

# Apically Linked Small Metallacarborane Clusters. Directed Synthesis and Structural Characterization of 7,7'-[Cp\*Co(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>)<sub>2</sub>] and [Cp\*Co(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>-7)]<sub>2</sub>X Complexes (X = MeCH, HC=CH, C≡C)<sup>†,1</sup>

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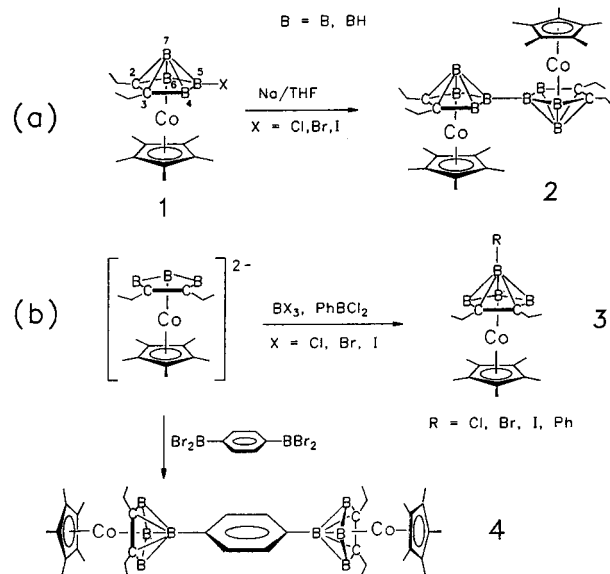
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A series of novel bis(cobaltacarboranyl) (CoC<sub>2</sub>B<sub>4</sub>)<sub>2</sub>X dicluster complexes whose B(7) (apex) atoms are linked by organic moieties involving sp-, sp<sup>2</sup>-, or sp<sup>3</sup>-hybridized carbon, or by a direct B(7)–B(7') bond, has been prepared by extension of the recently described "recapitation" method (Curtis, M. A.; *et al. Inorg. Chem.* **1996**, *35*, 6703) that entails treatment of 6-vertex *nido*-CoC<sub>2</sub>B<sub>3</sub> dianions with monoboron reagents. Reactions of Li<sub>2</sub>[*nido*-Cp\*Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>3</sub>)] in toluene with MeCH(BCl<sub>2</sub>)<sub>2</sub> and with *cis*-(BCl<sub>2</sub>)C<sub>2</sub>H<sub>2</sub> gave, respectively, [Cp\*Co(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>-7-)]<sub>2</sub>MeCH (**5**) and *cis*-[Cp\*Co(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>-7-)]<sub>2</sub>C<sub>2</sub>H<sub>2</sub> (**6a**) following chromatographic separation. Ultraviolet irradiation of **6a** induced partial conversion to the trans isomer **6b**, affording a 46:54 trans/*cis* equilibrium mixture in 84 h. Reactions of the same cobaltacarborane dianion with bis(catecholboryl)acetylene and with bis(catecholdiboryl) gave [Cp\*Co(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>-7-)]<sub>2</sub>C<sub>2</sub> (**7**) and [Cp\*Co(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>-7-)]<sub>2</sub> (**8**), respectively. The new complexes were isolated as air-stable, crystalline orange solids and were characterized from their <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C NMR, IR, UV–visible, and mass spectra, supported by X-ray crystallographic studies of **5**, **6a**, **7**, and **8**. Crystal data for **5**: space group *P2<sub>1</sub>ca* (orthorhombic); *a* = 14.220(10) Å, *b* = 15.690(10) Å, *c* = 16.860(10) Å, *Z* = 4; *R* = 0.041 for 7485 independent reflections. Crystal data for **6a**: space group *C2/c* (monoclinic); *a* = 12.849(6) Å, *b* = 11.435(6) Å, *c* = 25.619(13) Å, β = 96.230(10)°; *Z* = 4; *R* = 0.036 for 5440 independent reflections. Crystal data for **7**: space group *P2<sub>1</sub>/n* (monoclinic); *a* = 17.298(12) Å, *b* = 13.932(10) Å, *c* = 30.82(2) Å, β = 96.34(5)°; *Z* = 8; *R* = 0.070 for 9632 independent reflections. Crystal data for **8**: space group *P1* (triclinic); *a* = 9.150(10) Å, *b* = 10.270(10) Å, *c* = 10.340(10) Å, α = 84.52(5)°, β = 78.05(5)°, γ = 68.6(5)°; *Z* = 1; *R* = 0.056 for 5154 independent reflections.

## Introduction

Rational, controlled methods for linking small inorganic or organometallic units to form larger covalently bonded structures are of interest as routes to metal-containing chain polymers, polycluster compounds, and solid-state materials that can be tailored to exhibit useful electronic or other properties.<sup>2</sup> Transition metal complexes of organoborane or carborane ligands having two to four boron atoms are especially amenable to this kind of chemistry, as they are generally stable, soluble, and readily undergo linking and stacking reactions. Our two groups have explored this area extensively, both separately<sup>3,4</sup> and as part of an ongoing collaboration.<sup>5</sup> For example, metal stacking involving diborolyl (C<sub>2</sub>B<sub>2</sub>) ring ligands has produced polydecker sandwiches that are semiconducting,<sup>6</sup> while related chemistry

## Scheme 1



based on C<sub>2</sub>B<sub>3</sub> carborane rings has been employed to synthesize molecular stacks having two to six decks as well as soluble oligomeric linked-multisandwich complexes.<sup>7</sup>

Some recent developments in our work are of interest in this context. As outlined in Scheme 1a, Wurtz-type coupling of

<sup>†</sup> Dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday.

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(1) (a) Organotransition-Metal Metallacarboranes. 48. (b) For Part 47, see: Curtis, M. E.; Sabat, M.; Grimes, R. N. *Inorg. Chem.* **1996**, *35*, 6703.

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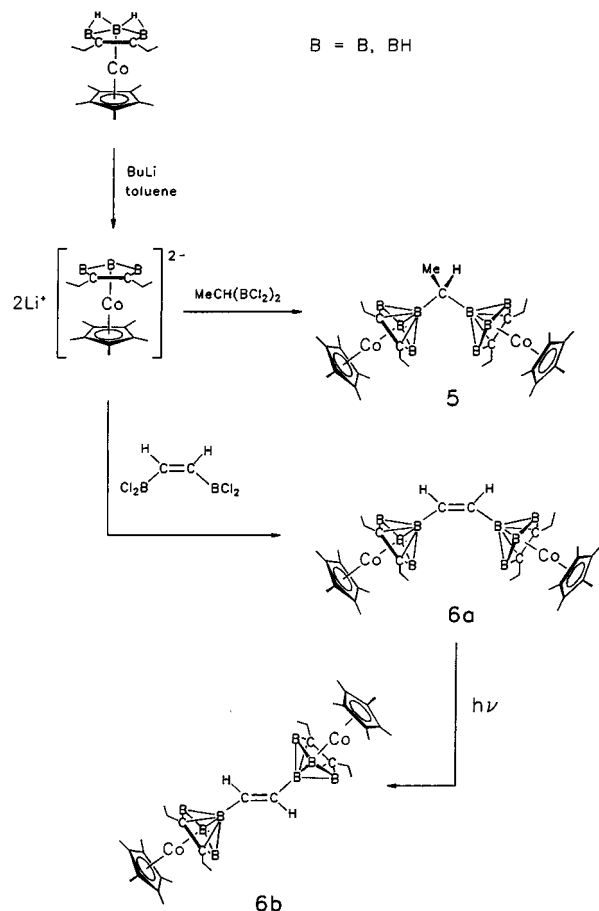
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(7) Grimes, R. N. *Appl. Organomet. Chem.* **1996**, *10*, 209, and references therein.

