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## Triple-Decker Sandwich Complexes of Cobalt, Rhodium, and Ruthenium Bridged by $C_2B_3$ or $C_3B_2$ Rings: Synthesis, Structure, and Electrochemistry

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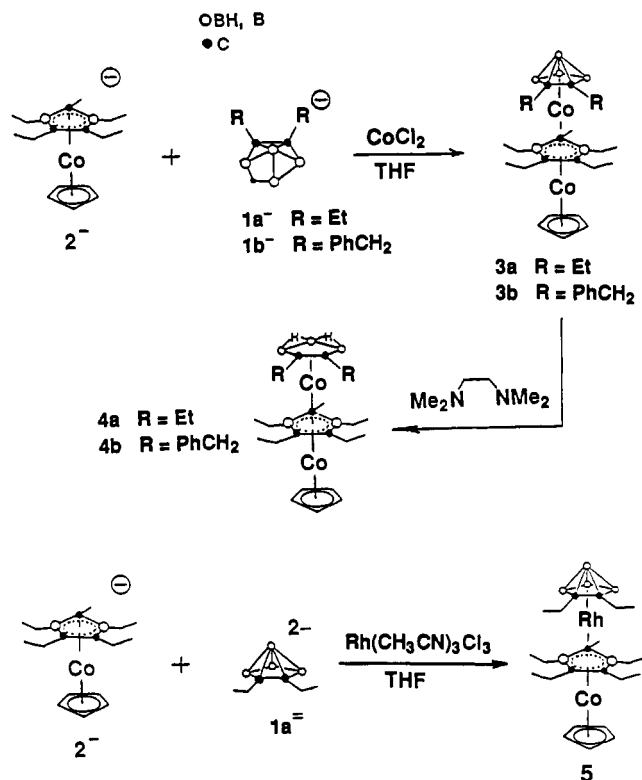
The planned syntheses, structural characterization, and electrochemistry of new homo- and heterobimetallic triple-decker species bridged by  $C_2B_3$  or  $C_3B_2$  rings are described. Reactions of the carborane monoanions *nido*- $R_2C_2B_4H_5^-$  (**1a<sup>-</sup>**, **1b<sup>-</sup>**) and the diboroly monoanion  $CpCo(Et_2MeC_3B_2Et_2)^-$  (**2<sup>-</sup>**) in cold THF produced the dicobalt diamagnetic 20-electron "hybrid" sandwiches ( $R_2C_2B_4H_4$ )Co(Et<sub>2</sub>MeC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub>)CoCp (**3a**, R = Et; **3b**, R = CH<sub>2</sub>Ph) as green crystalline solids. Decapitation (apex BH removal) of these complexes in TMEDA afforded yellow ( $R_2C_2B_3H_3$ )Co(Et<sub>2</sub>MeC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub>)CoCp (**4a**, R = Et; **4b**, R = CH<sub>2</sub>Ph). The reaction of the corresponding carborane dianion **1a<sup>2-</sup>** with **2<sup>-</sup>** and Rh<sup>3+</sup> gave brown (Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Rh(Et<sub>2</sub>MeC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub>)CoCp (**5**). The cobaltacarborane dianion (C<sub>5</sub>Me<sub>5</sub>)Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>3</sub>)<sup>2-</sup> (**6<sup>2-</sup>**) and [(C<sub>5</sub>Me<sub>5</sub>)RhCl<sub>2</sub>]<sub>2</sub> reacted in THF to form the green triple-decker complexes (C<sub>5</sub>Me<sub>5</sub>)Co(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>2</sub>-4-R)Rh(C<sub>5</sub>Me<sub>5</sub>) (**7a**, R = H; **7b**, R = Cl). In an alternative route to rhodium triple-deckers, the dianion **1a<sup>2-</sup>** reacted with [(C<sub>5</sub>Me<sub>5</sub>)RhCl<sub>2</sub>]<sub>2</sub> to generate the brown rhodacarborane (C<sub>5</sub>Me<sub>5</sub>)Rh(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>3</sub>) (**8**), which in turn was decapitated to give a *nido*-rhodacarborane complex (C<sub>5</sub>Me<sub>5</sub>)Rh(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>3</sub>) (**9**), isolated as a yellow oil. Deprotonation of **9** gave the dianion **9<sup>2-</sup>**, which reacted with [(C<sub>5</sub>Me<sub>5</sub>)RhCl<sub>2</sub>]<sub>2</sub> to form the red crystalline dirhodium triple-decker (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Rh<sub>2</sub>(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>3</sub>) (**10a**) and its orange 4-chloro derivative **10b**. Treatment of the **9<sup>2-</sup>** ion with (cymene)ruthenium(II) dichloride gave the red rhodium-ruthenium complex (C<sub>5</sub>Me<sub>5</sub>)Rh(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>3</sub>)Ru(MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>) (**11**), while **9<sup>2-</sup>** and [(C<sub>5</sub>Me<sub>5</sub>)CoCl]<sub>2</sub> reacted to form the cobalt-rhodium species **7a**. The new compounds **3-11** were isolated via column and plate chromatography and characterized from their <sup>11</sup>B and <sup>1</sup>H NMR, IR, and mass spectra, supported by an X-ray diffraction study of **5**. Most of the new complexes are stable indefinitely in air and undergo reversible electrochemical oxidation and reduction to give paramagnetic ions. Crystal data for **5**: mol wt 543.4; space group *Pbca*; Z = 8; a = 17.322 (7), b = 19.698 (13), c = 15.619 (9) Å; V = 5327 (9) Å<sup>3</sup>; R = 0.070 for 1714 reflections having F<sub>o</sub><sup>2</sup> > 2.5σ(F<sub>o</sub><sup>2</sup>).

### Introduction

Triple-decker sandwich complexes, characterized by the presence of planar bridging ligands that are coordinated to metal atoms on both faces, have drawn the attention of theoreticians<sup>2</sup> and synthetic chemists<sup>3</sup> since the syntheses of the original ionic<sup>4</sup> and electrically neutral<sup>5</sup> compounds (Ni<sub>2</sub>Cp<sub>3</sub><sup>+</sup> and Cp<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, respectively) nearly 2 decades ago. While a variety of triple-deckers are now known, incorporating bridging ligands as diverse as hydrocarbons, P<sub>n</sub> or As<sub>n</sub> rings, and others, those species bridged by carbon-boron heterocycles comprise by far the most extensive family. Most complexes of the latter type, of which several dozen examples have been characterized, contain cyclocarborane (C<sub>2</sub>B<sub>3</sub>), borole (C<sub>4</sub>B), diborole (C<sub>3</sub>B<sub>2</sub>), thiadiborole (C<sub>2</sub>B<sub>2</sub>S), or diborabenzene (C<sub>4</sub>B<sub>2</sub>) central ring systems.<sup>3</sup>

The boron-containing triple-deckers are of interest in several respects: as a class, they exhibit high chemical stability in solution; many of them undergo reversible electrochemical oxidation and reduction without decomposition, and those that have been studied in detail reveal high electron delocalization between the metal centers.<sup>6</sup> Our groups have been interested in developing practical,

### Scheme I



efficient routes to stable triple-decker systems having  $C_2B_3$  or  $C_3B_2$  bridging rings and, further, to exploit these synthetic and structural principles in order to construct more extended electron-delocalized systems such as tetradeccker and larger sandwiches,<sup>3a,7</sup> linked triple-deckers and related polymetallic complexes,<sup>8</sup> and polymers.<sup>9</sup>

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**Table I.** 115.8-MHz  $^{11}\text{B}$  FT NMR Data

compd <sup>a-c</sup>	$\delta(\text{J}_{\text{BH}}$ , Hz)	rel areas
(Et <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> )Co(Et <sub>2</sub> MeC <sub>3</sub> B <sub>2</sub> Et <sub>2</sub> )CoCp ( <b>3a</b> )	17.0, <sup>d</sup> 12.1 (153), 5.4 (148), 1.9 (158)	2:1:1:2
[(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ]Co(Et <sub>2</sub> MeC <sub>3</sub> B <sub>2</sub> Et <sub>2</sub> )CoCp ( <b>3b</b> )	15.4, <sup>d</sup> 9.2 (112), 2.7, <sup>e</sup> 0.6 <sup>e</sup>	2:1:1:2
(Et <sub>2</sub> C <sub>2</sub> B <sub>3</sub> H <sub>5</sub> )Co(Et <sub>2</sub> MeC <sub>3</sub> B <sub>2</sub> Et <sub>2</sub> )CoCp ( <b>4a</b> )	16.8, <sup>d</sup> 3.8, <sup>e</sup> 2.6 <sup>e</sup>	2:1:2
[(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>3</sub> H <sub>5</sub> ]Co(Et <sub>2</sub> MeC <sub>3</sub> B <sub>2</sub> Et <sub>2</sub> )CoCp ( <b>4b</b> )	15.5, <sup>d</sup> 3.0, <sup>e</sup> 2.0 <sup>e</sup>	2:1:2
(Et <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> )Rh(Et <sub>2</sub> MeC <sub>3</sub> B <sub>2</sub> Et <sub>2</sub> )CoCp ( <b>5</b> )	13.7, <sup>d</sup> 11.4 (~150), 10.0 (~150), 0.3 (154)	2:1:1:2
(C <sub>5</sub> Me <sub>5</sub> )Co(2,3-Et <sub>2</sub> C <sub>2</sub> B <sub>3</sub> H <sub>3</sub> )Rh(C <sub>5</sub> Me <sub>5</sub> ) ( <b>7a</b> )	54.9 (116), 6.4 (91)	1:2
(C <sub>5</sub> Me <sub>5</sub> )Co(2,3-Et <sub>2</sub> C <sub>2</sub> B <sub>3</sub> H <sub>2</sub> Cl)Rh(C <sub>5</sub> Me <sub>5</sub> ) ( <b>7b</b> )	51.7 (118), 16.1, <sup>f</sup> 9.7 (97)	1:1:1
(C <sub>5</sub> Me <sub>5</sub> )Rh(Et <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ) ( <b>8</b> )	11.3 (147), 8.1 (157), 2.5 (153)	1:1:2
(C <sub>5</sub> Me <sub>5</sub> )Rh(Et <sub>2</sub> C <sub>2</sub> B <sub>3</sub> H <sub>3</sub> ) ( <b>9</b> )	4.1 (145), 1.4 (130)	1:2
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> Rh <sub>2</sub> (Et <sub>2</sub> C <sub>2</sub> B <sub>3</sub> H <sub>3</sub> ) ( <b>10a</b> )	50.2 (124), 4.6 (103)	1:2
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> Rh <sub>2</sub> (Et <sub>2</sub> C <sub>2</sub> B <sub>3</sub> H <sub>2</sub> Cl) ( <b>10b</b> )	48.2 (83), 15.1, <sup>f</sup> 7.1 (114)	1:1:1
(C <sub>5</sub> Me <sub>5</sub> )Rh(Et <sub>2</sub> C <sub>2</sub> B <sub>3</sub> H <sub>3</sub> )Ru(MeC <sub>6</sub> H <sub>4</sub> CHMe <sub>2</sub> ) ( <b>11</b> )	44.9 (127), 4.8 (122)	1:2

