. Our efforts in this area are continuing.

Experimental Section

Except where otherwise indicated, materials, instrumentation, and general procedures were identical with those described in the preceding paper.[1a] All new products gave unit-resolution mass spectra exhibiting strong parent envelopes and intensity patterns in good agreement with calculated spectra based on natural isotopic distributions. In addition, the fragmentations exhibited in the unit-resolution spectra are consistent with the proposed structures, e.g., loss of ligand or M(ligand) units from the parent ions. Elemental analyses were provided by E&R Microanalytical Laboratory, Corona, NY 11368.

Synthesis of Cp*Co($Me_2C_2B_4H_4$) (1). A solution of LiC_5Me_5 was prepared by addition of 10.4 mmol of *n*-butyllithium (1.6 M in hexane) to 10.4 mmol of C_5Me_5H in dry THF. This solution was stirred for 1 h and added dropwise to anhydrous $CoCl_2$ (1.35 g, 10.4 mmol) in THF, and the combined solution was stirred for 45 min. To this was added a solution of $Na^+Me_2C_2B_4H_5^-$ (prepared via reaction of 1.08 g (10.4 mmol) of the neutral carborane with excess NaH in 50 mL of THF), and the mixture was stirred for 16 h. The reactor was opened in air, the solution rotary-evaporated to dryness, the residue dissolved in dichloromethane, and the solution filtered through 2 cm of silica gel. The eluent was evaporated to dryness, and the residue was taken up in 2:1 hexane/dichloromethane and eluted through a silica column. The second band obtained was bright orange **1** (0.861 g, 2.91 mmol, 28%). Anal. Calcd for $CoC_{14}B_4H_{25}$: C, 56.90; H, 8.53. Found: C, 56.75; H, 8.80.

Synthesis of Cp*Co($Me_2C_2B_3H_5$) (2). A solution of 0.861 g (2.91 mmol) of **1** in 30 mL of TMEDA was prepared, 3 drops of water were added via pipet, and the solution was stirred in air for 1.5 h. The solvent was removed under vacuum, and the product was suction-filtered through 2 cm of silica gel, yielding a bright yellow solution, which was rotary-

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(13) (a) Wong, K.-S.; Bowser, J. R.; Pipal, J. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 5045. (b) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 1936. (c) Piepgrass, K. W.; Curtis, M. A.; Wang, X.; Sabat, M.; Grimes, R. N. Manuscript in preparation.

(14) Grimes, R. N. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 55 and references therein.

evaporated to give crystalline yellow **2**, 0.631 g (2.21 mmol, 76%). Anal. Calcd for $CoC_{14}B_3H_{26}$: C, 58.85; H, 9.17. Found: C, 58.96; H, 9.33.

Syntheses of Cp*Co($Me_2C_2B_3H_4$-5-Me) (3), Cp*Co($Me_2C_2B_3H_3$-4/6,5-Me_2) (4), and Cp*Co($Me_2C_2B_3H_2$-4,5,6-Me_3) (5). A 1.830-g (6.41-mmol) sample of **2** was placed in a 2-neck 250-mL round-bottom flask fitted with a stopcock and a septum cap. The flask was evacuated and cooled in liquid nitrogen, THF was added by distillation, and the liquid nitrogen bath was removed. While the flask was warming, 6.4 mmol of butyllithium in hexane was added via syringe, and the solution was warmed to room temperature, producing a color change to bright orange. After the mixture was stirred for 20 min, 12.8 mmol of methyl iodide was added, the solution was stirred for 1 h, and the solvent was removed under vacuum. The residue was dissolved in hexane, and the solution was suction-filtered through 2 cm of silica gel, giving 1.751 g (5.84 mmol, 91%) of yellow, crystalline **3**. Compound **4** was prepared via an identical procedure from **3** (0.587 g, 1.96 mmol), using 1.96 mmol of butyllithium and 3.92 mmol of methyl iodide, affording 0.548 g (1.75 mmol, 89%) of yellow **4**. The same procedure employing 0.548 g (1.75 mmol) of **4**, 1.75 mmol of butyllithium, and 3.50 mmol of methyl iodide gave 0.448 g (1.37 mmol, 78%) of yellow **5**. Anal. Calcd for **3**, $CoC_{15}B_3H_{28}$: C, 60.10; H, 9.42. Found: C, 60.39; H, 9.71. Calcd for **5**, $CoC_{17}B_3H_{32}$: C, 62.29; H, 9.84. Found: C, 62.51; H, 10.08.