## Scheme 2



B(5)-halo monomers **1** cleanly afforded the B(5)–B(5′)-linked bis(cobaltacarborane) dimer **2**, which was crystallographically characterized.<sup>8</sup> There was no evidence of the corresponding B(7)–B(7′) apically linked dimer; however, the synthesis of this isomer has been achieved in the present study, as described below. In very recent work,<sup>1b</sup> Curtis et al. prepared apex-substituted derivatives of  $MC_2B_4$  *closo*-metallocarborane clusters, a previously unknown class, via boron insertion into the  $Cp^*Co(Et_2C_2B_3H_5)^{2-}$  dianion as shown in Scheme 1b. This “recapitation” approach furnishes a useful and, as will be shown, versatile entry to apically substituted  $Cp^*Co(2,3-Et_2C_2B_4H_3-7-X)$  compounds, including linked-cluster species such as **4**. In the present paper, we report a significant extension of the boron insertion strategy to generate, via straightforward synthetic procedures, a series of new B(7)-linked complexes in which the mode of cluster linkage varies from direct B–B bonding to coupling via  $sp^-$ ,  $sp^2$ , or  $sp^3$ -hybridized carbon atoms.

## Results and Discussion

**Synthesis of Methyl- and Ethenyl-Bridged Bis(cobaltacarboranyl) Complexes.** Deprotonation of *nido*- $Cp^*Co(2,3-Et_2C_2B_3H_5)$ <sup>9</sup> in toluene solution to give the dianion, followed by treatment with 1,1′-bis(dichloroboryl)ethane and chromatographic separation and workup, gave orange air-stable crystals of  $[Cp^*Co(2,3-Et_2C_2B_4H_3-7-)]_2MeCH$  (**5**) in 84% isolated yield (Scheme 2). The compound was characterized from <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C NMR, UV–visible, infrared, and mass spectra (Tables 1 and 2 and Experimental Section). The <sup>1</sup>H NMR spectrum of **5** is consistent with the assigned structure, showing equivalence

of the four ethyl groups and the two  $Cp^*$  ligands. The <sup>11</sup>B NMR spectrum displays two equal-area resonances, one of which arises from the equivalent B(4,6) borons while the other consists of overlapped nonequivalent B(5) and B(7) peaks. Both signals appear as broad singlets in the coupled as well as the proton-decoupled spectra, so that an unequivocal assignment of the peaks was not possible; from spectroscopic evidence alone, one could not rule out the possibility that **5** is linked through the equatorial borons B(5) and B(5′) rather than the apices (unlikely though this would be from a synthetic viewpoint). However, the apically connected geometry was unambiguously shown by an X-ray structure determination (Tables 3 and 4 and Figure 1).

The molecule exhibits normal distances and bond angles and has no crystallographically imposed symmetry, so that the two cobaltacarborane cages are independent. The main feature of interest is the bridging MeCH group, and the angles involving the bridgehead carbon atom C(4) (108–112°) reflect approximate  $sp^3$  orbital hybridization, as expected. The <sup>13</sup>C resonance for this carbon was not observed, but the proton NMR signal for its attached hydrogen ( $\delta -1.96$ ) as well as that of the adjacent methyl hydrogens ( $\delta -0.95$ ) appears at relatively high field compared to those typically observed in saturated hydrocarbons. These upfield shifts suggest a strong +I (electron-donating) effect<sup>10</sup> of the cobaltacarborane cage toward the methylene bridge, discounting resonance and conjugation as less likely mechanisms in systems of this type.

The ethylene-bridged complex **6a** was prepared by reaction of the cobaltacarborane dianion with *cis*-bis(dichloroboryl)-ethylene as shown in Scheme 2 and was isolated as orange air-stable crystals in 50% yield. NMR and mass spectrometric evidence supported an ethylene-bridged structure but could not distinguish between *cis* and *trans* geometry, although the former was certainly more likely in view of the starting reagent. However, the presence of a C=C infrared stretching band at 1608  $cm^{-1}$  indicated a *cis* isomer, since the *trans* species would be nonpolar and hence IR-inactive in the C=C region. The *cis* geometry was established by X-ray crystallography, as depicted in Figure 2 and summarized in Tables 3 and 5. The ethylene carbons C(4) and C(4′) are coplanar with their neighboring hydrogen and boron atoms (the sum of the angles around C(4) is 360.0°), and the C(4)–C(4′) distance is 1.346(3) Å, consistent with a CH=CH bridge. This picture is further augmented by the signals in the proton and carbon-13 NMR spectra (Table 1) corresponding to the vinyl CH protons ( $\delta$  4.31) and vinyl carbon atoms ( $\delta$  144.2), respectively. As in the case of **5**, these data suggest that the metallocarborane cluster is electron-donating to the organic bridging unit via an inductive mechanism.

Exposure of a  $C_6D_6$  solution of **6a** to ultraviolet radiation from a mercury vapor lamp resulted in partial isomerization to the *trans* complex **6b** (Scheme 2), which was detected by NMR spectroscopy. Integration of the proton NMR spectrum after 84 h of irradiation revealed a 46:54 **6b/6a** mixture, which is taken to represent an equilibrium since further irradiation to a total of 120 h produced no change in this ratio. Attempts to separate the isomers via chromatography were unsuccessful, but **6b** is identified as the *trans* isomer from its proton NMR signals, which are clearly distinguishable from those of **6a** (Table 1). Like the pure *cis* isomer **6a**, the mixture is an orange air-stable crystalline solid, and its mass spectrum is indistinguishable from that of **6a**.

**Synthesis of Ethenyl-Bridged and Directly Linked Bis(cobaltacarboranyl) Complexes.** The preparation of a  $-C\equiv C-$

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

(10) The characteristic electron donor properties of these metallocarboranes and related polyhedral boron clusters underline the fact that they are *not* (as still sometimes erroneously labeled) “electron deficient”.