<sup>a</sup> Shifts relative to BF<sub>3</sub>·OEt<sub>2</sub>, positive values downfield. <sup>b</sup> *n*-Hexane solution. <sup>c</sup> H–B coupling constant in Hz is given in parentheses, when resolved. <sup>d</sup> Diboroyl ring *B*-alkyl singlet resonance. <sup>e</sup> Superimposed/overlapped resonances. <sup>f</sup> B–Cl singlet resonance.

**Table II.** 300-MHz  $^1\text{H}$  FT NMR Data

compd	$\delta^{\text{a-c}}$
<b>3a</b>	4.64 s (C <sub>5</sub> H <sub>5</sub> ), 2.94 m (CH <sub>2</sub> ), 2.56 m (CH <sub>2</sub> ), 2.36 m (CH <sub>2</sub> ), 2.22 m (CH <sub>2</sub> ), 2.04 m (CH <sub>2</sub> ), 1.98 s (diboroyl C–CH <sub>3</sub> ), 1.59 t (ethyl CH <sub>3</sub> ), 1.31 t (ethyl CH <sub>3</sub> ), 0.97 t (ethyl CH <sub>3</sub> )
<b>3b</b>	7.08 m (C <sub>6</sub> H <sub>5</sub> ), 6.96 m (C <sub>6</sub> H <sub>5</sub> ), 4.70 s (C <sub>5</sub> H <sub>5</sub> ), 4.00 d (benzyl CH <sub>2</sub> ), 3.77 d (benzyl CH <sub>2</sub> ), 3.07 m (ethyl CH <sub>2</sub> ), 2.45 m (ethyl CH <sub>2</sub> ), 2.11 m (ethyl CH <sub>2</sub> ), 2.04 s (diboroyl C–CH <sub>3</sub> ), 2.03 m (ethyl CH <sub>2</sub> ), 1.64 t (diboroyl ethyl CH <sub>3</sub> ), 1.39 t (diboroyl ethyl CH <sub>3</sub> )
<b>4a</b>	4.70 s (C <sub>5</sub> H <sub>5</sub> ), 2.82 m (CH <sub>2</sub> ), 2.32 m (CH <sub>2</sub> ), 2.10 m (CH <sub>2</sub> ), 1.90 m (CH <sub>2</sub> ), 1.77 m (CH <sub>2</sub> ), 1.95 s (diboroyl C–CH <sub>3</sub> ), 1.53 t (ethyl CH <sub>3</sub> ), 1.33 t (ethyl CH <sub>3</sub> ), 0.91 t (ethyl CH <sub>3</sub> ), –7.20 <sup>d</sup> s
<b>4b</b>	7.02 m (C <sub>6</sub> H <sub>5</sub> ), 6.88 m (C <sub>6</sub> H <sub>5</sub> ), 4.78 s (C <sub>5</sub> H <sub>5</sub> ), 3.61 d (benzyl CH <sub>2</sub> ), 3.41 d (benzyl CH <sub>2</sub> ), 2.95 m (ethyl CH <sub>2</sub> ), 2.43 m (ethyl CH <sub>2</sub> ), 2.08 s (diboroyl C–CH <sub>3</sub> ), 1.90 m (ethyl CH <sub>2</sub> ), 1.58 t (ethyl CH <sub>3</sub> ), 1.41 t (ethyl CH <sub>3</sub> ), –6.92 <sup>d</sup> s
<b>5</b>	4.63 s (C <sub>5</sub> H <sub>5</sub> ), 2.51 m (CH <sub>2</sub> ), 2.39 m (CH <sub>2</sub> ), 2.31 m (CH <sub>2</sub> ), 2.21 m (CH <sub>2</sub> ), 1.96 s (diboroyl C–CH <sub>3</sub> ), 1.68 q (CH <sub>2</sub> ), 1.45 t (ethyl CH <sub>3</sub> ), 1.24 t (ethyl CH <sub>3</sub> ), 1.05 t (ethyl CH <sub>3</sub> )
<b>7a</b>	2.54 m (CH <sub>2</sub> ), 2.25 m (CH <sub>2</sub> ), 1.64 s (C <sub>5</sub> Me <sub>5</sub> ), 1.62 s (C <sub>5</sub> Me <sub>5</sub> ), 1.36 t (ethyl CH <sub>3</sub> )
<b>7b</b>	2.81 m (CH <sub>2</sub> ), 2.60 m (CH <sub>2</sub> ), 2.38 m (CH <sub>2</sub> ), 1.65 s (C <sub>5</sub> Me <sub>5</sub> ), 1.28 t (ethyl CH <sub>3</sub> ), 1.27 t (ethyl CH <sub>3</sub> )
<b>8</b>	2.52 m (CH <sub>2</sub> ), 2.26 m (CH <sub>2</sub> ), 1.88 s (C <sub>5</sub> Me <sub>5</sub> ), 1.24 (ethyl CH <sub>3</sub> )
<b>9</b>	2.02 m (CH <sub>2</sub> ), 1.79 m (CH <sub>2</sub> ), 1.88 s (C <sub>5</sub> Me <sub>5</sub> ), 1.11 t (ethyl CH <sub>3</sub> ), –5.2 <sup>d</sup> s
<b>10a</b>	2.28 q (CH <sub>2</sub> ), 1.69 s (C <sub>5</sub> Me <sub>5</sub> ), 1.26 t (ethyl CH <sub>3</sub> )
<b>10b</b>	2.42 q (CH <sub>2</sub> ), 2.35 q (CH <sub>2</sub> ), 1.70 s (C <sub>5</sub> Me <sub>5</sub> ), 1.23 t (ethyl CH <sub>3</sub> ), 1.20 t (ethyl CH <sub>3</sub> )
<b>11</b>	4.97 d (C <sub>6</sub> H <sub>4</sub> ring), 4.88 d (C <sub>6</sub> H <sub>4</sub> ring), 2.60 m (cymene isopropyl CH), 2.32 q (CH <sub>2</sub> ), 2.04 s (cymene CH <sub>3</sub> ), 1.67 s (C <sub>5</sub> Me <sub>5</sub> ), 1.31 t (ethyl CH <sub>3</sub> ), 1.20 d (cymene isopropyl CH <sub>3</sub> )

<sup>a</sup> CDCl<sub>3</sub> solution. <sup>b</sup> Shifts relative to (CH<sub>3</sub>)<sub>4</sub>Si. Integrated peak areas in all cases are consistent with the assignments given. Legend: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet. <sup>c</sup> B–H<sub>terminal</sub> resonances are broad quartets and mostly obscured by other signals. <sup>d</sup> B–H–B proton resonance.