Synthesis of Cp*$_2$Co$_2$($Me_2C_2B_3$-4,6-Me_2-5-Cl) (9) via Cp*Co($Me_2C_2B_3H_4$-5-Cl) (6), Cp*Co($Me_2C_2B_3H_3$-4/6-Me-5-Cl) (7), and Cp*Co($Me_2C_2B_3H_2$-4,6-Me_2-5-Cl) (8). A 369-mg (1.29-mmol) sample of **2** was placed in a 2-neck 250-mL round-bottom flask fitted with a stopcock and a septum cap. The flask was evacuated and cooled in liquid nitrogen, THF was added by distillation, and the liquid nitrogen bath was removed. While the flask was warming, 1.29 mmol of butyllithium was added via syringe, and the solution was warmed to room temperature, producing a color change to bright orange. After the mixture was stirred for 20 min, the flask was cooled in liquid nitrogen, 1.41 mmol of $MeSO_2$-Cl was injected, and the flask was allowed to warm to room temperature. The solution was stirred for 1 h, the solvent was removed under vacuum, the residue was dissolved in hexane, and the solution was suction-filtered through 2 cm of silica gel, giving 0.345 g (1.08 mmol, 83%) of yellow, crystalline **6**. Compound **7** was prepared via a similar procedure from **6** employing MeI in place of $MeSO_2Cl$. Compound **6** (0.341 g, 1.07 mmol) was reacted with 1.07 mmol of butyllithium and 1.13 mmol of methyl iodide, and the product was purified on a silica gel column in 5:1 hexane/CH_2Cl_2. The yield of **7** was 0.234 g (0.700 mmol, 66%). The same procedure employing 0.234 g (0.700 mmol) of **7**, 0.70 mmol of butyllithium, and 0.70 mmol of methyl iodide gave 0.126 g (0.362 mmol, 52%) of yellow **8**.

A solution of the $(Cp^*CoCl)_2$ dimer was prepared from 0.362 mmol each of butyllithium and pentamethylcyclopentadiene as described above in the synthesis of **1**. To this was added a solution of $Li^+[Cp^*Co(Me_2C_2B_3HMe_2Cl]^-$ (**8**$^-$), prepared from 0.362 mmol of the neutral carborane and an equimolar quantity of butyllithium with stirring for 15 min. The combined solution was stirred overnight. The reactor was opened in air, the solution was rotary-evaporated to dryness, the residue was dissolved in hexane, and the solution was filtered through silica gel in hexane followed by dichloromethane. The latter fraction was characterized from ^1H and ^{11}B NMR and mass spectra as **9**, 75 mg (0.14 mmol, 38%).

Synthesis of Cp*$_2$Co$_2$($Me_2C_2B_3Me_3$) (10). The procedure followed was the same as in the preparation of **9** except that **5** (0.148 g, 0.452 mmol) was employed in place of **8**. Equimolar quantities (0.274 mmol) of $CoCl_2$, C_5Me_5H, and butyllithium were used, affording 11 mg (0.021 mmol, 5%) of black **10**.

Synthesis of Cp*$_2$Co$_2$[$(Me_3Si)_2C_2B_3Me_3$] (13). The procedure given for the conversion of **8** to **9** was used to prepare **13** from **12**. A 0.221-mmol quantity of Cp*Co[$(Me_3Si)_2C_2B_3H_5$] (**12**, compound **9a** in the preceding paper[1a]) was deprotonated with an equimolar quantity of butyllithium in THF and added to a solution of 0.221 equiv of $(Cp^*CoCl)_2$ in hexane, prepared as described above, and allowed to stir 30 min before use. After mixing, the combined solution was stirred 5 h, opened to the air, and rotary-evaporated to give a dark red solid. This material was eluted in hexane through 2 cm of silica to give 0.126 g (0.212 mmol, 96%) of red crystalline **13**.