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

115.8-MHz $^{11}\text{B}$ NMR Data		
compound	$\delta^{a-c}$	rel areas
$\text{Cp}^*\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_4)$ ( <b>1</b> , X = H)	11.0, 3.0, 1.3	1:2:1
$[\text{Cp}^*\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_3\text{-7-})]_2\text{MeCH}$ ( <b>5</b> )	14.6, 3.6	2:2
<i>cis</i> - $[\text{Cp}^*\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_3\text{-7-})]_2\text{C}_2\text{H}_2$ ( <b>6a</b> )	13.9, 7.7, 3.8	1:1:2
$[\text{Cp}^*\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_3\text{-7-})]_2\text{C}_2$ ( <b>7</b> )	11.9, 3.2, -3.6	1:2:1
$7,7'$ - $[\text{Cp}^*\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_3)]_2$ ( <b>8</b> )	14.5, 3.8	2:2
$5,5'$ - $[\text{Cp}^*\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_3)]_2$ ( <b>2</b> ) <sup>d,e</sup>	20.2, 4.2	1:3

200.1-MHz $^1\text{H}$ NMR Data	
compd	$\delta^{b,f,g}$
<b>1</b> (X = H) <sup>h</sup>	2.51 (m, 2H, ethyl CH <sub>2</sub> ), 2.28 (m, 2H, ethyl CH <sub>2</sub> ), 1.77 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 1.19 (t, 6H, ethyl CH <sub>3</sub> )
<b>5</b>	2.16 (m, 4H, ethyl CH <sub>2</sub> ), 1.81 (m, 4H, ethyl CH <sub>2</sub> ), 1.71 (s, 30H, C <sub>5</sub> Me <sub>5</sub> ), 1.31 (t, 6H, $J_{\text{H,H}} = 7.3$ Hz, ethyl CH <sub>3</sub> ), 1.28 (t, 6H, $J_{\text{H,H}} = 7.3$ Hz, ethyl CH <sub>3</sub> ), -0.95 (d, 3H, $J_{\text{H,H}} = 7.6$ Hz, CH <sub>3</sub> CH), -1.96 (q, 1H, $J_{\text{H,H}} = 7.8$ Hz, CH <sub>3</sub> CH)
<b>6a</b>	4.31 (s, 2H, vinyl H), 2.27 (dq, 4H, $J_{\text{H,H}} = 7.7$ Hz, ethyl CH <sub>2</sub> ), 1.95 (dq, 4H, $J_{\text{H,H}} = 7.7$ Hz, ethyl CH <sub>2</sub> ), 1.76 (s, 30H, C <sub>5</sub> Me <sub>5</sub> ), 1.19 (t, 12H, $J_{\text{H,H}} = 7.7$ Hz, ethyl CH <sub>3</sub> )
<b>6a</b> <sup>i</sup>	4.78 (s, 2H, vinyl H), 2.21 (m, 4H, ethyl CH <sub>2</sub> ), 1.96 (m, 4H, ethyl CH <sub>2</sub> ), 1.54 (s, 30H, C <sub>5</sub> Me <sub>5</sub> ), 1.38 (t, 12H, $J_{\text{H,H}} = 7.8$ Hz, ethyl CH <sub>3</sub> )
<b>6b</b> <sup>i</sup>	4.92 (s, 2H, vinyl H), 2.21 (m, 4H, ethyl CH <sub>2</sub> ), 1.96 (m, 4H, ethyl CH <sub>2</sub> ), 1.47 (s, 30H, C <sub>5</sub> Me <sub>5</sub> ), 1.26 (t, 12H, $J_{\text{H,H}} = 7.7$ Hz, ethyl CH <sub>3</sub> )
<b>7</b>	2.28 (dq, 4H, $J_{\text{H,H}} = 7.4$ Hz, ethyl CH <sub>2</sub> ), 2.07 (dq, 4H, $J_{\text{H,H}} = 7.4$ Hz, ethyl CH <sub>2</sub> ), 1.70 (s, 30H, C <sub>5</sub> Me <sub>5</sub> ), 1.20 (t, 12H, $J_{\text{H,H}} = 7.4$ Hz, ethyl CH <sub>3</sub> )
<b>8</b>	2.06 (dq, 4H, $J_{\text{H,H}} = 7.7$ Hz, ethyl CH <sub>2</sub> ), 1.94 (dq, 4H, $J_{\text{H,H}} = 7.7$ Hz, ethyl CH <sub>2</sub> ), 1.64 (s, 30H, C <sub>5</sub> Me <sub>5</sub> ), 1.28 (t, 12H, $J_{\text{H,H}} = 7.5$ Hz, ethyl CH <sub>3</sub> )
<b>2</b> <sup>d</sup>	2.57 (dq, 4H, ethyl CH <sub>2</sub> ), 2.39 (dq, 4H, ethyl CH <sub>2</sub> ), 1.80 (s, 30H, C <sub>5</sub> Me <sub>5</sub> ), 1.20 (t, 12H, ethyl CH <sub>3</sub> )

50.3-MHz $^{13}\text{C}$ NMR Data	
compd	$\delta^{b,f,j}$
<b>5</b>	94.6 (C <sub>2</sub> B <sub>4</sub> , br), 94.2 (C <sub>2</sub> B <sub>4</sub> , br), 91.0 (C <sub>5</sub> Me <sub>5</sub> ), 22.9 (CH <sub>2</sub> ), 22.8 (CH <sub>2</sub> ), 15.4 (ethyl CH <sub>3</sub> ), 15.2 (ethyl CH <sub>3</sub> ), 14.8 (CH <sub>3</sub> CH), 11.1 (C <sub>5</sub> Me <sub>5</sub> ), CH <sub>3</sub> CH not observed
<b>6a</b>	144.2 (vinyl, br), 93.2 (C <sub>2</sub> B <sub>4</sub> , br), 90.1 (C <sub>5</sub> Me <sub>5</sub> ), 21.7 (CH <sub>2</sub> ), 14.6 (CH <sub>3</sub> ), 10.1 (C <sub>5</sub> Me <sub>5</sub> )
<b>7</b>	93.5 (C <sub>2</sub> B <sub>4</sub> , br), 90.7 (C <sub>5</sub> Me <sub>5</sub> ), 21.8 (CH <sub>2</sub> ), 14.4 (CH <sub>3</sub> ), 10.0 (C <sub>5</sub> Me <sub>5</sub> ), C≡C not observed
<b>8</b>	94.2 (C <sub>2</sub> B <sub>4</sub> , br), 89.6 (C <sub>5</sub> Me <sub>5</sub> ), 21.9 (CH <sub>2</sub> ), 15.1 (CH <sub>3</sub> ), 10.0 (C <sub>5</sub> Me <sub>5</sub> )

<sup>a</sup> Shifts relative to  $\text{BF}_3\cdot\text{OEt}_2$ , positive values downfield. <sup>b</sup>  $\text{CDCl}_3$  solution except where otherwise indicated. <sup>c</sup> In all cases inequivalent, broad signals are overlapped or superimposed. <sup>d</sup> Reference 8. <sup>e</sup>  $\text{CH}_2\text{Cl}_2$  solution. <sup>f</sup> Shifts relative to  $(\text{CH}_3)_4\text{Si}$ . <sup>g</sup> B-H<sub>terminal</sub> resonances are broad quartets and mostly obscured by other signals. <sup>h</sup> Reference 9. <sup>i</sup> 300 MHz,  $\text{C}_6\text{D}_6$  solution. <sup>j</sup> All spectra proton-decoupled.