While separately developing the respective areas of carboranyl and diboroyl multidecker chemistry, we have recently sought to merge them via the synthesis of “hybrid” sandwiches that incorporate both carboranes and boron heterocycles, thereby further expanding the scope of synthetic possibilities and creating novel electronic molecular systems. In a recent paper,<sup>10</sup> we described the synthesis and chemistry of the first such hybrid species, (R<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Fe(Et<sub>2</sub>MeC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub>)CoCp and (R<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>)Fe(Et<sub>2</sub>MeC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub>)CoCp (R = PhCH<sub>2</sub>, Et). Here we extend this chemistry, employing a different synthetic approach, to related Co–Co and Co–Rh carboranyl–diboroyl systems and also report the designed synthesis and characterization of new (C<sub>5</sub>Me<sub>5</sub>)M–

**Table III.** Infrared Absorptions (cm<sup>-1</sup>, Neat Films on KBr Plates)<sup>a,b</sup>

compd	absorptions
<b>3a</b>	3094 m, 2960 s, 2924 s, 2914 sh, 2866 s, 2541 vs, 1447 s, 1372 m, 1288 m, 1170 m, 1110 w, 965 m, 860 s, 820 s
<b>3b</b>	2967 s, 2934 vs, 2870 s, 2572 sh, 2536 vs, 2370 s, 2340 s, 2000–1200, <sup>c</sup> 1300 s, 1174 s, 1090 m, 1075 m, 1030 m, 1005 m, 950 m, 867 s, 836 s, 697 s
<b>4a</b>	2958 s, 2925 vs, 2853 vs, 2521 m, br, 1448 s, 1190 w, 826 m
<b>5</b>	2966 s, 2930 s, 2890 m, 2871 s, 2854 m, 2553 s, 1376 m, 1371 m, 1297 m, 1166 m, 1060 m, 959 m, 891 w, 875 m, 833 w, 789 w, 721 w, 718 w
<b>7a</b>	2960 s, 2919 s, 2867 s, 2826 w, 2461 s, 1375 s, 1023 m, 821 s
<b>7b</b>	2969 s, 2963 s, 2906 s, 2868 s, 2469 s, 1646 m, 1447 s, 1425 m, 1379 s, 1264 m, 1028 s, 813 s, 741 s
<b>8</b>	2954 s, 2924 s, 2853 s, 2541 m, 2361 w, 2340 w, 2337 w, 2332 w, 1457 s, 1377 m, 1026 w, 894 w
<b>9</b>	2960 s, 2925 s, 2869 s, 2854 s, 2551 m, 1454 m, 1377 m, 1026 w, 909 w, 741 w
<b>10a</b>	2960 s, 2923 s, 2868 s, 2458 s, 1465 m, 1375 s, 1265 s, 1072 w, 1024 m, 909 m, 819 s, 740 s
<b>10b</b>	2961 s, 2920 s, 2854 s, 2470 s, 2447 sh, 1446 s, 1379 s, 1260 m, 1121 m, 1087 m, 1073 m, 1027 s, 966 m, 924 m, 849 w, 805 s
<b>11</b>	2959 s, 2924 s, 2869 s, 2826 s, 2462 m, 1473 s, 1464 s, 1437 s, 1380 s, 1029 m, 826 s, 801 m

<sup>a</sup> Microcrystalline films obtained by evaporation of solutions. <sup>b</sup> Legend: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad. <sup>c</sup> Complex multiplet structure.

(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>)M/L triple-decker sandwiches in which M is Co or Rh and M/L is Rh(C<sub>5</sub>Me<sub>5</sub>) or Ru(*p*-MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>).

## Results and Discussion

**Synthesis of Carboranyl–Diboroyl “Hybrid” Complexes.** The previously described iron–cobalt hybrid species (vide supra) were obtained<sup>10</sup> via thermal displacement of cyclooctatriene from (R<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Fe(C<sub>8</sub>H<sub>10</sub>) complexes (R = Et, CH<sub>2</sub>Ph) by the neutral dihydrodiborole–cobalt reagent CpCo(Et<sub>2</sub>MeHC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub>). In the present work, *nido*-R<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>5</sub><sup>-</sup> (**1a**<sup>-</sup>, **1b**<sup>-</sup>) and CpCo(Et<sub>2</sub>MeC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub>)<sup>-</sup> (**2**<sup>-</sup>) monoanions (prepared via bridge deprotonation of the neutral carborane<sup>11</sup> and the diborole–cobalt complex,<sup>12</sup> respectively) were reacted with CoCl<sub>2</sub> in cold THF solution. Extraction of the crude products in dichloromethane followed by chromatographic separation on silica gave, in each case, one major band, which on further purification afforded dark green crystals of (R<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Co(Et<sub>2</sub>MeC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub>)CoCp (**3a**, R = Et; **3b**, R = CH<sub>2</sub>Ph), as shown in Scheme I. Yields of the pure products were ca. 30%. The characterization of **3a** and **3b** via unit- and high-

(11) (a) Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>: Boyter, H. A. Jr.; Swisher, R. G.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1985**, *24*, 3810. (b) (PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>: Spencer, J. T.; Grimes, R. N. *Organometallics* **1987**, *6*, 328.

(12) (a) Siebert, W.; Edwin, J.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 148. (b) Edwin, J.; Boehm, M. C.; Chester, N.; Hoffman, D.; Hoffmann, R.; Pritzkow, H.; Siebert, W.; Stumpf, K.; Wadepohl, H. *Organometallics* **1983**, *2*, 1666.

(10) Attwood, M. D.; Fonda, K. K.; Grimes, R. N.; Brodt, G.; Hu, D.; Zenneck, U.; Siebert, W. *Organometallics* **1989**, *8*, 1300.

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

<i>Mr</i>	543.4	reflcn's retd	1714
space group	<i>Pbca</i>	<i>F</i> (000)	2248
<i>a</i> , Å	17.322 (7)	<i>R</i>	0.070
<i>b</i> , Å	19.698 (13)	<i>R<sub>w</sub></i>	0.057
<i>c</i> , Å	15.619 (9)	av shift:error	0.03
<i>V</i> , Å <sup>3</sup>	5327 (9)	max shift:error	0.18
$\mu$ , mm <sup>-1</sup> (Mo K $\alpha$ )	1.19	largest peak in	0.4
$\lambda$ , Å	0.7107	finel diff map,	
<i>D</i> (cald), g cm <sup>-3</sup>	1.355 (2)	<i>e</i> /Å <sup>3</sup>	
2 $\theta$ range, deg	1–45	<i>Z</i>	8
reflcn's obsd	3513		

**Table V.** Positional and Equivalent Thermal Parameters for Non-Hydrogen Atoms in **5<sup>a</sup>**

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B<sub>eq</sub></i> , Å <sup>2</sup>
Rh	0.11466 (7)	0.14221 (6)	0.14596 (8)	4.7
Co	0.2703 (1)	0.04296 (11)	0.1233 (1)	5.1
C2	0.0565 (8)	0.2352 (10)	0.1978 (11)	6.7
C3	0.0532 (7)	0.2425 (7)	0.0993 (12)	5.5
B4	0.0153 (10)	0.1687 (11)	0.0584 (16)	7.0
B5	-0.0113 (10)	0.1212 (11)	0.1514 (15)	7.6
B6	0.0196 (10)	0.1674 (9)	0.2379 (14)	5.4
B7	-0.0239 (10)	0.2082 (10)	0.1549 (14)	6.1
B8	0.1647 (10)	0.0426 (9)	0.1828 (13)	5.1
C9	0.2224 (8)	0.1019 (8)	0.2128 (10)	5.6
C10	0.2444 (7)	0.1408 (7)	0.1389 (13)	4.7
B11	0.2070 (11)	0.1133 (11)	0.0552 (13)	6.1
C12	0.1584 (8)	0.0514 (8)	0.0848 (10)	4.9
C2M	0.0807 (9)	0.2972 (8)	0.2480 (13)	7.3
C2E	0.0131 (10)	0.3317 (9)	0.2871 (13)	9.1
C3M	0.0805 (9)	0.2946 (9)	0.0466 (13)	7.9
C3E	0.0128 (10)	0.3352 (9)	0.0180 (12)	7.8
C8M	0.1343 (11)	-0.0191 (10)	0.2405 (14)	9.8
C8E	0.0828 (11)	-0.0016 (10)	0.3127 (12)	9.2
C9M	0.2570 (10)	0.1098 (10)	0.3059 (9)	7.5
C9E	0.2175 (9)	0.1627 (9)	0.3545 (12)	7.9
C10M	0.3104 (8)	0.1986 (8)	0.1382 (14)	7.9
C10E	0.2755 (9)	0.2659 (7)	0.1415 (16)	9.7
C11M	0.2142 (12)	0.1445 (14)	-0.0436 (11)	12.7
C11E	0.2585 (17)	0.1339 (16)	-0.1017 (14)	19.2
C12M	0.1140 (11)	0.0044 (9)	0.0241 (14)	8.3
C1R	0.3412 (11)	-0.0212 (10)	0.1888 (14)	10.2
C2R	0.3013 (9)	-0.0552 (8)	0.1257 (18)	11.3
C3R	0.3187 (10)	-0.0256 (11)	0.0409 (13)	9.3
C4R	0.3707 (10)	0.0273 (10)	0.0593 (12)	8.5
C5R	0.3837 (10)	0.0288 (9)	0.1489 (15)	9.7

<sup>a</sup>Standard deviations in the last significant digit are in parentheses.

resolution mass spectra and <sup>11</sup>B NMR (Table I), <sup>1</sup>H NMR (Table II), and infrared spectra (Table III) is consistent with the structure shown in Scheme I having a vertical mirror plane (time-averaged symmetry in solution) defined by the metal atoms and the C–Me group of the diborolyl ring. In contrast to the analogous 29-electron paramagnetic Fe–Co species reported earlier,<sup>10</sup> **3a** and **3b** are diamagnetic, as expected for Co<sub>2</sub> 30-electron triple-decker systems, and exhibit normal NMR spectra. The assigned geometry (Scheme I) corresponds to that proposed<sup>10</sup> for the iron–cobalt complexes, but no X-ray structure determination has been obtained for the latter compounds. Consequently, crystallographic data were collected<sup>13</sup> on **3a**. Severe disorder in several of the alkyl substituents on the diborolyl ligand precluded an acceptable level of precision for the structural analysis, but the proposed triple-decker geometry (Scheme I) was confirmed. Subsequently, a satisfactory crystal structure analysis was conducted on a cobalt–rhodium analogue of **3a** as described below.