Synthesis of Cp*$_2$Co$_2$($C_2B_3H_5$) (14). (a) Via Desilylation of 13. A 0.118-g (0.199-mmol) sample of **13** in THF was treated with 0.398 mmol of TBAF (1.0 M in THF) in air, the mixture was stirred for 5 min, and the volatiles were removed by distillation in vacuo. The black residue was suction filtered through 2 cm of silica gel in CH_2Cl_2 solution until the eluent was clear. The eluent was stripped of solvent, the residue was taken up in 2:1 hexane/CH_2Cl_2, and the solution was eluted through a silica column, affording a black band of **14** (12 mg, 0.027 mmol, 14%).

(b) Via Complexation of 16. The procedure described above for the synthesis of **13** from **12** was followed with Cp*Co($C_2B_3H_7$) (**16**, compound **11a** in the preceding paper[1a]) as the starting complex. Using 54 mg (0.202 mmol) of **16** and equimolar quantities of butyllithium, $CoCl_2$, and C_5Me_5H, workup as before, with final purification via chromatography on a silica gel column in 1:1 hexane/CH_2Cl_2, gave black, crystalline **14** (20 mg, 0.044 mmol, 22%). Exact mass: calcd for $^{59}Co_2{}^{12}C_{22}{}^{11}B_3{}^1H_{35}{}^+$, *m/z* 450.1682; found, 450.1665.

Attempted Synthesis of [Cp*Co($C_2B_3H_4Cl$)]$_2$Ni. A solution of 137 mg (0.469 mmol) of Cp*Co($C_2B_3H_6$-5-Cl) (compound **11b** in the preceding paper[1a]) was deprotonated with 0.469 mmol of butyllithium and stirred for 30 min, after which 51 mg (0.234 mmol) of $NiBr_2$ was added and the mixture stirred for 4 h. The solvent was removed by rotary-evaporation and the residue filtered through 2 cm of silica gel in hexane followed by CH_2Cl_2 and methanol. The CH_2Cl_2 fraction was chromatographed on silica in 1:1 hexane/CH_2Cl_2, and the third band to elute was black, crystalline **17**. Anal. Calcd for $Co_2Cl_2C_{24}B_6H_{38}$: C, 49.68; H, 6.60. Found: C, 49.32; H, 6.88.

Synthesis of [Cp*Co($Me_2C_2B_3H_2$-5-Me)]$_2$Ni (18). The procedure in the preceding synthesis was followed, employing **3** (0.243 g, 0.811 mmol), 0.811 mmol of butyllithium, and 89 mg (0.406 mmol) of $NiBr_2$. The CH_2Cl_2 fraction from the suction filtration was pure **18**, 22 mg (0.034 mmol, 8%). Anal. Calcd for $Co_2C_{30}B_6H_{52}$: C, 55.08; H, 8.01. Found: C, 55.63; H, 8.58.

X-ray Structure Determination on 5. Measurements were carried out on a Rigaku AFC6S diffractometer at 25 °C using Mo Kα radiation. Table IV lists information on the data collection and structure determination. Preliminary measurements indicated a triclinic unit cell, and cell reduction calculations using the program TRACER II did not show a cell of higher symmetry. Unit cell dimensions were obtained using the setting angles of 25 high-angle reflections. The intensities of three standard reflections were monitored, showing neither significant decay or instrument instability. Absorption corrections were applied via the program DIFABS. The structure was solved by the Patterson technique employing the TEXSAN 5.0 crystallographic software package.[15] Full-matrix least-squares calculations with anisotropic thermal displacement parameters for all non-hydrogen atoms yielded the final values of R and R_w, given in Table IV. Hydrogen atoms were located from difference Fourier maps and included as fixed contributions to the structure factors, except for the bridging hydrogen atoms in the carborane ring, which were refined with isotropic thermal displacement parameters. The final difference Fourier map was featureless.

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Supplementary Material Available: Tables of anisotropic thermal parameters and mean planes for **5** (2 pages). Ordering information is given on any current masthead page.

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[15] TEXSAN: *Single Crystal Structure Analysis Software, Version 5.0*; Molecular Structure Corp.: The Woodlands, TX 77381, 1989.