**Table 2.** UV-Visible and Infrared Data

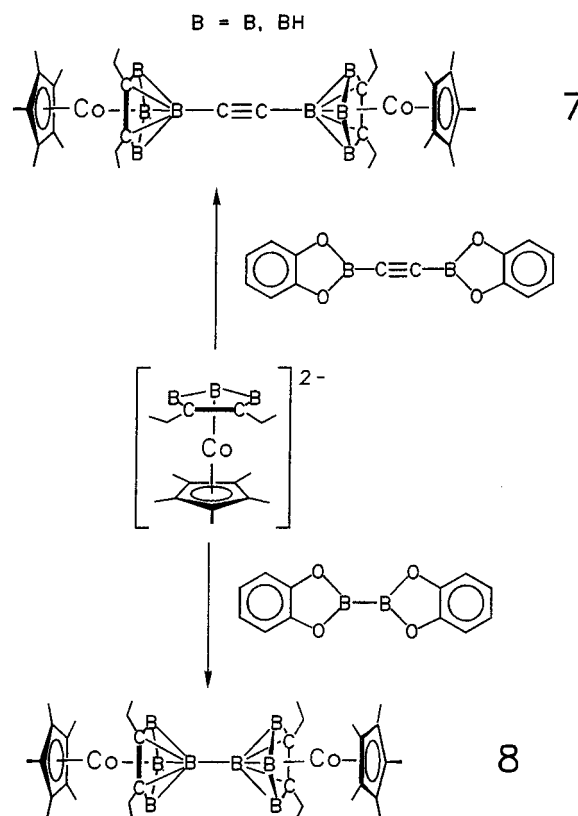
UV-Visible Absorptions ( $\text{CH}_2\text{Cl}_2$ Solution)		
compd	$\lambda$ , nm (rel intensity)	$\epsilon^a$
<b>1</b> <sup>b</sup>	418 (3), 292 (100), 248 (19)	11 718
<b>2</b> <sup>c</sup>	466 (10), 354 (64), 294 (100)	24 469
<b>5</b>	298 (100), 232 (30)	56 840
<b>6a</b>	310 (100), 292 (sh), 230 (36)	52 447
<b>7</b>	312 (100), 230 (17)	85 855
<b>8</b>	320 (100), 290 (sh), 232 (43)	30 339

Infrared Absorptions ( $\text{cm}^{-1}$ , $\text{CH}_2\text{Cl}_2$ solution vs $\text{CH}_2\text{Cl}_2$ ) <sup>d</sup>	
compd	
<b>5</b>	2972 s, 2939 s, 2910 vs, 2877 w, 2543 vvs, 1480 m, 1456 m, 1433 w, 1385 s
<b>6a</b>	3682 m, 3056 vvs, 2969 s, 2933 s, 2906 s, 2874 m, 2534 vvs, 1608 m, 1481 m, 1449 s, 1426 s, 1386 s
<b>7</b>	2975 vs, 2962 s, 2913 vs, 2533 vvs, 1725 w, 1478 m, 1454 s, 1383 vs
<b>8</b>	3687 w, 2968 vs, 2929 vvs, 2872 m, 2524 vvs, 1480 m, 1456 s, 1433 w, 1380 s

<sup>a</sup> Extinction coefficient in  $\text{cm}^{-1} \text{M}^{-1}$  for the most intense band. <sup>b</sup> Reference 9 (spectrum recorded in  $\text{CHCl}_3$  solution). <sup>c</sup> Reference 8. <sup>d</sup> Legend: s, strong; m, medium; w, weak; sh, shoulder; v, very; br, broad.

connected complex could not be accomplished via a route analogous to that of **5** and **6a** since bis(dichloroboryl)acetylene is inaccessible. However, treatment of the cobaltacarborane dianion with bis(catecholboryl)acetylene generated the desired complex **7** in 15% yield (Scheme 3). As in the cases of **5** and **6a**, the multinuclear NMR data indicated a symmetrical

**Scheme 3**

**Table 3.** Experimental X-ray Diffraction Parameters and Crystal Data

	<b>5</b>	<b>6a</b>	<b>7</b>	<b>8</b>
empirical formula	Co <sub>2</sub> C <sub>34</sub> B <sub>8</sub> H <sub>60</sub>	Co <sub>2</sub> C <sub>34</sub> B <sub>8</sub> H <sub>58</sub>	Co <sub>2</sub> C <sub>34</sub> B <sub>8</sub> H <sub>56</sub>	Co <sub>2</sub> C <sub>32</sub> B <sub>8</sub> H <sub>56</sub>
fw	673.2	671.1	669.1	645.1
crystal dimensions (mm)	0.70 × 0.60 × 0.40	0.60 × 0.55 × 0.55	0.50 × 0.40 × 0.15	0.70 × 0.50 × 0.2
space group	<i>P2<sub>1</sub>ca</i>	<i>C2/c</i>	<i>P2<sub>1</sub>/n</i>	<i>P1</i>
<i>a</i> , Å	14.220 (10)	12.849 (6)	17.298 (12)	9.150 (10)
<i>b</i> , Å	15.690 (10)	11.435 (6)	13.932 (10)	10.270 (10)
<i>c</i> , Å	16.860 (10)	25.619 (13)	30.82 (2)	10.340 (10)
$\alpha$ , deg				84.52 (5)
$\beta$ , deg		96.23 (1)	96.34 (5)	78.05 (5)
$\gamma$ , deg				68.65 (5)
<i>V</i> , Å <sup>3</sup>	3762 (4)	3742 (3)	7382 (9)	885 (2)
<i>Z</i>	4	4	8	1
transmission factors	0.87–1.00	0.86–1.00	0.70–1.00	0.72–1.00
<i>D</i> (calcd), g cm <sup>-3</sup>	1.19	1.19	1.20	1.21
$\theta$ range, deg	1.77–29.01	1.60–29.99	1.61–22.50	2.13–30.10
no. of independ reflectns	7485	5440	9632	5154
no. of obsd reflectns <sup>a</sup>	6179	4496	4849	4516
<i>R</i> 1 <sup>b</sup>	0.041	0.036	0.070	0.056
w <i>R</i> 2 <sup>c</sup>	0.107	0.098	0.197	0.158
largest peak in final diff map, e/Å <sup>3</sup>	0.41	0.35	0.46	0.99

<sup>a</sup>  $I > 2\sigma(I)$ . <sup>b</sup>  $R1 = \sum ||E_o| - |E_c|| / \sum |F_o|$ . <sup>c</sup>  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ .

**Table 4.** Selected Bond Distances and Bond Angles for [Cp\*Co(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>-7-)]<sub>2</sub>MeCH (**5**)

Distances, Å			
Co(1)–C(2)	2.035(4)	C(4)–B(7)	1.577(6)
Co(1)–C(3)	2.041(4)	C(4)–B(17)	1.575(6)
Co(1)–B(4)	2.096(5)	Co(11)–C(12)	2.028(5)
Co(1)–B(5)	2.125(5)	Co(11)–C(13)	2.028(4)
Co(1)–B(6)	2.096(5)	Co(11)–B(14)	2.086(5)
C(2)–C(3)	1.485(6)	Co(11)–B(15)	2.113(5)
C(2)–B(4)	1.560(6)	Co(11)–B(16)	2.100(5)
C(2)–B(7)	1.791(6)	C(12)–C(13)	1.467(6)
C(2)–C(2M)	1.506(6)	C(12)–B(14)	1.572(8)
C(3)–B(6)	1.549(7)	C(12)–B(17)	1.814(6)
C(3)–B(7)	1.782(5)	C(12)–C(12M)	1.498(7)
C(3)–C(3M)	1.521(6)	C(13)–B(16)	1.552(7)
B(4)–B(5)	1.667(7)	C(13)–B(17)	1.814(5)
B(4)–B(7)	1.801(6)	C(13)–C(13M)	1.503(7)
B(5)–B(6)	1.674(7)	B(14)–B(15)	1.632(8)
B(5)–B(7)	1.753(6)	B(14)–B(17)	1.794(7)
B(6)–B(7)	1.802(6)	B(15)–B(16)	1.667(7)
C(2M)–C(2E)	1.515(8)	B(15)–B(17)	1.751(7)
C(3M)–C(3E)	1.485(8)	B(16)–B(17)	1.792(6)
C(4)–C(5)	1.552(6)	C(12M)–C(12E)	1.49(2)
C(4)–H(4A)	1.03(4)	C(13M)–C(13E)	1.489(11)