Complexes **3a** and **3b** were readily converted to the corresponding open-faced species (R<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>)Co(Et<sub>2</sub>MeC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub>)CoCp (**4a**, R = Et; **4b**, R = CH<sub>2</sub>Ph) via “decapitation” (removal of the apex BH unit<sup>3b</sup>) with tetramethylethylenediamine (TMEDA) in THF solution (Scheme I). The green solid complexes **4a** and **4b**

**Table VI.** Bond Distances (Å) and Selected Bond Angles (deg) in **5**

Bond Distances			
Rh–C2	2.24 (2)	C2–C3	1.54 (2)
Rh–C3	2.20 (1)	C2–C2M	1.51 (3)
Rh–B4	2.26 (2)	C2–B7	1.77 (2)
Rh–B5	2.22 (2)	C3–C3M	1.55 (2)
Rh–B6	2.24 (2)	C3–B4	1.56 (3)
Rh–B8	2.22 (2)	C3–B7	1.79 (2)
Rh–C9	2.28 (1)	B4–B5	1.79 (3)
Rh–C10	2.25 (1)	B8–C12	1.55 (3)
Rh–B11	2.21 (2)	B8–C8M	1.60 (3)
Rh–C12	2.16 (1)	C9–B8	1.58 (2)
Co–B8	2.05 (2)	C9–C9M	1.58 (2)
Co–C9	2.00 (2)	C9–C10	1.44 (2)
Co–C10	1.99 (1)	C10–B11	1.56 (2)
Co–B11	2.06 (2)	C10–C10M	1.61 (2)
Co–C12	2.04 (1)	B11–C11M	1.67 (3)
Co–C1R	2.04 (2)	B11–C12	1.55 (2)
Co–C2R	2.01 (2)	C12–C12M	1.53 (2)
Co–C3R	2.05 (2)	C8M–C8E	1.48 (3)
Co–C4R	2.03 (2)	C9M–C9E	1.46 (2)
Co–C5R	2.02 (2)	C10M–C10E	1.46 (2)
B4–B7	1.89 (3)	C11M–C11E	1.21 (3)
B5–B7	1.76 (3)	C1R–C2R	1.38 (3)
B6–C2	1.61 (3)	C1R–C5R	1.38 (3)
B6–B5	1.71 (3)	C2R–C3R	1.48 (3)
B6–B7	1.78 (3)	C3R–C4R	1.41 (3)
C2M–C2E	1.49 (2)	C4R–C5R	1.42 (3)
C3M–C3E	1.49 (2)		

Bond Angles			
C2–C3–B4	117 (2)	B8–C9–C10	109 (1.5)
C3–B4–B5	101 (2)	C9–C10–B11	112 (1.5)
B4–B5–B6	107 (2)	C10–B11–C12	104 (1.5)
B5–B6–C2	105 (2)	B11–C12–B8	110 (1.5)
B6–C2–C3	110 (2)	C9–B8–C12	105 (1.5)
C1R–C2R–C3R	110 (2)	C10–C10M–C10E	110 (1.5)
C2R–C3R–C4R	104 (2)	B11–C11M–C11E	133 (2.5)
C3R–C4R–C5R	109 (2)	C9–C9M–C9E	112 (1.5)
C4R–C5R–C1R	110 (2)	B8–C8M–C8E	117 (2.0)
C5R–C1R–C2R	107 (2)	C2–C2M–C2E	111 (1.5)
C3–C2–C2M	124 (1.5)	C3–C3M–C3E	110 (1.5)
B6–C2–C2M	125 (2)	B4–C3–C3M	123 (2.0)
C2–C3–C3M	120 (1.5)	C9–B8–C8M	126 (2)
C12–B8–C8M	128 (2)	B8–C9–C9M	125 (1.5)
C10–C9–C9M	126 (1.5)	C9–C10–C10M	125 (1.5)
B11–C10–C10M	122 (1.5)	C10–B11–C11M	128 (2)
C12–B11–C11M	127 (2)	B11–C12–C12M	124 (1.5)
B8–C12–C12M	126 (2)		

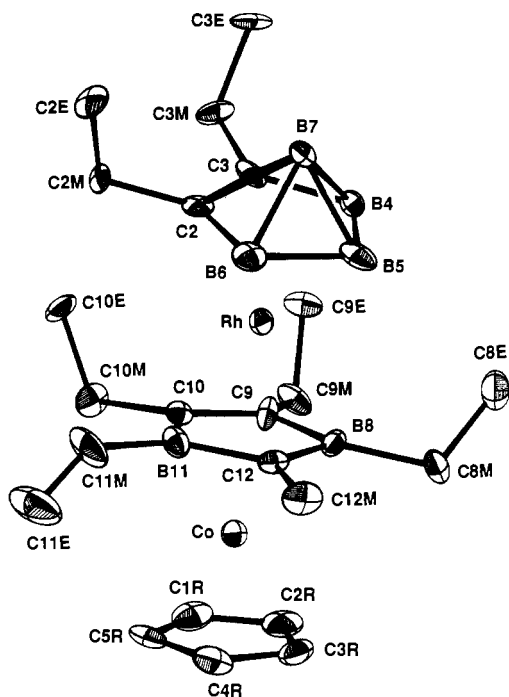
were isolated in about 70% yield and characterized spectroscopically (Tables I–III and Experimental Section).

A similar approach was employed to prepare a cobalt–rhodium sandwich analogous to **3a**, except that in this case the carborane dianion (generated by removal of both bridge protons<sup>14</sup>) was required for coordination with the rhodium(III) reagent; this corresponds to observations in earlier work<sup>8a,8b</sup> on the synthesis of ruthenium and osmium complexes of R<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub><sup>2-</sup>. As shown at the bottom of Scheme I, the reaction of the cobalt diborolyl anion **2-** and tris(acetonitrile)rhodium trichloride with the Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub><sup>2-</sup> ion (**1a<sup>2-</sup>**) in cold THF gave one major product, isolated by chromatography on silica and characterized as brown crystalline (Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Rh(Et<sub>2</sub>MeC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub>)CoCp (**5**).

**Molecular Structure of 5.** The <sup>11</sup>B spectrum (Table I) is closely similar to that of the dicobalt complexes **3a** and **3b**, and the 2:1:1:2 pattern supports the structure in Scheme I. This geometry has been established by X-ray diffraction, and a drawing of the molecule is given in Figure 1 (data collection parameters and atomic parameters are listed in Tables IV and V). The bond distances and angles (Table VI) are within normal ranges, and the seven-vertex pentagonal-bipyramidal RhC<sub>3</sub>B<sub>2</sub>Co and RhC<sub>2</sub>B<sub>4</sub> clusters exhibit no distortions other than those attributable to the large atomic radius of rhodium. The regular closo geometry of both clusters is consistent with the presence of 16 skeletal electrons

(13) Pritzkow, H. Unpublished results.

(14) Siriwardane, U.; Islam, M. S.; West, T. A.; Hosmane, N. S.; Maguire, J. A.; Cowley, A. H. *J. Am. Chem. Soc.* **1987**, *109*, 4600.



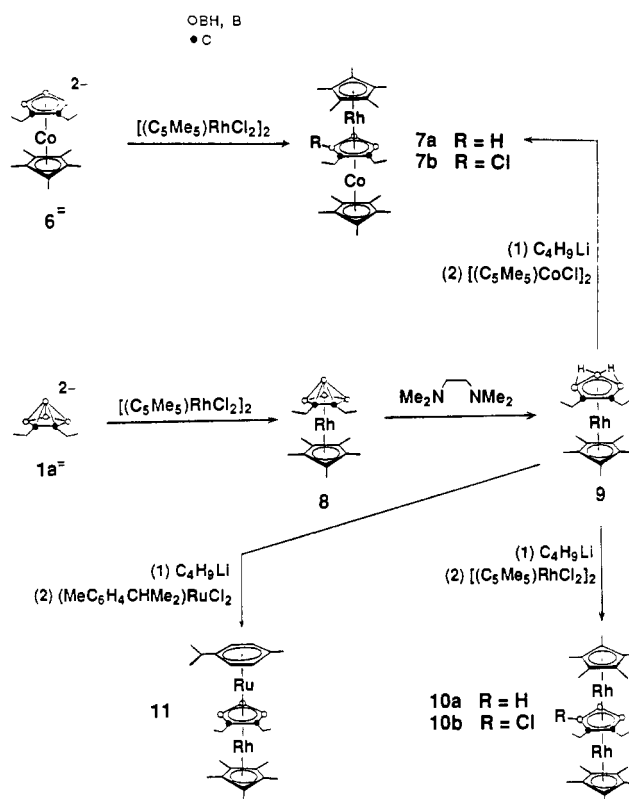
**Figure 1.** ORTEP drawing of the molecular structure of **5** (non-hydrogen atoms) showing 20% thermal ellipsoids.

in each, according to skeletal electron-counting theory;<sup>15</sup> moreover, the molecular geometry and diamagnetism of **5** are consistent with formal oxidation states of +3 for both metals. Viewed as a triple-decker complex, **5** is a 30-electron system<sup>2,3</sup> whose carboranyl ( $C_2B_4$ ) and diboroly ( $C_3B_2$ ) ligands are comparable to those in earlier structure determinations on triple-decker systems.<sup>3,5a,8</sup>

The rhodium atom is nearly centered over its two coordinated rings and is approximately equidistant from the  $C_2B_3$  and  $C_3B_2$  planes (1.76 and 1.80 Å, respectively). However, the  $C_2B_4$  carborane unit is tilted away from the  $C_3B_2$  ring ( $C_3B_2$ - $C_2B_3$  dihedral angle =  $8.6^\circ$ ) so as to increase the separation between its cage carbons (C2 and C3) and the nearest carbon atoms in the  $C_3B_2$  ring (C9 and C10); this effect is ascribed to relief of interligand steric crowding involving the C-ethyl groups. The cyclopentadienyl and  $C_3B_2$  planes are nearly parallel (dihedral angle  $1.9^\circ$ ), as expected in the absence of significant interligand contacts. There are no unusually short intermolecular distances, the closest being 3.551 Å between C5R and C8E.