Angles, deg			
C(3)–C(2)–C(2M)	121.6(4)	C(12M)–C(12)–Co(11)	135.8(4)
C(2M)–C(2)–B(4)	126.1(4)	C(13)–C(12)–B(14)	111.3(4)
C(2M)–C(2)–B(7)	133.2(4)	C(12)–C(13)–C(13M)	121.9(5)
C(2M)–C(2)–Co(1)	135.1(3)	C(13M)–C(13)–B(16)	125.4(5)
C(3)–C(2)–B(4)	111.9(3)	C(13M)–C(13)–B(17)	132.9(4)
C(2)–C(3)–C(3M)	118.9(4)	C(13M)–C(13)–Co(11)	135.2(4)
C(3M)–C(3)–B(6)	128.2(4)	C(12)–C(13)–B(16)	112.2(4)
C(3M)–C(3)–B(7)	131.9(4)	B(17)–C(4)–B(7)	112.2(3)
C(3M)–C(3)–Co(1)	135.9(3)	B(17)–C(4)–H(4A)	109(2)
C(2)–C(3)–B(6)	112.5(3)	C(5)–C(4)–B(7)	109.5(3)
C(13)–C(12)–C(12M)	119.8(6)	C(5)–C(4)–B(17)	111.3(2)
C(12M)–C(12)–B(14)	128.3(6)	C(5)–C(4)–H(4A)	107(2)
C(12M)–C(12)–B(17)	132.0(5)	B(7)–C(4)–H(4A)	108(2)

molecule with equivalent CoC<sub>2</sub>B<sub>4</sub> cages, each having local mirror symmetry, but were consistent with both B(5)–C≡C–B(5') and B(7)–C≡C–B(7') linkage. The latter geometry was confirmed by an X-ray structural analysis that revealed a unit cell containing two independent molecules, one of which is pictured in Figure 3 while relevant data are given in Tables 3 and 6. Drawings of both molecules are available as Supporting Information.

Although it is clear from NMR that only one isomer of **7** is present in solution, the two solid-state molecules I and II exhibit significantly different conformations. Molecule I (shown in Figure 3) deviates sharply from the expected linearity of the

**Table 5.** Selected Bond Distances and Bond Angles for *cis*-[Cp\*Co(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>-7-)]<sub>2</sub>C<sub>2</sub>H<sub>2</sub> (**6a**)

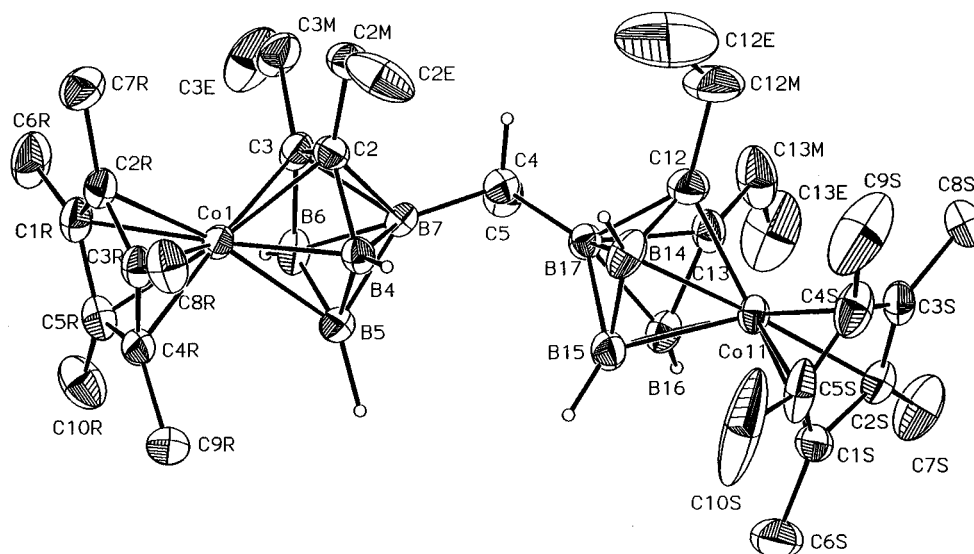
Distances, Å			
Co(1)–C(2)	2.041(2)	C(3)–C(3M)	1.509(2)
Co(1)–C(3)	2.042(2)	B(4)–B(5)	1.681(3)
Co(1)–B(4)	2.089(2)	B(4)–B(7)	1.807(3)
Co(1)–B(5)	2.121(2)	B(5)–B(6)	1.688(3)
Co(1)–B(6)	2.101(2)	B(5)–B(7)	1.750(3)
C(2)–C(3)	1.477(2)	B(6)–B(7)	1.795(3)
C(2)–B(4)	1.556(3)	C(2M)–C(2E)	1.503(3)
C(2)–B(7)	1.801(2)	C(3M)–C(3E)	1.522(3)
C(2)–C(2M)	1.509(2)	C(4)–C(4')	1.346(3)
C(3)–B(6)	1.560(3)	C(4)–H(4A)	0.97(2)
C(3)–B(7)	1.790(2)	C(4)–B(7)	1.562(2)

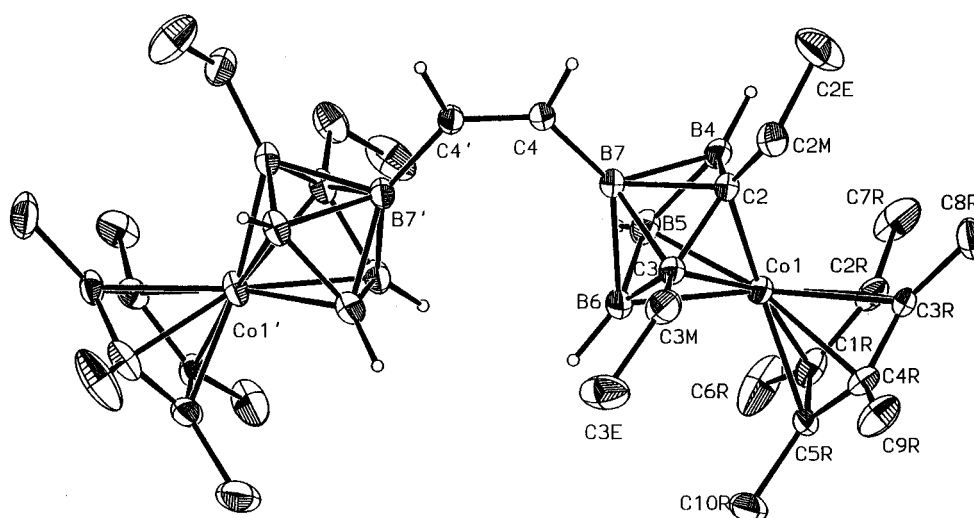
Angles, deg			
C(3)–C(2)–C(2M)	119.1(2)	C(3M)–C(3)–B(7)	133.0(1)
C(2M)–C(2)–B(4)	128.1(2)	C(3M)–C(3)–Co(1)	135.6(1)
C(2M)–C(2)–B(7)	132.7(1)	C(2)–C(3)–B(6)	112.8(1)
C(2M)–C(2)–Co(1)	136.0(1)	C(4')–C(4)–H(4A)	116.9(11)
C(3)–C(2)–B(4)	112.3(1)	C(4')–C(4)–B(7)	130.8(1)
C(2)–C(3)–C(3M)	119.9(2)	B(7)–C(4)–H(4A)	112.3(1)
C(3M)–C(3)–B(6)	126.9(2)		