**Synthesis of Homo- and Heterobimetallic Rhodium Triple-Decker Complexes.** The approach that was employed in the designed synthesis of triple-decker complexes of cobalt, ruthenium, and osmium<sup>8a,b</sup> was applied in the current work to prepare structurally analogous complexes incorporating rhodium. While the chemistry of small cobaltacarboranes derived from  $R_2C_2B_4H_6$  is extensive, their rhodium counterparts have been virtually unknown.<sup>16</sup> In this work, the cobaltacarborane dianion  $(C_5Me_5)Co(Et_2C_2B_3H_3)^{2-}$  ( $6^{2-}$ ) and  $[(C_5Me_5)RhCl_2]_2$  reacted in THF solution to generate two major products, characterized as the green triple-decker complexes  $(C_5Me_5)Co(2,3-Et_2C_2B_3H_2-4-R)Rh-(C_5Me_5)$  (**7a**, R = H; **7b**, R = Cl) in a combined isolated yield of 68%. The structures in Scheme II are consistent with the  $^{11}B$  and  $^1H$  NMR spectra, which are typical of  $C_2B_3$ -bridged triple-decker complexes (e.g., the shift of the unique B(5) resonance to very low field) and are similar to the spectra of previously reported complexes of this class.<sup>8a,b</sup> The formation of a B-chlorinated product following extraction in  $CH_2Cl_2$  is not surprising, since

**Scheme II**



Davis et al. had found that halogenation of triple-deckers at B(4) often occurs in the presence of  $RuCl_3$  or  $OsCl_3$  and/or on workup of the products in dichloromethane.<sup>8a</sup>

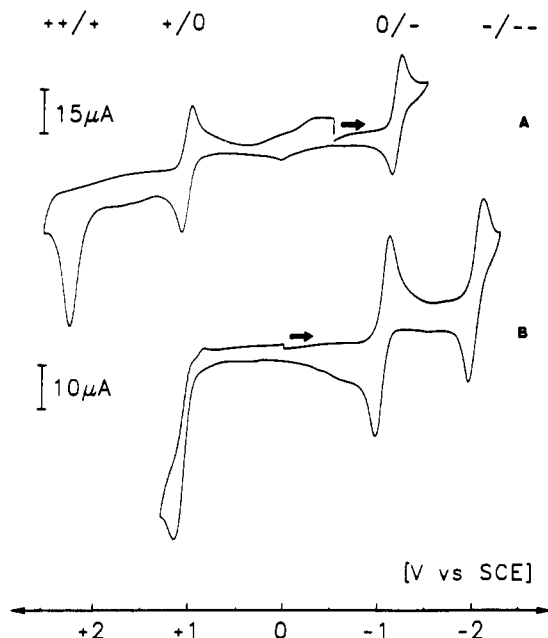
As an alternative route to rhodium-containing triple-deckers, which can be used to prepare homobimetallic as well as heterobimetallic species, we prepared the small rhodacarborane  $(C_5Me_5)Rh(Et_2C_2B_4H_4)$  (**8**) via the reaction of the carborane dianion  $1a^{2-}$  with  $[(C_5Me_5)RhCl_2]_2$  (Scheme II). Compound **8** was isolated in 41% yield as brown crystals that deteriorated in air over several days, and its structural assignment based on  $^{11}B$  and  $^1H$  NMR and mass spectra was straightforward. The decapitation of **8** by treatment with TMEDA proceeded normally to give the *nido*-rhodacarborane complex  $(C_5Me_5)Rh(Et_2C_2B_3H_5)$  (**9**), isolated as a yellow oil. Complex **9** was, in turn, converted to triple-decker complexes as shown in Scheme II. Treatment of **9** with 2 equiv of butyllithium removed the two bridge protons to give the dianion  $9^{2-}$ , which reacted with  $[(C_5Me_5)RhCl_2]_2$  to produce the desired dirhodium species  $(C_5Me_5)_2Rh_2(Et_2C_2B_3H_3)$  (**10a**), a red crystalline solid, and its orange 4-chloro derivative **10b**, in a combined 46% yield. The proposed structure is supported by the NMR data, which correlate well with triple-decker geometry (vide supra) and also clearly indicate the high symmetry created by the presence of identical  $(C_5Me_5)Rh$  groups.

Similar reactions of the  $9^{2-}$  ion with (cymene)ruthenium(II) dichloride and with  $[(C_5Me_5)CoCl]_2$  gave, respectively, the rhodium-ruthenium complex  $(C_5Me_5)Rh(Et_2C_2B_3H_3)Ru-(MeC_6H_4CHMe_2)$  (**11**) and the cobalt-rhodium species **7a** described above; the latter reaction thus furnishes an alternative route to **7a**. Red **11** was isolated in 16% yield, accompanied by a small amount of its chlorinated derivative (identified by mass spectra only). Again, the structure of **11** as shown in Scheme II is fully consistent with the spectroscopic data.

**Electrochemistry.** Compounds **3a**, **3b**, **4a**, **4b**, **7a**, **10a**, and **11** were investigated by cyclic voltammetry in 0.1 M  $Bu_4NPF_6/CH_2Cl_2$  and 0.1 M  $Bu_4NPF_6/1,2$ -dimethoxyethane (DME) solutions at platinum or glassy-carbon working electrodes. The data suggest that the electron-transfer reactions are very rapid, i.e., electrochemically reversible. Differences between cathodic and anodic peak potentials of a redox couple ( $\Delta E_p$ ) were generally 60–70 mV at moderate scan rates (0.05–0.2 V  $s^{-1}$ ). In DME

(15) (a) 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. (b) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.

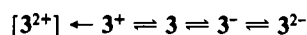
(16) A rhodium-bridged complex,  $\mu-(Ph_3P)_3Rh-C_2B_4H_7$ , has been prepared: Magee, C. P.; Sneddon, L. G.; Beer, D. C.; Grimes, R. N. *J. Organomet. Chem.* **1975**, *86*, 159.



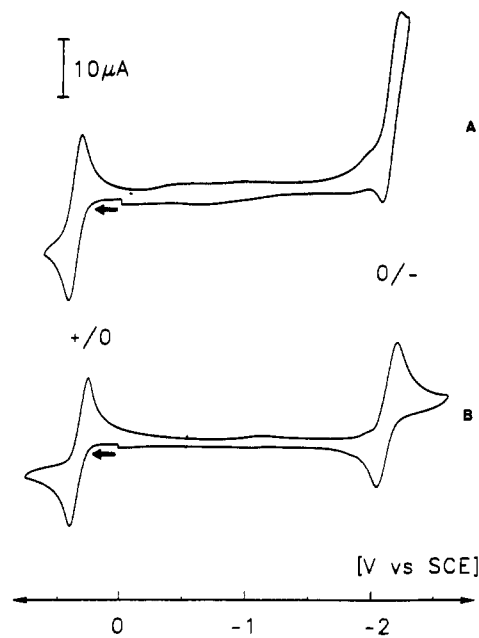
**Figure 2.** Cyclic voltammograms of **3b** at Pt electrodes vs SCE at 20 °C ( $\nu = 0.1 \text{ V s}^{-1}$ ): (A) in 0.1 M  $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ ; (B) in 0.1 M  $\text{Bu}_4\text{NPF}_6/\text{DME}$ .

solutions,  $\Delta E_p$  values for reversible signals varied between 90 and 130 mV. As  $\text{Cp}_2\text{Fe}^{+/-}$  displayed the same behavior, this effect is attributed to uncompensated  $iR$  drop. In addition to the evidence from  $\Delta E_p$  values (see data in Table VII), the 1-electron nature of the redox steps was established from the observed peak currents of the waves. The voltage range accessible for investigation with a ground current sensitivity of  $5 \mu\text{A}/\text{cm}$  was +2.60 to -2.20 V in  $\text{CH}_2\text{Cl}_2$  and +2.00 to -3.00 V in DME.

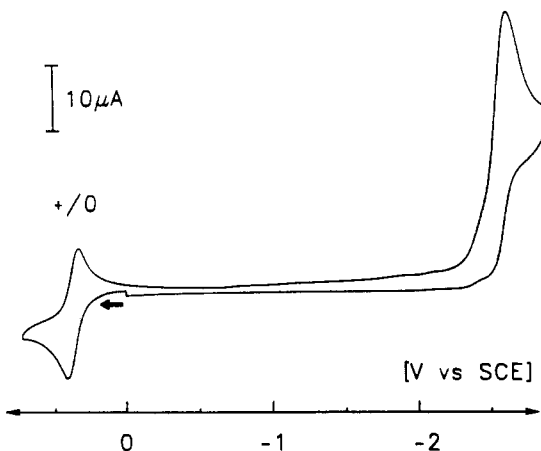
$(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)\text{Co}(\text{Et}_2\text{MeC}_3\text{B}_2\text{Et}_2)\text{CoCp}$  (**3a**, **3b**). The dicobalt triple-decker complexes exhibited solvent-dependent redox behavior, with corresponding potentials within 0.2 in each case. In  $\text{CH}_2\text{Cl}_2$ , **3a** and **3b** underwent reversible oxidation to form the monocations and a second irreversible oxidation forming the dications. Due to the limitation of the voltage range in  $\text{CH}_2\text{Cl}_2$ , only the first (reversible) reductions were observable; thus, the singly charged species are both stable (Figure 2). In DME solutions, the reversible formation of both mono- and dianions was observed. The oxidations yielded short-lived monocations for both compounds (**3a**, +1.19 V; **3b**, +1.22 V). A similar solvent effect has been observed for the iron-cobalt analogues,<sup>10</sup> and in the case of the 33-valence-electron dinickel triple-decker complex  $(\text{Et}_2\text{HC}_3\text{B}_3\text{Me}_3)_2\text{Ni}_2(\text{Et}_2\text{HC}_3\text{B}_2\text{Me}_2)$ , the cleavage by DME of the electrochemically generated 32-valence-electron cation has been utilized in synthesis.<sup>17</sup> The electron-transfer series for **3a/3b** encompasses five members in a voltage range of 5.00 V (+2.60 to -2.40 V), from the 28-valence-electron dication to the 32-valence-electron dianion.



$(\text{R}_2\text{C}_2\text{B}_3\text{H}_5)\text{Co}(\text{Et}_2\text{MeC}_3\text{B}_2\text{Et}_2)\text{CoCp}$  (**4a**, **4b**). The decapitated complexes **4a** and **4b** exhibited reversible reductions forming 31-valence-electron monoanions in both solvents, with similar redox potentials: ( $\text{CH}_2\text{Cl}_2$ : **4a**, -1.42 V; **4b**, -1.38 V. DME: **4a**, -1.24 V; **4b**, -1.18 V). A second reversible reduction forming the dianions were observable only in DME (**4a**, -2.30 V; **4b**, -2.24 V). At a scan rate of  $0.1 \text{ V s}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ , values of 1.00 and 0.98 were measured for the ratio of peak currents ( $i_a/i_c$ ), indicating that the anions as well as the dianions are stable under the chosen conditions at room temperature. However, at low temperatures and with scan rates up to  $1 \text{ V s}^{-1}$ , only irreversible signals for the oxidations were observed in both solvents, and peaks arising from

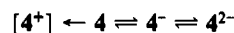


**Figure 3.** Cyclic voltammograms of **7a** at GC electrodes vs SCE at 20 °C (A) and at -60 °C (B) in 0.1 M  $\text{Bu}_4\text{NPF}_6/\text{DME}$ . Scan rate:  $0.1 \text{ V s}^{-1}$ .



**Figure 4.** Cyclic voltammogram of **11** at GC electrodes vs SCE at 20 °C in 0.1 M  $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ . Scan rate:  $0.1 \text{ V s}^{-1}$ .

products of these additional reactions were observed. Clearly, absorption processes alter the surface of the working electrode in these measurements. We conclude that, in contrast to **3a/3b**, the decapitated derivatives **4a/4b** do not survive electrochemical oxidation to form 29-valence-electron monocations; thus, the electron-transfer series for these compounds consists of just three electrochemically stable species ranging from the neutral complexes to the 32-valence-electron dianions.



$(\text{C}_5\text{Me}_5)\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Rh}(\text{C}_5\text{Me}_5)$  (**7a**),  $(\text{C}_5\text{Me}_5)_2\text{Rh}_2(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)$  (**10a**), and  $(\text{C}_5\text{Me}_5)\text{Rh}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Ru}(\text{MeC}_6\text{H}_4\text{CHMe}_2)$  (**11**). Cyclic voltammetry on these triple-decker complexes exhibited generally reversible first oxidation waves, indicating that the 29-valence-electron species are stable in DME and  $\text{CH}_2\text{Cl}_2$  solutions under the experimental conditions at room temperature. In all cases, the  $\Delta E_p$  values ranged between 60 and 70 mV and the current ratios were 1.00. Compounds **7a** and **11** exhibited a second, irreversible oxidation (Figures 3 and 4), which remained irreversible even at low temperatures and with scan rates up to  $1 \text{ V s}^{-1}$ . Electrochemical reduction of these compounds revealed significant differences: although **10a** and **11** exhibited only irreversible signals (**10a**, -1.12 V; **11**, -2.61 V), **7a** gave a reversible wave at -2.15 V in DME. This redox equilibrium is fully reversible only at low temperatures.

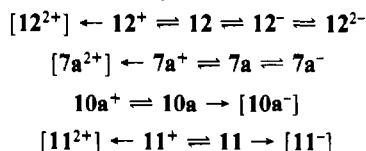
(17) Zwickler, J.; Kuhlmann, T.; Pritzkow, H.; Siebert, W.; Zenneck, U. *Organometallics* 1988, 7, 2316.

Table VII. Cyclic Voltammetric Data<sup>a</sup>

compd	couple	$E_1^{a,b}$	$\Delta E_p^c$	current ratio <sup>d</sup>	$v^e$	solvent	electrolyte
3a	2+/+	+2.40	<i>f</i>		0.05	CH <sub>2</sub> Cl <sub>2</sub>	Bu <sub>4</sub> NPF <sub>6</sub>
	+0	+1.05	63	0.96	0.05		
	0/-	-1.16	71	1.06	0.05		
3a	+0	+1.19	<i>f</i>		0.1	DME	Bu <sub>4</sub> NPF <sub>6</sub>
	0/-	-1.09	130	1.04	0.1		
	-2/-	-2.12	130	~1	0.1		
3b	2+/+	+2.25	<i>f</i>		0.05	CH <sub>2</sub> Cl <sub>2</sub>	Bu <sub>4</sub> NPF <sub>6</sub>
	+0	+1.09	66	0.90	0.05		
	0/-	-1.11	71	1.04	0.05		
3b	+0	+1.22	<i>f</i>		0.1	DME	Bu <sub>4</sub> NPF <sub>6</sub>
	0/-	-1.06	109	1	0.1		
	-2/-	-2.19	110	~1	0.1		
4a	+0	+1.00	<i>f</i>		0.1	CH <sub>2</sub> Cl <sub>2</sub>	Bu <sub>4</sub> NPF <sub>6</sub>
	0/-	-1.42	79	0.95	0.1		
4a	+0	+1.18	<i>f</i>		0.1	DME	Bu <sub>4</sub> NPF <sub>6</sub>
	0/-	-1.24	83	1	0.1		
	-2/-	-2.30	92	1	0.1		
4b	+0	+1.07	<i>f</i>		0.1	CH <sub>2</sub> Cl <sub>2</sub>	Bu <sub>4</sub> NPF <sub>6</sub>
	0/-	-1.38	75	0.96	0.1		
	+0	+1.25	<i>f</i>		0.1		
0/-	-1.18	95	1	0.1			
-2/-	-2.24	100	0.98	0.1			
7a	2+/+	+1.67	<i>f</i>		0.2	CH <sub>2</sub> Cl <sub>2</sub>	Bu <sub>4</sub> NPF <sub>6</sub>
	+0	-0.27	60	1	0.1		
7a	2+/+	+1.49	<i>f</i>		0.2	DME	Bu <sub>4</sub> NPF <sub>6</sub>
	+0	+0.37	75	1	0.1		
	0/-	-2.15	109	1	0.1		
10a	+0	+0.44	66	1	0.1	CH <sub>2</sub> Cl <sub>2</sub>	Bu <sub>4</sub> NPF <sub>6</sub>
	0/-	-1.04	<i>f</i>		0.2		
10a	+0	+0.52	125	1	0.1	DME	Bu <sub>4</sub> NPF <sub>6</sub>
	0/-	-1.12	<i>f</i>		0.1		
11	2+/+	+1.66	<i>f</i>		0.5	CH <sub>2</sub> Cl <sub>2</sub>	Bu <sub>4</sub> NPF <sub>6</sub>
	+0	+0.31	64	1	0.1		
11	2+/+	+1.12	<i>f</i>		0.2	DME	Bu <sub>4</sub> NPF <sub>6</sub>
	+0	+0.36	64	1	0.5		
	0/-	-2.61	<i>f</i>		0.5		

<sup>a</sup>Data reported for Pt or glassy-carbon working electrodes at room temperature; electrolyte concentration is 0.1 M. <sup>b</sup> $v$  vs SCE;  $E^o$  reported for reversible system; peak potentials ( $E_p^{ox}$ ,  $E_p^{red}$ ) reported for irreversible signals. <sup>c</sup>Separation in mV of cathodic and anodic peaks;  $\Delta E_p$  exceeds 60–70 mV for reversible signals in DME due to uncompensated  $iR$  drop;  $E_p$  for Cp<sub>2</sub>Fe<sup>+10</sup> is 100–110 mV under the same conditions. <sup>d</sup> $i_c/i_a$  for reductions;  $i_c/i_a$  for oxidations. <sup>e</sup>Scan rate is V/s. <sup>f</sup>Irreversible.

The electrochemistry of **7a**, **10a**, and **11** may be compared with that of the isoelectronic triple-decker complex CpCo(2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>3</sub>)CoCp (**12**).<sup>5,18</sup> Complex **12** can exist in four stable redox states (**12**<sup>+</sup>, **12**, **12**<sup>-</sup>, **12**<sup>2-</sup>), of which only the oxidation of **12**<sup>+</sup> is irreversible. In contrast, compounds **7a**, **10a**, and **11**, in which CpCo units in **12** are formally replaced by (C<sub>3</sub>Me<sub>3</sub>)Rh or (MeC<sub>3</sub>H<sub>4</sub>CHMe<sub>2</sub>)Ru groups, are more limited in having only two or three redox states in the same voltage range. The following equations summarize these systems.