B–C≡C–B chain, with a calculated angle of Co–X–Co angle of 158°, where X represents the midpoint of the C≡C bond; in II this angle is 172°, much closer to linear geometry. Another measure of the crystal packing effect is given by the intramolecular dihedral angle subtended by the C<sub>2</sub>B<sub>3</sub> ring planes, which in a perfectly linear conformation would be parallel (as they are in **8** described below). In **7**, the dihedral angles are 31 and 12° for molecules I and II, respectively. The observation that relatively weak intermolecular forces can produce a substantial distortion from linear geometry indicates that the binding between the acetylenic carbons and the apex boron atoms is mostly  $\sigma$  in character and nonrigid, with little or no  $\pi$ -interaction; this is consistent with the corresponding B–C bond distances (1.50–1.53 Å). The acetylenic C–C bond lengths in I and II are 1.205 (12) and 1.214 (13) Å, respectively, within the normal range for such values.

Direct linkage of the two cobaltacarborane cages at the apex borons was achieved by reaction of bis(catecholboronyl) with the dianion to generate **8** (Scheme 3), isolated in 19% yield as an air-stable orange solid. Again the NMR data indicated a symmetrical dimer with equivalent cluster units and mirror symmetry in each cage; in this case, it was possible to distinguish spectroscopically between the B(7)–B(7') and B(5)–B(5') linked isomers, since the latter compound, previously prepared and structurally characterized,<sup>8</sup> (see **2** in Scheme 1) is



**Figure 1.** Molecular structure of  $[\text{Cp}^*\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_3\text{-}7\text{-})]_2\text{MeCH}$  (**5**, 30% thermal ellipsoids) with hydrogen atoms omitted for clarity.



**Figure 2.** Molecular structure of *cis*- $[\text{Cp}^*\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_3\text{-}7\text{-})]_2\text{C}_2\text{H}_2$  (**6a**).

clearly different from **8**. Nonetheless, an X-ray analysis was carried out, yielding the structure depicted in Figure 4 (see also Tables 3 and 7). The molecule possesses a crystallographic inversion center which imposes a linear conformation, as mentioned above. The B(7)–B(7') bond length of 1.674(6) Å is in the expected range for a single boron–boron bond, and hence there is no indication of a significant  $\pi$ -interaction between the cages.

To our knowledge, **8** is the first crystallographically characterized boron cage dimer involving 7-vertex polyhedra joined at the apices. Indeed, **8** and its isomer **2** provide one of the very rare cases of isomeric linked-cluster carboranes in which X-ray structural data are available for both isomers, allowing direct comparison between them. In terms of crystallographic bond distances and angles, there are no striking differences; the intercage B–B bond length in **2** is 1.690(6) Å, insignificantly longer than that in **8**, and the other structural parameters in the two isomers are also closely comparable. There is, however, some divergence in their spectroscopic properties, showing that linkage at equatorial vs apical boron locations does affect the electronic structure of the  $\text{CoC}_2\text{B}_4$  framework to a measurable degree. Comparison of the  $^{11}\text{B}$  NMR spectra of **2**, **8**, and the parent monomer **1** (Table 1) shows a marked deshielding in the dimers, particularly **2**, relative to the monomer, suggesting a transfer of electron density from the boron skeleton to the intercage B–B bond in these compounds.

**UV–Visible Spectra.** All of the bis(cobaltacarborane) complexes are orange, air-stable crystalline solids, but their UV–visible spectra (Table 2) show some clear differences from each other and from the parent cluster **1** (X = H). Each compound exhibits a moderate red shift in its major band relative to **1**. Those linked by organic moieties—**5**, **6a**, and **7**—show very high extinction coefficients that are consistent with charge-transfer excitation, probably involving filled cobaltacarborane MOs and empty antibonding MOs on the linking organic groups. The contrast in the spectra of the two B–B linked dimers, involving a red shift of 26  $\text{cm}^{-1}$  in the major band in going from the equatorially linked species **2** to the apically connected isomer **8**, is interesting. The spectrum of **2** is similar to that of the monomer **1** in that the major absorbance near 290 nm is virtually unchanged, implying that linkage at the B(5) vertices produces no large electronic perturbation of the cages; the situation in **8** is clearly different, and perhaps reflects greater p character in the apex–apex vs equatorial–equatorial interaction. Pending the development of reliable MO methods that are applicable to metallaboron clusters involving first-row transition metals, which have yet to be demonstrated,<sup>11</sup> we are not yet in a position to interpret these data in detail.

(11) See, for example: Mebel, A. M.; Musaev, D. G.; Koga, N.; Morokuma, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3259.

**Table 6.** Selected Bond Distances and Bond Angles for [Cp\*Co(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>-7-)]<sub>2</sub>C<sub>2</sub> (7)

Distances, Å			
Co(11)–C(12)	2.036(9)	Co(21)–C(22)	2.035(8)
Co(11)–C(13)	2.040(8)	Co(21)–C(23)	2.028(9)
Co(11)–B(14)	2.098(11)	Co(21)–B(24)	2.098(11)
Co(11)–B(15)	2.121(10)	Co(21)–B(25)	2.134(12)
Co(11)–B(16)	2.099(10)	Co(21)–B(26)	2.085(11)
C(12)–C(13)	1.524(12)	C(22)–C(23)	1.490(12)
C(12)–B(14)	1.541(14)	C(22)–B(24)	1.56(2)
C(12)–B(17)	1.779(13)	C(22)–B(27)	1.765(13)
C(12)–C(12M)	1.518(12)	C(22)–C(22M)	1.508(12)
C(13)–B(16)	1.555(14)	C(23)–B(26)	1.556(14)
C(13)–B(17)	1.784(13)	C(23)–B(27)	1.793(13)
C(13)–C(13M)	1.502(12)	C(23)–C(23M)	1.532(12)
B(14)–B(15)	1.66(2)	B(24)–B(25)	1.71(12)
B(14)–B(17)	1.80(2)	B(24)–B(27)	1.80(2)
B(15)–B(16)	1.67(2)	B(25)–B(26)	1.63(2)
B(15)–B(17)	1.75(2)	B(25)–B(27)	1.76(2)
B(16)–B(17)	1.80(2)	B(26)–B(27)	1.81(2)
C(12M)–C(12E)	1.54(2)	C(22M)–C(22E)	1.502(13)
C(13M)–C(13E)	1.50(2)	C(23M)–C(23E)	1.536(13)
B(17)–C(1)	1.526(13)	B(27)–C(2)	1.518(14)
C(1)–C(2)	1.205(12)		
Angles, deg			
C(13)–C(12)–C(12M)	117.4(8)	C(22M)–C(22)–B(24)	127.2(9)
C(12M)–C(12)–B(14)	130.1(9)	C(22M)–C(22)–B(27)	130.5(7)
C(12M)–C(12)–B(17)	132.8(8)	C(22M)–C(22)–Co(21)	137.3(7)
C(12M)–C(12)–Co(11)	134.6(7)	C(23)–C(22)–B(24)	112.5(9)
C(13)–C(12)–B(14)	112.1(8)	C(22)–C(23)–C(23M)	119.0(8)
C(12)–C(13)–C(13M)	119.4(8)	C(23M)–C(23)–B(26)	128.9(9)
C(13M)–C(13)–B(16)	129.0(9)	C(23M)–C(23)–B(27)	131.8(7)
C(13M)–C(13)–B(17)	131.7(8)	C(23M)–C(23)–Co(21)	136.3(7)
C(13M)–C(13)–Co(11)	136.4(6)	C(22)–C(23)–B(26)	111.4(8)
C(12)–C(13)–B(16)	111.0(4)	C(2)–C(1)–B(17)	174.0(11)
C(23)–C(22)–C(22M)	119.7(8)	C(1)–C(2)–B(27)	174.6(10)