### Concluding Remarks

The preparative routes employed in this work to prepare hybrid carborane–diborole sandwich complexes, which involve reactions of anionic substrates in solution, are complementary to the approach used in our earlier paper in the synthesis of iron–cobalt hybrid species<sup>10</sup> wherein a cyclooctatriene ligand was thermally displaced from ( $\eta^6$ -C<sub>8</sub>H<sub>10</sub>)Fe(R<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>) by the dihydrodiborole complex (Et<sub>2</sub>MeC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub>)CoCp. A large variety of metal sandwich structural types are potentially accessible by combining these two methods. Indeed, in the area of arene–metallacarborane chemistry,

the combination of C<sub>8</sub>H<sub>10</sub> displacement and ionic solution reactions has allowed the construction of multilevel, homo- and heterotrimeric (Fe<sub>3</sub> and FeRu<sub>2</sub>) complexes.<sup>8d</sup> In addition, the general robustness and air stability of these hybrid complexes and their ability to undergo multistep reversible electrochemical oxidations and reductions without decomposition extend the scope of this chemistry still further. These properties strengthen the feasibility of using such compounds as steppingstones to larger structures, including tetradecar sandwich complexes as described in the following article.<sup>19</sup>

### Experimental Section

**Instrumentation.** <sup>11</sup>B (115.8 MHz) and <sup>1</sup>H (300 MHz) NMR spectra were acquired on Nicolet NT-360 and GE QE300 spectrometers respectively, and visible–ultraviolet spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer with HP Vectra computer interface. Unit-resolution mass spectra were obtained on a Finnegan MAT 4600 GC/MS spectrometer using perfluorotributylamine (FC43) as a calibration standard. Simulated mass spectra based on natural isotopic abundances were calculated on an AT&T 3B5 computer using the program MASPEC by R.N.G. In all cases, strong parent envelopes were observed, and the calculated and observed unit-resolution spectral patterns were in close agreement. High-resolution mass measurements were obtained on a Finnegan MAT 8230 instrument using an SSX 300 data system with perfluorokerosene as a reference standard. ESR spectra were recorded on a Varian E3 spectrometer fitted with an electrolytic cell. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrometer. Column chromatography was conducted on silica gel 60 (Merck), and thick-layer chromatography was carried out on precoated silica gel plates (Merck).

Electrochemical measurements were conducted using a Princeton Applied Research (PAR, EG+G) Model 173 potentiostat, a Model 179 digital coulometer, a Model 175 function generator, a Metrohm electrochemical cell, and Metrohm rotating disk electrodes (Pt, glassy carbon) for polarography and cyclic voltammetry (without rotating). All potentials are given in V vs an SCE reference electrode that was equipped with a salt bridge (Metrohm) of identical composition with that of the investigated solution. Moderate sweep rate cyclic voltammograms were recorded on a Houston Instrument Series 2000 X-Y recorder and rapid scan rate data were obtained on a Hameg HM 208 two-channel storage oscilloscope. The potential scale was calibrated with Cp<sub>2</sub>Fe<sup>+/-</sup>.

**Materials and Procedures.** Dichloromethane and *n*-hexane were anhydrous grade and were stored over 4-Å molecular sieves prior to use. THF was distilled from sodium–benzophenone immediately prior to use. *nido*-2,3-Diethyl-2,3-dicarbahexaborane(8) [Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>] and the corresponding 2,3-dibenzyl derivative were prepared as described elsewhere.<sup>11</sup> The cobalt–diborole complex CpCo(Et<sub>2</sub>MeC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub>) (**2**) was prepared by a literature procedure.<sup>12</sup> Sodium hydride was used as a 50% dispersion in mineral oil. *tert*-Butyllithium and sodium cyclopentadienide were purchased as standard solutions from Aldrich. Except where otherwise indicated, all syntheses were conducted under vacuum or an atmosphere of nitrogen, using Pyrex apparatus of the type described in ref 8a, Figure 3, which consist of several vessels and sintered glass filters attached to a vacuum line and interconnected so as to permit successive steps to be conducted without exposure of materials to the atmosphere. Workup of products was generally conducted in air by using benchtop procedures.

**Electrochemical Procedures.** Purification of electrolytes and solvents and all measurements were conducted under argon. Bu<sub>4</sub>NPF<sub>6</sub> (Fluka electrochemical reagent grade) was dried at 110 °C for 20 h in vacuo before use. Dichloromethane (Merck p.a.; Riedel-deHaen 99+%) was distilled from CaH<sub>2</sub> and stored under argon in the dark. DME (Aldrich 99+%) was passed through a column of activated basic alumina (ICN Alumina B Super 1, activated at 280 °C for 2 days under vacuo) and distilled twice before use. Solvents were stored under argon, and freshly prepared solutions of electrolytes were stored in Schlenk tubes equipped with Teflon valves.

**Preparation of (Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Co(Et<sub>2</sub>MeC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub>)CoCp (**3a**).** The diethylcarborane **1a** (Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, 31 mg, 0.24 mmol) was deprotonated with excess dry NaH in THF, and the solution was filtered in vacuo into a second vessel. The cobalt–diborole complex (67 mg, 0.213 mmol) was deprotonated by stirring for ca. 1 h in THF at 0 °C over excess potassium metal, followed by stirring for 2 h at room temperature, which produced a color change from green to yellow. The solution was filtered in vacuo into the carborane anion solution frozen in a liquid-nitrogen bath, after which CoCl<sub>2</sub> (31 mg, 0.24 mmol) was added from a side arm, and the

(19) Fessenbecker, A.; Attwood, M. D.; Grimes, R. N.; Stephan, M.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Inorg. Chem.*, following paper in this issue.

reaction mixture was stirred at  $-78^{\circ}\text{C}$  for 1 h, during which little color change was noted. The mixture was then stirred overnight at  $0^{\circ}\text{C}$ , which produced a sharp color change from yellow to brown. The mixture was filtered through silica and the residue extracted with  $\text{CH}_2\text{Cl}_2$ , after which the crude product was chromatographed on a silica plate with 2:1 hexane/ $\text{CH}_2\text{Cl}_2$  as eluent. Only one dark green/orange band ( $R_f$  0.30) was observed, which was shown by analytical HPLC to be pure. Recrystallization of this material from hexane gave dark green crystals of **3a**, yield 34 mg (32% based on carborane reagent used). Exact mass: calcd for  $^{59}\text{Co}_2^{12}\text{C}_{23}^{11}\text{B}_6^1\text{H}_{42}^+$ , 502.2509; found, 502.2520. Visible-UV absorptions (nm, in  $\text{CH}_2\text{Cl}_2$ ): 652 (1%), 364 (96%), 310 (100%), 260 (48%).

**Preparation of  $[(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_4]\text{Co}(\text{Et}_2\text{MeC}_3\text{B}_2\text{Et}_2)\text{CoCp}$  (**3b**).** In a procedure identical with that used for **3a**, 83 mg (0.32 mmol) of the dibenzylcarborane **1b**, 92 mg (0.29 mmol) of **2**, and 42 mg (0.32 mmol) of  $\text{CoCl}_2$  were employed to generate, on plate chromatography, a red-orange band ( $R_f$  0.57 in 1:1  $\text{CH}_2\text{Cl}_2$ /hexane) and a small amount of colorless  $(\text{PhCH}_2)_4\text{C}_2\text{B}_8\text{H}_8$  ( $R_f$  0.74), a product known to form by fusion<sup>20</sup> of the dibenzylcarborane anion. The red band was pure **3b**, 54 mg (0.086 mmol), yield 29%. Exact mass: calcd for  $^{59}\text{Co}_2^{12}\text{C}_{33}^{11}\text{B}_6^1\text{H}_{46}^+$ , 626.2822; found, 626.2828. Visible-UV absorptions (nm, in  $\text{CH}_2\text{Cl}_2$ ): 646 (4%), 364 (100%), 308 (88%), 252 (42%), 234 (48%).

**Conversion of **3a** and **3b** to  $(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Co}(\text{Et}_2\text{MeC}_3\text{B}_2\text{Et}_2)\text{CoCp}$  (**4a**) and  $[(\text{PhCH}_2)_2\text{C}_2\text{B}_3\text{H}_3]\text{Co}(\text{Et}_2\text{MeC}_3\text{B}_2\text{Et}_2)\text{CoCp}$  (**4b**).** A 0.178-g (0.354 mmol) sample of **3a** was stirred in excess wet TMEDA for 1 h at room temperature, producing a color change from orange/brown to dark green. The volatiles were removed by rotary evaporation, and the product was filtered through silica and extracted with  $\text{CH}_2\text{Cl}_2$  and eluted on silica plates with 50%  $\text{CH}_2\text{Cl}_2$  in hexane. Green **4a** ( $R_f$  0.82) was collected in 73% yield (0.128 g, 0.260 mmol). Exact mass: calcd for  $^{59}\text{Co}_2^{12}\text{C}_{23}^{11}\text{B}_5^1\text{H}_{43}^+$ , 492.2494; found, 492.2510. Visible-UV absorptions (nm, in  $\text{CH}_2\text{Cl}_2$ ): 596 (4%), 378 (60%), 312 (100%), 234 (46%). A 24-mg sample of **3b** was stirred in wet TMEDA for 20 min at room temperature, during which a color change similar to that observed with **3a** was observed. Workup, as for **4a** above, gave green **4b**, 16 mg, 0.026 mmol (68%). Exact mass: calcd for  $^{59}\text{Co}_2^{12}\text{C}_{33}^{11}\text{B}_5^1\text{H}_{47}^+$ , 616.2807; found, 616.2817. Visible-UV absorptions (nm, in  $\text{CH}_2\text{Cl}_2$ ): 600 (4%), 378 (67%), 314 (100%), 236 (44%).