## Conclusions

The work described in this paper and its predecessor<sup>1b</sup> demonstrates the versatility of the “recapitulation” approach as a method for generating apically connected cobaltacarborane dimers, and we anticipate that it can be applied to analogous compounds of other metals as well. In combination with Wurtz-type cage coupling and Cp\*–Cp\* intercage linkage,<sup>8</sup> previously described, as well as multidecker sandwich construction via controlled synthesis,<sup>3–7</sup> a very large array of carborane- and organoborane-based polymers and covalently bonded networks now seems accessible.

## Experimental Section

**Instrumentation.** <sup>1</sup>H NMR (200.1 MHz) and <sup>13</sup>C NMR (50.3 MHz) spectra were recorded on a Bruker AC-200 spectrometer, while <sup>11</sup>B NMR (115.8 MHz) spectra were obtained on a Nicolet NT-360 instrument. All spectra were recorded in CDCl<sub>3</sub> solution. Unit resolution mass spectra were obtained on Varian MAT CH7 and MAT 8230 spectrometers. Each compound exhibited a strong parent envelope whose intensity pattern was consistent with the calculated spectrum based on natural isotopic abundances. Elemental analyses were conducted on a Perkin-Elmer 2400 CHN analyzer using 2,4-dinitrophenylhydrazine 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 in CH<sub>2</sub>Cl<sub>2</sub> solution on a Mattson Cygnus FTIR spectrometer.

**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) and on silica gel 60 plates (ICN). The complex *nido*-Cp\*(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>) was obtained via the literature synthesis.<sup>9</sup> MeCH(BCl<sub>2</sub>)<sub>2</sub>, *cis*-C<sub>2</sub>H<sub>2</sub>(BCl<sub>2</sub>)<sub>2</sub>, [(C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)B]<sub>2</sub>C<sub>2</sub>, and [(C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)B]<sub>2</sub> were prepared according to published procedures.<sup>12</sup> Solvents were distilled from appropriate drying agents under an inert atmosphere.

**Synthesis of [Cp\*Co(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>-7-)]<sub>2</sub>MeCH (5).** A solution containing 200 mg (0.64 mmol) of Cp\*Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>) in 25 mL of

toluene at 0 °C was treated with 0.51 mL (1.28 mmol) of 2.5 M *n*-butyllithium. The solution turned dark red-orange as it was warmed to room temperature over a 1.5 h period. The solution was cooled to 0 °C, and 61 mg of MeCH(BCl<sub>2</sub>)<sub>2</sub> was added. The solution became cloudy and turned orange as the flask was warmed to room temperature. The contents were stirred for 16 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 CH<sub>2</sub>Cl<sub>2</sub>. The hexane wash contained only Cp\*Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>) (152 mg). The CH<sub>2</sub>Cl<sub>2</sub> wash was column-chromatographed on silica in 2:3 hexane/CH<sub>2</sub>Cl<sub>2</sub>, giving a major orange band that was characterized as **5** (43 mg, 0.06 mmol, 84% based on starting complex consumed). MS: *m/z* 673 (molecular ion envelope). Anal. Calcd for Co<sub>2</sub>C<sub>34</sub>B<sub>8</sub>H<sub>60</sub>: C, 60.66; H, 8.98. Found: C, 59.50; H, 9.72.

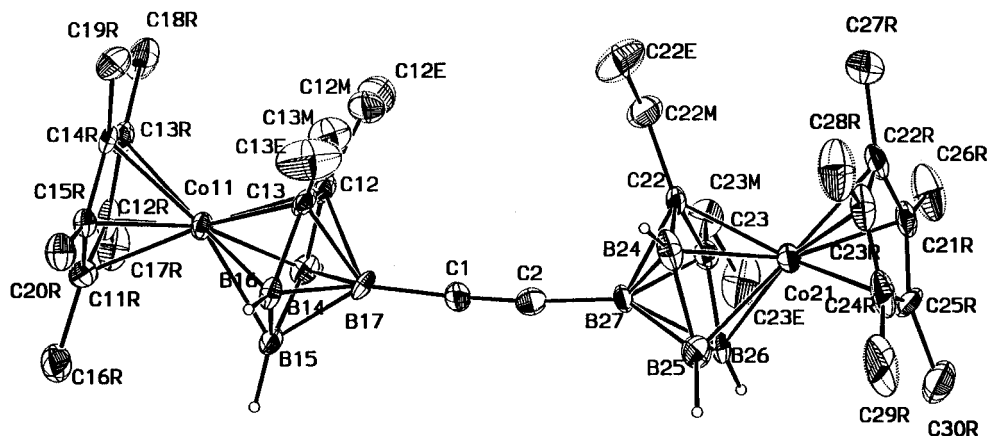
**Synthesis of *cis*-[Cp\*Co(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>-7-)]<sub>2</sub>C<sub>2</sub>H<sub>2</sub> (6a).** The preceding procedure was followed using 300 mg (0.96 mmol) of Cp\*Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>) and 0.76 mL (1.91 mmol) of 2.5 M *n*-butyllithium. The cobaltacarborane dianion solution was stirred at room temperature for 2 h, after which 90 mg (0.48 mmol) of *cis*-C<sub>2</sub>H<sub>2</sub>(BCl<sub>2</sub>)<sub>2</sub> was added dropwise at room temperature, producing a cloudy solution that turned orange. Stirring was continued for 12 h, and workup as above yielded 156 mg (0.23 mmol, 50% based on starting complex consumed) of **6a** following chromatography on silica. MS: *m/z* 671 (molecular ion envelope). Anal. Calcd for Co<sub>2</sub>C<sub>34</sub>B<sub>8</sub>H<sub>58</sub>: C, 60.84; H, 8.71. Found: C, 59.57; H, 9.10.

**Synthesis of [Cp\*Co(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>-7-)]<sub>2</sub>C<sub>2</sub> (7).** A solution containing 300 mg (0.96 mmol) of Cp\*Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>) in 30 mL of toluene at 0 °C was treated with 0.76 mL (1.91 mmol) of 2.5 M *tert*-butyllithium. The cobaltacarborane dianion solution was stirred at room temperature for 2 h, after which 125 mg (0.48 mmol) of [(C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)B]<sub>2</sub>C<sub>2</sub> was added at room temperature, producing a cloudy solution that turned orange. The contents were stirred for 12 h, after which the 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 CH<sub>2</sub>Cl<sub>2</sub>. The hexane wash contained only Cp\*Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>) (211 mg). The CH<sub>2</sub>Cl<sub>2</sub> wash was column-chromatographed on silica in 1:4 hexane/CH<sub>2</sub>Cl<sub>2</sub>, yielding a major orange band that was characterized as **7** (15 mg, 0.02 mmol, 16% based on starting complex consumed). MS: *m/z* 670 (molecular ion envelope). Anal. Calcd for Co<sub>2</sub>C<sub>34</sub>B<sub>8</sub>H<sub>56</sub>: C, 61.03; H, 8.44. Found: C, 59.99; H, 8.97.

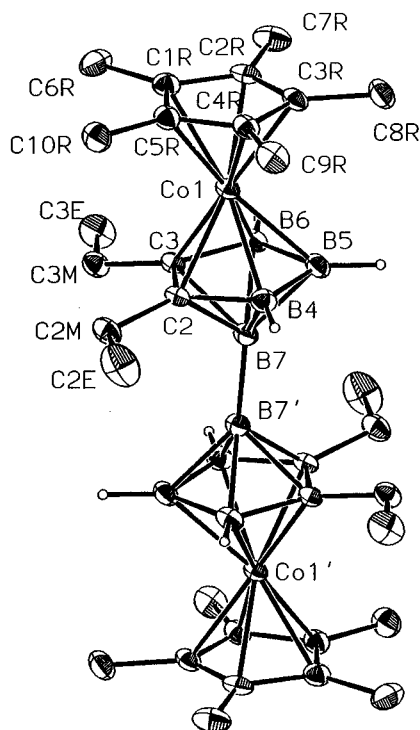
**Synthesis of [Cp\*Co(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>-7-)]<sub>2</sub> (8).** A solution containing 300 mg (0.96 mmol) of Cp\*Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>) in 30 mL of toluene at 0 °C was treated with 0.76 mL (1.91 mmol) of 2.5 M *tert*-butyllithium. The cobaltacarborane dianion solution was stirred at room temperature for 2 h, after which 114 mg (0.48 mmol) of [(C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)B]<sub>2</sub> was added at room temperature, producing a cloudy solution that turned orange. The contents were refluxed for 2 h, after which the 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 CH<sub>2</sub>Cl<sub>2</sub>. The hexane wash contained only Cp\*Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>) (94 mg). The CH<sub>2</sub>Cl<sub>2</sub> wash was column-chromatographed on silica TLC plates in 1:1 hexane/CH<sub>2</sub>Cl<sub>2</sub>, affording a major yellow band that was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Removal of solvent gave 40 mg (0.06 mmol, 19%) of **8**. MS: *m/z* 645 (molecular ion envelope). Anal. Calcd for Co<sub>2</sub>C<sub>32</sub>B<sub>8</sub>H<sub>56</sub>: C, 59.58; H, 8.75. Found: C, 58.25; H, 9.43.

**X-ray Structure Determinations.** Diffraction data were collected on a Siemens-Stoe AED2 diffractometer equipped with a graphite monochromator at –70 °C using Mo Kα radiation. Structures were solved by direct methods (SHELXS-86<sup>13</sup>), and refinement was by full-matrix least-squares on F<sup>2</sup> with all measured reflections (SHELXL-93<sup>14</sup>). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the methyl groups were placed in calculated positions and were refined as rigid CH<sub>3</sub> groups with common isotropic temperature factors for the hydrogens. All other hydrogen atoms were located in

- (12) (a) Soundarajan, R.; Matteson, D. S. *J. Org. Chem.* **1990**, *55*, 2274. (b) Siebert, W.; Hildenbrand, M.; Hornbach, P.; Karger, G.; Pritzkow, H. *Z. Naturforsch.* **1989**, *44B*, 1179. (c) Schulz, H.; Gabbert, G.; Pritzkow, H.; Siebert, W. *Chem. Ber.* **1993**, *126*, 1593. (d) Welch, C. N.; Shore, S. G. *Inorg. Chem.* **1968**, *7*, 225.
- (13) SHELXS-86: Sheldrick, G. M., University of Göttingen, Göttingen, Germany, 1986.
- (14) SHELXL-93: Sheldrick, G. M., University of Göttingen, Göttingen, Germany, 1993.



**Figure 3.** Molecular structure of  $[\text{Cp}^*\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_3\text{-7-})]_2\text{C}_2$  (**7**), showing one of the two independent molecules in the unit cell.



**Figure 4.** Molecular structure of  $[\text{Cp}^*\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_3\text{-7-})]_2$  (**8**).

difference Fourier maps and refined isotropically. The hydrogen atoms in one methyl group in **5**, as well as some of the hydrogens in **7** (molecule II), were not found and were omitted from the refinements. In **6a**, the two cluster units are related through a crystallographic twofold axis that bisects the C(4)–C(4') bond. The Cp\* ring in this structure is disordered and was refined using two sets of rigid rings. In **7**, there are two independent molecules in the asymmetric unit which are nearly transformed into each other by a 0.5, 0.0, 0.0 translation that results in very weak reflections for *hkl* with odd *h*. In **8**, the molecule has a center of inversion at the midpoint of the B(7)–B(7') bond.

**Table 7.** Selected Bond Distances and Bond Angles for  $[\text{Cp}^*\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_3\text{-7-})]_2$  (**8**)

Distances, Å			
Co(1)–C(2)	2.040(3)	B(4)–B(5)	1.674(5)
Co(1)–C(3)	2.044(3)	B(4)–B(7)	1.807(4)
Co(1)–B(4)	2.110(4)	B(4)–H(4)	1.03(4)
Co(1)–B(5)	2.140(4)	B(5)–B(6)	1.694(5)
Co(1)–B(6)	2.110(3)	B(5)–B(7)	1.773(4)
C(2)–C(3)	1.474(4)	B(5)–H(5)	1.10(4)
C(2)–B(4)	1.573(4)	B(6)–B(7)	1.802(5)
C(2)–B(7)	1.777(4)	B(6)–H(6)	1.07(4)
C(2)–C(2M)	1.507(4)	B(7)–B(7')	1.674(6)
C(3)–B(6)	1.561(4)	C(2M)–C(2E)	1.520(5)
C(3)–B(7)	1.776(4)	C(3M)–C(3E)	1.519(5)
C(3)–C(3M)	1.528(4)		
Angles, deg			
C(3)–C(2)–C(2M)	119.5(2)	C(3M)–C(3)–Co(1)	136.1(2)
C(2M)–C(2)–B(4)	127.3(2)	C(2)–C(3)–B(6)	112.5(2)
C(2M)–C(2)–B(7)	131.2(2)	B(7)–B(7)–C(3)	122.7(3)
C(2M)–C(2)–Co(1)	136.5(2)	B(7')–B(7)–C(2)	122.3(3)
C(3)–C(2)–B(4)	112.5(2)	B(7')–B(7)–B(5)	140.2(3)
C(2)–C(3)–C(3M)	119.2(2)	B(7')–B(7)–B(6)	132.4(3)
C(3M)–C(3)–B(6)	127.7(2)	B(7')–B(7)–B(4)	131.4(3)
C(3M)–C(3)–B(7)	131.6(2)		

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**Supporting Information Available:** Tables of atomic coordinates, isotropic and anisotropic thermal parameters, complete bond distances and angles, and calculated mean planes for **5**, **6a**, **7**, and **8** and drawings of **7**, forms I and II (33 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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