**Preparation of  $(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{Rh}(\text{Et}_2\text{MeC}_3\text{B}_2\text{Et}_2)\text{CoCp}$  (**5**).** A solution of the carborane dianion **1a**<sup>2-</sup> in THF was prepared from 70 mg (0.5 mmol) of **1a** as described elsewhere.<sup>8a</sup> A THF solution of the **2**<sup>-</sup> ion was obtained by deprotonation of 0.15 g (0.48 mmol) of **2** with 1 equiv of butyllithium at  $-78^{\circ}\text{C}$  and stirred for 30 min at that temperature, after which the green solution was added slowly to a yellow solution of 0.16 g (0.48 mmol) of  $\text{Rh}(\text{MeCN})_3\text{Cl}_3$  in THF at  $-78^{\circ}\text{C}$ . The combined solutions were stirred for 15 min as the color changed to dark red; the solution of **1a**<sup>2-</sup> was then added in small portions at  $-78^{\circ}\text{C}$ , and the mixture was stirred overnight while gradually warming to room temperature. The solvent was removed by rotary evaporation, leaving a brown residue, which was chromatographed on a silica plate in hexane to give three major brown bands. The slowest moving band ( $R_f$  0.10) was the desired product **5**, obtained as brown crystals, 35 mg (0.064 mmol, 14%). The remaining bands were identified as starting materials and a trace of **3a**). The structure proposed from spectroscopic data was established by X-ray crystallography (vide infra).

**Preparation of  $(\text{C}_5\text{Me}_5)\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Rh}(\text{C}_5\text{Me}_5)$  (**7a**) and  $(\text{C}_5\text{Me}_5)\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_3\text{H}_3\text{-4-Cl})\text{Rh}(\text{C}_5\text{Me}_5)$  (**7b**).** A solution of the cobalt diborolyl dianion **6**<sup>2-</sup> was prepared by treatment of the neutral complex (0.10 g, 0.30 mmol) was 2 equiv of butyllithium in THF at  $0^{\circ}\text{C}$  followed by stirring for 10 min. The solution was cooled to  $-78^{\circ}\text{C}$ , and 0.10 g (0.16 mmol) of solid  $[(\text{C}_5\text{Me}_5)\text{RhCl}_2]_2$  was added. The mixture was stirred overnight with slow warming to room temperature, after which the solvent was removed by rotary evaporation and the residue extracted with  $\text{CH}_2\text{Cl}_2$ , giving a green solution which was filtered through silica. Subsequent chromatography on a silica plate in 3:1 hexane/ $\text{CH}_2\text{Cl}_2$  gave two major green bands, the first being the chlorinated derivative **7b** (30 mg, 18%) and the second identified as the desired product **7a** (70 mg, 40%). Exact mass for **7a**: calcd for  $^{103}\text{Rh}^{59}\text{Co}^{12}\text{C}_{26}^{11}\text{B}_3^1\text{H}_{43}^+$ , 550.2031; found, 550.2072. Exact mass for **7b**: calcd for  $^{103}\text{Rh}^{59}\text{Co}^{37}\text{Cl}^{12}\text{C}_{26}^{11}\text{B}_3^1\text{H}_{42}^+$ , 586.1612; found, 586.1627.

**Preparation of  $(\text{C}_5\text{Me}_5)\text{Rh}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)$  (**8**).** A solution of the carborane dianion **1**<sup>2-</sup> in THF was prepared from 0.12 g (0.9 mmol) of **1a** as described earlier<sup>8a</sup> and cooled to  $-78^{\circ}\text{C}$ . Solid  $[(\text{C}_5\text{Me}_5)\text{RhCl}_2]_2$  (0.28 g (0.45 mmol) was added under vacuum from a side-arm tube. After 30 min of stirring at  $-78^{\circ}\text{C}$ , the red solution was warmed to room temperature; above ca.  $-20^{\circ}\text{C}$ , the color changed to green, and overnight stirring produced a brown solution. Removal of the THF solvent, ex-

traction of the brown residue in  $\text{CH}_2\text{Cl}_2$ , and filtration through silica gave a solution that was evaporated to a dry solid. When this solid was dissolved in  $\text{CH}_2\text{Cl}_2$  and plated on silica in 3:1 hexane/ $\text{CH}_2\text{Cl}_2$ , one major band was obtained which afforded **8** as a brown crystalline solid (0.136 g, 41%) which deteriorates on standing several days in air. Exact mass for **8**: calcd for  $^{103}\text{Rh}^{12}\text{C}_{16}^{11}\text{B}_4^1\text{H}_{29}^+$ , 368.1697; found 368.1679.

**Conversion of **8** to  $(\text{C}_5\text{Me}_5)\text{Rh}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)$  (**9**).** A 0.13-g (0.36 mmol) sample of **8** was dissolved in wet TMEDA and stirred at room temperature for 30 min. Removal of the TMEDA on a rotary evaporator gave a yellow oil, which was dissolved in hexane, filtered through silica, and chromatographed on a silica plate in hexane to give **9** as a yellow oil, 79 mg (61%). Exact mass for **9**: calcd for  $^{103}\text{Rh}^{12}\text{C}_{16}^{11}\text{B}_3^1\text{H}_{30}^+$ , 358.1682; found, 358.1680.

**Preparation of  $(\text{C}_5\text{Me}_5)_2\text{Rh}_2(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)$  (**10**).** Complex **9** (70 mg, 0.20 mmol) was deprotonated in THF solution by addition of 2 equiv of butyllithium at  $0^{\circ}\text{C}$  followed by stirring for 20 min. To the solution of **9**<sup>2-</sup> was added  $[(\text{C}_5\text{Me}_5)\text{RhCl}_2]_2$  (62 mg, 0.10 mmol) in a single portion at  $-78^{\circ}\text{C}$ , and the mixture was warmed to room temperature overnight with stirring. The solution was opened to the air and stirred for 10 min, and the THF was removed in vacuum. The residue was extracted with  $\text{CH}_2\text{Cl}_2$  and the solution filtered through silica and chromatographed on silica plates in 3:1 hexane/ $\text{CH}_2\text{Cl}_2$  to give red and orange bands, the first of which was the desired **10a** (40 mg, 34%) while the latter band was the 4-chloro derivative **10b** (15 mg, 12%). Exact mass for **10a**: calcd for  $^{103}\text{Rh}_2^{12}\text{C}_{26}^{11}\text{B}_3^1\text{H}_{43}^+$ , 594.1754; found, 594.1747. Exact mass for **10b**: calcd for  $^{103}\text{Rh}_2^{37}\text{Cl}^{12}\text{C}_{26}^{11}\text{B}_3^1\text{H}_{42}^+$ , 630.1335; found, 630.1340.

**Preparation of  $(\text{C}_5\text{Me}_5)\text{Rh}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Ru}(\text{MeC}_6\text{H}_4\text{CHMe}_2)$  (**11**).** A solution of the dianion **9**<sup>2-</sup> was prepared as described above from 60 mg (0.17 mmol) of **9** and stirred for 15 min at  $0^{\circ}\text{C}$ , after which the solution was placed in a  $-78^{\circ}\text{C}$  bath and 50 mg (0.17 mmol) of solid  $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2^{8a}$  was added in vacuo from a side-arm tube. The mixture was allowed to warm to room temperature overnight with stirring, following which the red-brown mixture was opened to the air and stirred for 10 min. The solvent was removed by rotary evaporation, the residue extracted with  $\text{CH}_2\text{Cl}_2$ , and the extract passed through a short silica column. The red filtrate was chromatographed on silica plates in 3:1 hexane/ $\text{CH}_2\text{Cl}_2$  to give two red bands of which the first was the desired **11** (15 mg, 16%) while the second was a monochloro derivative of the latter compound (identified mass spectroscopically), 7 mg (7%). Exact mass for **11**: calcd for  $^{104}\text{Ru}^{103}\text{Rh}^{12}\text{C}_{26}^{11}\text{B}_3^1\text{H}_{42}^+$ , 594.1675; found, 594.1670.

**X-ray Structure Determination on **5**.** A crystal grown from dichloromethane was used to determine the space group, which was uniquely established from the systematic absences  $0kl$ ,  $k = 2n$ ;  $h0l$ ,  $l = 2n$ ; and  $hk0$ ,  $h = 2n$ . A single octant of reciprocal space, bounded by  $0 \leq h \leq 18$ ,  $0 \leq k \leq 21$ , and  $0 \leq l \leq 16$ , was surveyed via the  $\theta/2\theta$  scan technique on a Nicolet P3m diffractometer equipped with a graphite monochromator. Relevant parameters are listed in Table IV. Only those reflections for which  $F_o^2 > 2.5\sigma(F_o^2)$  were used in the refinement of structural parameters. The intensities of two symmetry-related reflections showed a random variation of  $\pm 2.7\%$  about their mean value. Absorption corrections were made following refinement with isotropic thermal parameters,<sup>21</sup> but had little effect, lowering  $R$  for all data from 0.147 to 0.139. The structure was solved by the heavy-atom method using the Patterson function option of program SHELXS-86.<sup>22</sup> Because of the high thermal parameters of the boron and carbon atoms, no attempt was made to locate hydrogen atoms, and hence they were not included in refinement. Refinement including anisotropic thermal parameters was by the block-diagonal least-squares method, the model converging to the  $R$  values in Table IV. Scattering factors were taken from Cromer and Waber.<sup>23</sup> All computations, except for specifically referenced programs, were carried out by using programs written at the University of Virginia for an AT&T 3B15 computer.

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**Supplementary Material Available:** A table of mean planes (4 pages); a table of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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